DOCTORAL THESIS

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Environmental assessment of construction with recycled materials

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PREFACE

ABSTRACT

The use of industrial residues as raw materials in construction raises concerns over the potential leaching and dispersal of hazardous constituents from them into the environment. Their leaching behaviour has been studied in laboratory assays, but leaching processes in the field over larger spatial and temporal scales are more complex due to variations in the conditions the materials are exposed to, and less well understood. Hence, estimates of the potential environmental loads associated with the use of such materials based on laboratory tests may be inaccurate. This thesis addresses the environmental implications of using recycled materials in road and landfill cover constructions. The focus is primarily on the leaching of inorganic constituents from six types of materials: incineration ashes, copper smelter slag, blast-furnace slag, recycled concrete, natural rock and contaminated soil. The leaching behaviour of constituents from these materials were assessed in both laboratory batch leaching tests and monitoring programs in which the water percolating through them in field applications were sampled over one to ten years. Leaching data were evaluated using statistical and geochemical modelling. In addition, assessment methods and criteria to judge the environmental suitability of substituting natural materials for recycled materials in construction were reviewed. It was found that leachates from recycled materials in the constructions contain higher concentrations of several constituents than natural water and leachates from conventional materials. However, the rates and extent of constituent leaching were affected by the application methods in various ways that are explored and discussed. The results of simplified leaching tests did not always reflect the leaching behaviour in the field, which highlight the importance of developing assessment methods that allow case-specific factors to be taken into account. The environmental impacts of leaching must also be considered in relation to the expected impacts of the default alternative, *i.e.* landfilling of industrial residues and exploitation of natural resources. Combinations of case-specific assessments and system analyses would be the ideal approaches to evaluate impacts at both local and regional scales.

SAMMANFATTNING

Användningen av industriella restprodukter som konstruktionsmaterial inom anläggningsbyggande väcker frågan om möjlig utlakning och spridning av förorenande ämnen från materialen till omgivande miljö. Materialens lakningspotential bestäms vanligen genom lakförsök utförda under kontrollerade förhållanden i laboratorium. Lakningsprocesser i fält sker dock över större rums- och tidskalor och är mer komplexa på grund av variationer i miljön som materialen exponeras för. Uppskattningar av materialens möjliga miljöpåverkan baserade på laboratorietester kan därför vara felaktiga. Den här avhandlingen handlar om den miljömässiga betydelsen av att använda återvunna material som konstruktionsmaterial i vägar och deponisluttäckningar. Fokus är i huvudsak på utlakningen av oorganiska ämnen från sex typer av material: förbränningsaskor, kopparslagg, hyttsten, återvunnen betong, naturligt berg och förorenad jord. Utlakningen från dessa material undersöktes med hjälp av både skakförsök i laboratorium och kontrollprogram där vatten som perkolerade materialen i fältapplikationer (sk. lakvatten) provtogs under ett till tio år. Lakvattendata utvärderades med hjälp av statistisk och geokemisk modellering. Dessutom granskades olika bedömningsmetoder och kriterier som kan användas för att bedöma den miljömässiga lämpligheten av att använda återvunna istället för naturliga material i anläggningskonstruktioner. Lakvatten från återvunna material i de undersökta konstruktionerna innehöll högre koncentrationer av flera ämnen än naturliga vatten och lakvatten från naturliga material. Dock var hastigheten och omfattningen av utlakningen beroende av hur materialet användes, vilket har undersökts och diskuteras i avhandlingen. Resultaten från förenklade skakförsök överensstämde inte alltid med observationerna i fält, vilket understryker vikten av att utveckla bedömningsmetoder där fallspecifika faktorer kan tas i beaktande. Miljöpåverkan orsakad av lakning måste också ses i relation till den påverkan som kan uppstå om restprodukterna istället deponeras och naturliga material exploateras. Kombinationer av fallspecifika och systemövergripande analyser skulle därför vara det ideala sättet att utvärdera både lokala och regionala effekter av en möjlig användning av återvunna material.

LIST OF PAPERS

This thesis is based on the following scientific papers which are referred to in the text by their Roman numerals.

Paper I   Lidelöw, S., Lagerkvist, A., 2007. Evaluation of leachate emissions from crushed rock and municipal solid waste incineration bottom ash used in road construction. *Waste Management* 27, 1356-1365.

Paper II   Lidelöw, S., Ragnvaldsson, D., Leffler, P., Tesfalidet, S., Maurice, C., 2007. Field trials to assess the use of iron-bearing industrial by-products for stabilisation of chromated copper arsenate-contaminated soil. *The Science of the Total Environment* 387, 68-78.

Paper III   Travar, I., Lidelöw, S. Andreas, L., Tham, G., Lagerkvist, A. Assessing the environmental impact of ashes used in a landfill cover construction. Accepted for publication in *Waste Management*.

Paper IV   Lidelöw, S., Mácsik, J., 2008. Leaching behaviour of copper slag, blast-furnace slag and recycled concrete used in a full-scale road construction. Submitted to *The Science of the Total Environment*, June 2008.

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Appendices: Paper I-IV

1   INTRODUCTION

Every year, an estimated total of 90 Mt of construction aggregates is consumed in Sweden (SGU, 2007a), which corresponds to about 10 t or one lorry load per inhabitant. Recent statistics suggest that across Europe the total annual consumption of aggregates exceeds 3 Gt (UEPG, 2007). The aggregates are used for constructing roads, railways, bridges, tunnels, embankments, buildings, car parks, airfields, squares, noise barriers etc. The road construction industry is responsible for about half of the aggregate consumption, while the rest is used in concrete, filling and other applications (SGU, 2007a). An emerging area of application is landfill covering. The introduction of stricter EU regulations for landfilling waste (EU Council, 1999) has led to the closure of many old landfills that have to be covered to reduce the emission of landfill gas into the atmosphere and the infiltration of water into the waste. In Sweden alone, an estimated 100 Mt of mineral materials is needed for this purpose (Lagerkvist, 2000).

At present, most aggregates are obtained from natural bedrock, till, sand and gravel resources, while the remainder is derived mainly from mobile crushers at road construction sites, mine waste rock and surplus material generated during the production of industrial minerals and dimensional stone (Table 1; SGU, 2007a). In the 1990s, concerns were aroused about the adverse environmental impacts of quarrying operations and the depletion of natural resources, especially in densely populated areas. Several measures were introduced to promote recycling efforts, including the establishment of national targets to limit exploitation of natural deposits, and taxation of virgin materials and waste sent to landfill. Collectively these measures have strongly encouraged the use of recycled materials as substitutes for natural aggregates in construction.

In Sweden, industrial activities annually generate almost 80 Mt of residues, which could potentially be used as construction materials (Table 1), for example: air-cooled blast-furnace slag, recycled concrete from sorted demolition waste and bottom ashes all have

Table 1   Annual deliveries of aggregates and production of industrial residues with potential to serve as substitutes for natural aggregates in Sweden.

	Amount (Mt y^{-1})	Source of data
Delivered aggregates		
Crushed bedrock	57	SGU (2007a)
Natural sand and gravel	20	SGU (2007a)
Till	2	SGU (2007a)
Others[a]	13	SGU (2007a)
Total	92	
Industrial waste produced		
Mining (tailings and waste rock)	63	SGU (2007b); Swedish EPA (2007)
Construction and demolition[b]	10	RVF (2007)
Metal industry	2	SGI (2003)
Natural stone industry	2	SGI (2003)
Incineration	1	Ribbing (2007)
Others[c]	1	SGI (2003); ETRMA (2007)
Total	79	

[a] Mainly obtained from mobile crushers at road construction, mine waste rock and surplus material from the production of industrial minerals and dimensional stone (SGU, 2007a).
[b] Including excavation residues and reclaimed asphalt.
[c] Including tyre shreds (ETRMA, 2007), waste from the pulp, paper and foundry industries, and others (SGI, 2003).

suitable physical properties for use in unbound layers (Arm, 2003; Sherwood, 1995); ground granulated blast furnace slag and fly ash can serve as cementitious materials in concrete (Hale *et al.*, 2008; Yazlcl *et al.*, 2008) or liners for waste containment (Palmer *et al.*, 2000; Prashanth *et al.*, 2001); lime by-products and fly ash can be used as stabilising agents (Goswami and Mahanta, 2007; Zhou *et al.*, 2000); and waste soils can be used as filling materials (Song *et al.*, 2003; Tuncan *et al.*, 2000).

However, their utilisation raises concerns about the potential leaching and dispersal of hazardous constituents, such as trace metals and organic compounds, from them into the environment. In order to accurately predict long-term constituent leaching parameters, several factors related to the properties of relevant constituents, material matrices, the applications and the environmental conditions must be considered. Many studies on leaching properties of materials and constituents have been performed using laboratory leaching tests and geochemical modelling under equilibrium conditions (Apul *et al.*, 2005; Chandler *et al.*, 1997; Dijkstra *et al.*, 2008; Kosson *et al.*, 1996; Van der Sloot *et al.*, 1997). However, the nature and extent of leaching progresses in the field over larger spatial and temporal scales, and the effects of variations in the conditions the materials may be exposed to, are less well known. This deficiency may lead to inaccurate estimation (either over- or under-estimation) of the true environmental costs of substituting natural materials for recycled materials in construction. Overestimation of constituent release may lead to disposal of materials that are suitable for recycling, and thus unnecessarily reduce the disposal capacity, while underestimation may result in future needs for remediation.

2   OBJECTIVES AND SCOPE OF THE THESIS

The overall objective of this thesis was to acquire knowledge regarding the environmental implications of using recycled materials as aggregates in (i) road construction and (ii) landfill cover constructions.

The following questions are discussed:
- What is the environmental significance of leachates from recycled materials used in construction?
- What factors influence constituent leaching from the materials used in a construction?
- What are the most useful methods for assessing the environmental suitability of an intended use?

Scope and demarcation

The main focus of this thesis is on the leaching of inorganic constituents from recycled materials applied as construction materials in different applications. The transport and migration of these constituents into the surrounding environment is considered to a limited degree. The environmental impacts associated with the extraction, treatment and transport of the materials are not discussed, and neither are the fate and environmental burden of the materials after their service life as construction materials.

3   MATERIAL AND METHODS

This chapter presents an overview of the materials and methods used in the studies. Detailed descriptions can be found in the corresponding papers.

3.1   Material

In four case studies (described in Paper I-IV), six types of materials were studied: incineration ashes, chromated copper arsenate (CCA)-contaminated soil, copper smelter slag, blast-furnace slag, recycled concrete and natural rock (Table 2). The materials were tested for their potential use in either road bases (Paper I and IV) or landfill cover constructions (Paper II and III).

Table 2   Overview of the materials investigated in the case studies I-IV.

Material	Origin	Abbreviation	Case
Bottom ash	Municipal solid waste incineration	BA1	Dåva
Crushed rock	Natural bedrock	CR	(Paper I)
Fayalite slag	Copper smelter	FS	Björsbyn
Blast furnace slag	Steel plant	BFS	(Paper IV)
Crushed recycled concrete	Building demolition waste	RC	
Crushed rock	Natural bedrock	CR	
Chromated copper arsenate (CCA)-contaminated soil "F"	Former wood-impregnation site at Forsmo (F)	CSF	CCA (Paper II)
CSF mixed with 1% SA (spent steel abrasive; 97% Fe^0)	SA from a steel plant	CSF+1%SA	
CSF mixed with 8% OSG (oxygen scarfing granulate; 69% Fe oxides)	OSG from a steel plant	CSF+8%OSG	
CCA-contaminated soil "R"	Former wood-impregnation site at Robertsfors (R)	CSR	
CSR mixed with 1% SA (spent steel abrasive; 97% Fe^0)	SA from a steel plant	CSR+1%SA	
CSR mixed with 8% OSG (oxygen scarfing granulate; 69% Fe oxides)	OSG from a steel plant	CSR+8%OSG	
Bottom ash (sieved to <10 mm)	Municipal solid waste incineration	BA2	Tveta
Bottom ash (sieved to >10 mm)	Municipal solid waste incineration	BA3	(Paper III)
Fly ash	Refuse-derived fuel incineration	FA	
Bottom ash	Refuse-derived fuel incineration	BA4	
Sewage sludge	Municipal sewage treatment plant	SS	

3.2   Methods

Laboratory leaching tests

Standard compliance batch leaching tests (CEN, 2002) were applied in studies I-III to estimate the water soluble fraction of constituents in the materials. Two-step leaching tests at liquid-to-solid (L/S) ratios of 2 and 10 were applied to the materials investigated in studies I and II, while one-step leaching tests at L/S 10 were applied to the materials investigated in study III. In all of these tests distilled water was used as a leachant, thus the pH of the leachate was dictated by the material itself.

Field tests

Field tests were used in all studies to assess the leaching of constituents from the materials in road or landfill cover constructions.

Two full-scale test roads were monitored: the Dåva test road, which is divided into sections built with BA1 or CR (Paper I) and the Björsbyn test road, where FS, BFS, CC and CR were used in separate road test sections (Paper IV). To collect leachate, 30 m² lysimeters were installed, partly under the open roadside slopes, in each section (Figure 1). Lysimeters were also installed in the middle of the road sections constructed with BA1 and CR (Paper I). Leachate was transported by gravity to sampling wells on the side of the road.
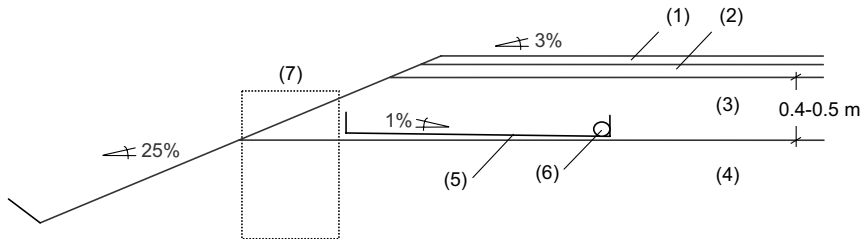
Figure 1   Schematic cross-section of a road test section with a lysimeter positioned under the roadside slope (Papers I and IV): (1) Wearing course, asphalt; (2) base, crushed rock; (3) sub-base, recycled aggregates or crushed rock; (4) subgrade; (5) lysimeter; (6) drainage pipe; (7) position of sampling well.

In the Tveta case study, three test areas of a full-scale cover construction built with sewage sludge and various types of ashes, were monitored (Figure 2; Paper III). Samples of water draining from the top of the liner (drainage) under gravity were collected in wells installed at the bottom of the landfill slope. Samples of water that percolated through the liner into the landfill (leachate) were collected by pumping from 1m² lysimeters placed randomly below the liner.
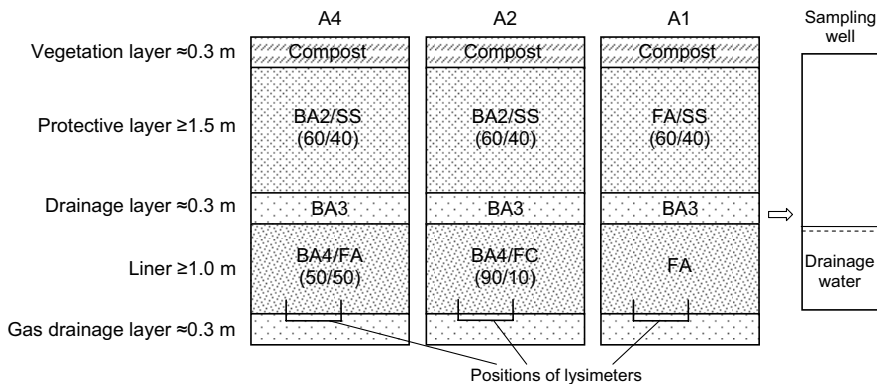
Figure 2   Schematic cross-section of the landfill cover test areas A1, A2 and A4 at the Tveta landfill indicating units for sampling drainage water and leachate. Abbreviations according to Table 2; FC = Friedland clay.

The potential use of untreated or treated soils contaminated with CCA from two sites, at Forsmo (F) and Robertsfors (R) (designated CSF and CSR, respectively) in the protective layer of a landfill cover was studied using outdoor, pilot-scale (1m³) lysimeters (Paper II). In order to evaluate the leachability of the soil mixtures, each lysimeter was equipped with triplicate soil moisture samplers for collection of pore water samples.

A summary of the water samples obtained in the field tests can be seen in Table 3.

Table 3   Monitoring programs of the case studies I-IV.

| Case	Length of sampling period	No. of samples	Analyses
Dåva (Paper I)	3 yr (2001-2004)[a] + 1 yr (2006-2007)[a]	21 + 5	pH, EC, T, alkalinity, elements (23), Cl⁻, SO₄²⁻, TS, VS, TOC, COD, BOD, nitrogen species
Björsbyn (Paper IV)	4 yr (1998-2002) + 1 yr (2006-2007)	10 + 6	pH, EC, T, Eh, alkalinity, elements (25), Cl⁻, SO₄²⁻,
CCA (Paper II)	2 yr (2005-2006) for CSF 2 yr (2006-2007) for CSR[b]	7 5	pH, EC, Eh, elements (9), DOC, As species
Tveta (Paper III)	2 yr (2004-2006) for A1 and A2 1 yr (2005-2006) for A4	10(A1), 11(A2), 5(A4)	pH, EC, alkalinity, elements (12), Cl⁻, nitrogen species

[a] Results for 2006-2007 were not included in Paper I.
[b] Results for 2007 were not included in Paper II.

Geochemical modelling

Geochemical equilibrium modelling was applied to leachates collected from the field lysimeters in order to: (i) identify minerals that may control the solubility of targeted constituents and (ii) to evaluate the possible neo-formation of minerals over time. Mineral saturation indices (SI) were calculated using the geochemical equilibrium speciation models PHREEQC-2 (Paper III; Parkhurst and Appelo, 1999) and Visual Minteq (Paper IV; Gustafsson, 2007) with the Minteq v4 database. The data for the calculations included measured elemental concentrations, pH, alkalinity, redox potential and temperature of the leachates.

Statistical analyses

Two-sample *t*-tests (Paper II) and Tukey's multiple comparison tests (Paper IV) were applied to determine the statistical significance of differences in means of variables of interest (with a significance threshold of $p < 0.05$).

In Paper I, multivariate data analyses were performed ($p < 0.05$) using partial least squares (PLS) projection to latent structures (Eriksson *et al.*, 2001) to evaluate the effects of factors such as the material (BA1 or CR) and lysimeter position on the leachate composition. These analyses were performed using Simca-P software developed by Umetrics AB (Umeå, Sweden).

4 RESULTS AND DISCUSSION

4.1 Environmental significance of the leachates

The significance of leachate emissions can be evaluated by applying either generic or case-specific criteria. The former generally consists of quantitatively expressed maximum recommended (or permitted) concentrations, or cumulative releases, of constituents from the source, while the latter may be applied to relate the restrictions to case-specific conditions (*e.g.* the state of the recipient). Comparisons of leaching from the investigated materials and normal conditions in affected recipients, *e.g.* background values of surface and ground waters, or toxicity values, can then be used to assess the potential environmental impact of an intended use.

Faced with decisions about whether to use recycled materials the default alternative is generally not to refrain from undertaking a planned construction, but to use conventional materials. Hence, it may also be pertinent to compare the leaching arsing from the use of recycled and conventional materials.

Constituents exceeding regulatory limits under compliance test leaching

Since no specific regulation for geotechnical applications of recycled materials have been established in Sweden as yet, the limit values for materials that can be deposited in inert waste landfills set by the EU Council (2003) were used in initial assessments of the leachates. These criteria aim to protect groundwater. It might therefore seem reasonable to assume that materials deemed to be acceptable for landfilling as inert will also be acceptable in construction applications. However, the criteria were derived from generic environmental scenarios (Hjelmar *et al.*, 2001), which are not necessarily relevant to the field applications discussed here.

Results of compliance leaching tests (CEN, 2002) indicated that only one of the tested materials met the acceptance criteria for inert waste landfills (Table 4). The CCA-contaminated soils and one of the ash mixtures used at Tveta even exceeded the criteria for disposal in non-hazardous waste landfills.

Iron treatment of the CCA-contaminated soils substantially reduced As mobility due to the high affinity of As for Fe oxides (Paper II). Leaching of As from CSF decreased by 54% after addition of SA (spent steel abrasive; Table 2), but it still exceeded limits for hazardous waste landfills (Table 4). Treatment of CSF with OSG (oxygen scarfing granulate; Table 2) decreased As leaching by 94%, to levels deemed acceptable for inert waste landfills, but increased Ni leaching by two orders of magnitude. The treatments were less successful for CSR. For example, after addition of OSG, the leaching of As from CSR still exceeded limits for inert waste landfills and the concentration leached from CSF by an order of magnitude (Paper II).

From the ashes investigated in the Tveta and Dåva case studies (Papers I and III), the release of salt-forming species such as Cl^- and SO_4^{2-} was high due to their abundance in the ashes and their high water solubility. Releases of the oxyanion forming elements Mo and Sb were also elevated, which may be due to the alkaline conditions (pH 9.5-12) established during the tests. Mo and Sb have high affinities for sorption onto Al- and Fe-(hydr)oxides, but their sorption decreases with increasing pH (Comans *et al.*, 2000;

Meima and Comans, 1998). The fly ash (FA), which was used in its fresh state, generated a strongly alkaline leachate (pH ~12). This probably explains the elevated leaching of Pb observed from the FA and its mixture with bottom ash (FA/BA4) since the solubility of Pb is lowest at intermediate pH (9-10), and increase with increasing pH.

Table 4   Classification of materials according to waste acceptance criteria for landfills based on compliance leaching tests (**x**). Analysed constituents exceeding corresponding landfill class are given in parenthesis.

		Landfill class		
		Inert	Non-hazardous	Hazardous
CCA	CSF	(Zn)	(As)	**x**
	CSF+1%SA		(As)	**x**
	CSF+8%OSG	(Ni)	**x**	
	CSR		(As)	**x**
	CSR+1%SA	(As)	**x**	
	CSR+8%OSG	(As)	**x**	
Tveta	BA2	**x**		
	BA3	(Cu, Cl⁻, SO_4^{2-})	**x**	
	FA	(Ba, Mo, Pb, Cl⁻)	**x**	
	BA4	(Cl⁻, SO_4^{2-})	**x**	
	BA4/FA	(SO_4^{2-})	(Pb, Cl⁻)	**x**
	SS	(SO_4^{2-})	**x**	
Dåva	BA1	(Mo, Sb, Cl⁻, SO_4^{2-})	**x**	
	CR	(As)	**x**	
Björsbyn	FS[a]	(As, Cu, Ni, Pb, Zn)	**x**	
	BFS[b]	(SO_4^{2-})	**x**	

[a] Based on data from Fällman and Carling (1998).
[b] Based on data from Fällman (1997).

Fayalite slag (FS) investigated in the Björsbyn case study (Paper IV), released elevated levels of several trace elements, exceeding the limit values for inert waste landfills (Table 4). In contrast, the concentrations leached from blast-furnace slag (BFS) were low. However, the BFS contains 1-2% S, causing elevated leaching of SO_4^{2-}. The CEN leaching test was not applied to the crushed recycled concrete (RC) and crushed rock (CR) used at Björsbyn, but results of previous two-step batch leaching tests performed at accumulated L/S ratios of 4 and 8 (Jacobsson and Mácsik, 1997) indicate that both materials would have met the acceptance criteria for inert waste landfills.

Comparison of the use of recycled and the conventional materials

Since the road test sections with recycled and conventional materials were identical in terms of design and were situated at the same site, they likely received similar external contamination loads from sources such as atmospheric deposition and road runoff. Thus, it seems reasonable to assume that any differences in their leachate compositions arise from the tested materials.

According to the field tests, the use of recycled materials as substitutes for conventional CR in the road sub-bases led to significantly higher leaching of several constituents (Table 5). However, the CR released similar, or even higher, concentrations, of some species, *e.g.* Ba, Mg and Zn than the recycled materials. Leachate from the Dåva bottom ash (BA1) was more alkaline and contained higher amounts of salts, organic matter,

nitrogen, Al, Cr and Cu than the CR leachate. SO_4^{2-}, which readily dissolved from the BA1 in the laboratory tests, was released in similar amounts from the Dåva CR in the field. This may be due to the presence of sulphide minerals in the CR, which release SO_4^{2-} and associated metals (*e.g.* Zn) upon oxidation in the field.

In accordance with the laboratory leaching test, high levels of metal(loid)s leached from the FS, exceeding those from the CR by more than an order of magnitude (Table 5). The BFS released high amounts of several constituents, including some metals, which was unexpected due to the low total concentrations of these elements in this material (Paper IV) and their low solubility in the laboratory tests (Table 4). This discrepancy may be related to the pH of the BFS leachate, which was significantly lower in the field than in the laboratory leaching tests (see chapter 4.2). RC generated the least polluted leachate, but it released higher levels of Cr and As than the CR.

Table 5   Comparison of average constituent concentrations in leachates from road sections with recycled and natural materials at Dåva and Björsbyn, respectively. --, -, +, ++ and +++ = >10-fold lower, 2-10-fold lower, 2-10-fold higher, 10-100-fold higher, and >100-fold higher, respectively. The differences were statistically significant (p<0.05).

		--	-	+	++	+++
Dåva	BA	Mg, Mn, Zn	Ba, NO$_3$-N	pH, EC, Alk, K, TOC, N$_{tot}$, NO$_2$-N	Al, Cl$^-$, Cr, Cu, Na, NH$_4$-N	
Björsbyn	FS		Mg	Ba	Cd, Mo, Ni, Sb	Cu, Zn
	BFS		pH, Ba	EC, Ca, Mg, SO$_4^{2-}$, Cd, Pb, Se, V	Al, Fe, K	Mn
	RC		Ba	As	Cr, Na	

For many constituents, the difference between leachates from BA1 and CR decreased over time, mainly due to changes in the ash leachate composition (Paper I). For example, after three years, the levels of Cu and Cl$^-$ were in the same range in both leachates, while those of Al and Cr were still ten-fold higher in leachate from BA1. The release of some species (*e.g.* Cu, Mo, Ni and Zn) from the FS decreased by 50-90% over ten years, but at least tenfold higher quantities of these elements were still being released from the FS than from the CR after ten years (Paper IV). The leaching of many constituents from the BFS varied as a function of pH, but generally decreased with time due to depletion of the fraction available for leaching (Paper IV). For example, the amounts of Al and Pb released from BFS and CR became similar after ten years. In addition, although the leaching of Cr from the RC decreased considerably over time, it was an order of magnitude higher than that from the CR throughout the sampling period.

Data on leaching emissions from landfill covers built with natural materials and geomembranes are not available. Hence, the contaminant loads of the alternative covers cannot currently be related to those of conventional solutions.

Discrepancies between the source and the state of the recipient

In Sweden, the water that comes into contact with the road base materials is usually discharged, without prior treatment, either to surface water via roadside drainage ditches or to groundwater via infiltration in the subsoil. Therefore, in order to assess the pollu-

tion potential of the field leachates their levels of pollutants were compared to criteria for priority pollutants of natural freshwater quality (Table 6), which are similar to, or lower than, those cited in the WHO drinking water quality criteria (WHO, 2006), but in the upper range of the normal background concentrations in Swedish groundwater (Aastrup *et al.*, 1995).

Concentrations of several constituents most strongly exceeded levels stipulated in freshwater toxicity criteria in leachates from the field applications of BA1, FS and BFS. In the FS leachate, Cu and Zn exceeded these criteria, while Al and Cu were the major pollutants in leachates from the BA1 and BFS. In fact, the concentrations of Al and Cu were elevated in leachates from all investigated materials, including the CR. The toxicity of Mo and Sb in natural water is not well documented, but releases of both of these elements from the BA1, and Mo from FS appeared to exceed the limits. Sb, Se and V were only analysed in the leachate samples collected during the sixth and tenth years of leaching, respectively. Although leached in moderate concentrations in this late stage they should not be overlooked in future environmental evaluations since most elements are leached in higher concentrations in the initial leaching phase.

The temporal leaching trends differed between the materials. For example, the BA1 released very high concentrations of Cl$^-$ (~16 mg l^{-1}) and Cu (~2 mg l^{-1}) in the initial phase, but the concentrations of both these constituents declined to about 0.2 mg l^{-1} in less than three years (Paper I). In a mung bean assay, Ore *et al.* (2007) showed that the first leachate from the roadside slope with BA1 could be acutely toxic to plants due to its high salinity. In contrast, the leaching of Cu from the FS showed a moderate decrease, from 0.5 mg l^{-1} to 0.2 mg l^{-1}, over ten years. Elevated releases of constituents from the BFS were associated with the occasional generation of acid leachates (pH<4, see chapter 4.2). Acid leachates may in themselves be of environmental concern, due to (*inter alia*) the risk of mobilisation of heavy metals in roadside soil.

Saline water such as BA leachates may also cause secondary effects through the mobilisation of metals such as organic- or oxide-bound Cu, Pb and Zn in roadside soil (Amrhein *et al.*, 1992; Bauske and Goetz, 1993; Norrström and Jacks, 1998). It may also enhance the mobility of Cd in the soil due to complexation with Cl$^-$ (Doner, 1978; Lumsdon *et al.*, 1995). In the long-term, however, the cumulative salt load originating from the BA may be negligible compared with that originating from road salt application. For example, as shown in (Paper I), the amount of Cl$^-$ available for leaching in BA1 per meter of the test road corresponds to the amount applied in 4.5 years of road salting at the average rate in Sweden of 6 kg of salt per meter road and year in (Bjelkås and Lindmark, 1994).

Leaching of constituents from the road base materials is expected to occur mainly from the roadside slopes, since asphalt pavement can reduce water infiltration by about 90% (Reid *et al.*, 2001). Hence, although leachates with highly elevated concentrations of constituents can occur under the road pavement (Paper I), this will probably be of minor environmental relevance as long as the pavement remains intact.

Attenuation processes such as dilution/dispersion of contaminants and sorption to soil particles may occur close to the source, thereby reducing their concentrations to acceptable levels. Modelling of reactive transport, by Apul *et al.* (2007), in a road base application of steel slag built on moderately attenuating soil (assuming a K$_d$ value of 50 l kg^{-1}

Table 6 Comparison of average constituent concentrations in field leachates and threshold values for freshwater quality.

-, ±, +, ++ and +++ = <2-fold lower, ±2-fold, 2-10-fold higher, 10-100-fold higher, and >100-fold higher, respectively.

		Minor constituents (µg l⁻¹)											Major constituents (mg l⁻¹)		
		As^{III}/As^{V} 15[a]	Cd 0.25[b]	Cr^{III}/Cr^{VI} 74/11[b]	Cu 9[b]	Mo 73[c]	Ni 52[b]	Pb 2.5[b]	Sb 20[d]	Se 5[b]	V 160[e]	Zn 120[b]	Al 0.087[b]	Cl 230[b]	SO_4^{2-} 400[f]
Dåva	BA1	±	+	±/+	++	+	-	+	-	+	-	-	+++	+	-
	CR	±	+	-/-	+	+	-	+	-	+	-	+	+	-	-
Björsbyn	FS	-	+	-/-	++	+	+	+	+	+	-	++	+	-	+
	BFS	-	+	-/±	++	-	-	+	-	+	±	+	++	-	-
	RC	±	-	±/+	+	-	-	±	-	+	-	-	+	-	-
	CR	-	-	-/-	±	-	-	±	-	±	-	-	±	-	±
CCA	CSF	++	+[g]	-/±	±	n.a.	±	±[g]	n.a.	n.a.	n.a.	++	n.a.	n.a.	n.a.
	CSF+1%SA	+	+[g]	-/-	-	n.a.	+	±[g]	n.a.	n.a.	n.a.	+	n.a.	n.a.	n.a.
	CSF+8%OSG	±	+[g]	-/-	+	n.a.	++	±[g]	n.a.	n.a.	n.a.	+	n.a.	n.a.	n.a.
	CSR	±	+[g]	-/-	+	n.a.	-	±[g]	n.a.	n.a.	n.a.	+	n.a.	n.a.	n.a.
	CSR+1%SA	±	+[g]	-/-	-	n.a.	+	±[g]	n.a.	n.a.	n.a.	+	n.a.	n.a.	n.a.
	CSR+8%OSG	±	+[g]	-/-	-	n.a.	+	±[g]	n.a.	n.a.	n.a.	+	n.a.	n.a.	n.a.
Tveta	FA+SS	+	+	-/±	++	+	+	+	±	++	n.a.	++	+	++	+
	BA2+SS (A2)[h]	+	++	-/±	+++	++	+	++	+	+++	n.a.	++	+	++	++
	BA2+SS (A4)[h]	+	++	-/-	+++	+	+	++	+	++	n.a.	++	++	++	n.a.

n.a. – not available

[a] Guideline values for an increased risk of biological effects, *e.g.* impacts on the reproduction or survival of freshwater organisms, issued by the Swedish EPA (2000).

[b] Threshold values for chronic toxicity of natural freshwater to aquatic life issued by the US EPA (2006).

[c] Canadian interim freshwater criteria issued by CCME (1999).

[d] WHO drinking water quality criteria (WHO, 2006).

[e] Proposed by Beusen and Neven (1987) as a water quality criterion based on V toxicity to different freshwater organisms. Similar to the WHO drinking water quality criteria (70 µg l⁻¹).

[f] Maximum tolerable level for sensitive aquatic moss in soft water (<19 mg CaCO3 l⁻¹; Davies, 2007). Concentrations up to 1500 mg l⁻¹ may be tolerable in water of increasing hardness (up to 105 mg CaCO3 l⁻¹).

[g] Range of concentrations: <0.5-16 µg Cd l⁻¹ and <0.5-4 µg Pb l⁻¹. The difference between treatments was not significant (α<0.05).

[h] Refers to the protective layer of Tveta landfill cover test areas 2 and 4, respectively (Figure 2).

for metals) indicated that less than 10% of the initial mass of any constituent in the base layer reaches shallow groundwater after 20 years, unless the pavement is severely damaged. While metals were strongly retarded by the subsoil, salts were eroded from the edges (under the shoulders) without any significant retardation and could reach the groundwater within a few years.

In contrast to water percolating through a road pavement, water discharged from a landfill cover may be collected and treated together with the landfill leachate. However, before being discharged to a treatment plant, leachate from the liner will percolate through the de posited waste. This can cause changes in its composition due to processes such as the trapping of trace metals by organic matter complexation and formation of low-solubility sulphides in the waste. Further, the amounts of leachate generated are low. At the Tveta landfill, volumes of <3-30 l $(m^2 \ yr)^{-1}$ were observed below the compacted ash liner (Paper III). The leachate is therefore expected to have a minor influence on the overall leachate as long as the landfill is in operation, but this awaits field verification. Any environmental impact caused by leachate from the liner is dependent on the long-term performance of the liner (see chapter 4.2).

The use of ashes in the protective layer is of greater concern than their use in the liner. Based on an average precipitation of 600 mm yr^{-1}, an estimated 150 l $(m^2 \ yr)^{-1}$ of drainage water can be expected from the Tveta test areas (Paper III). Compared to the freshwater quality criteria, drainage water contained high concentrations of Cl^- and trace elements such as Cd, Cu, Pb, Se and Zn (Table 6). It also contained relatively high amounts of nitrogen (N_{tot}), likely due to the use of SS since the leaching of N_{tot} from the ashes was comparatively low (Paper III). The elevated release of trace metals could be related to their complexation with dissolved organic matter originating from the ashes and SS (c.f. chapter 4.2). The use of FA rather than BA in the protective layer led to lower availability of dissolved organic matter in the drainage (as indicated by the concentration of TOC; Paper III), which may explain the lower release of trace elements from the mixture with FA and SS than from that with BA and SS (Table 6). However, this needs to be evaluated further. Since the leaching of most constituents showed no clear tendency to decline over time, assessing required durations of treatment for the drainage water is difficult. Highly water-soluble species such as Cl^- and nitrogen may be depleted when an L/S of 2 is reached, *i.e.* within one to two decades (Paper III; Andreas *et al.*, 2007). Rates of decline of trace element leaching are more difficult to predict since they are dependent on factors such as the rate of organic matter degradation in the protective layer.

Results of the pilot-scale lysimeter tests indicate that the use of treated CCA-contaminated soil instead of ash mixtures in the protective layer would result in lower leaching of many constituents and, hence, reduce the need for treatment (Table 6). Nevertheless, the water discharged showed elevated concentrations, to varying extents (depending on soil type and amendment), of As, Cd, Ni and Zn. The addition of iron-bearing materials such as SA and OSG effectively reduced the leaching of some species, *e.g.* As and Zn (Paper II). However, OSG and (to a lesser degree) SA also contain chemical impurities, *e.g.* Mn and Ni, which were released upon oxidation of OSG and SA in the soils (Table 6; Paper II). In order to improve the efficiency of the iron stabilisation and minimise the risks of undesirable side-effects, increased proportions or use of smaller particles of metallic iron such as the SA would probably be the best alternative (Paper III). Before application in a landfill cover, factors related to the functional per-

formance of the soil mixtures (*e.g.* water permeability) need to be verified and possibly modified using additional materials. Any further amendments made may also affect, either negatively or positively, the mobility of the critical constituents, which must not be overlooked.

Concluding remarks

The use of recycled materials as substitute aggregates for conventional materials in the constructions led to increased leaching of several environmentally relevant constituents. However, this does not provide definitive indications that their leachates would have unacceptable environmental impacts, since (i) conventional CR can also release elevated concentrations of some constituents (*e.g.* Zn from the Dåva CR), and (ii) constituents may be leached at higher concentrations from the recycled materials without necessarily being environmentally significant (*e.g.* As from the RC). As discussed in section 4.3, the significance of leaching emissions from the recycled materials can also be seen in the context of other environmental impacts related to the default alternative, *i.e.* landfilling of industrial residues and extraction, pre-processing and transport of the CR.

Leachates from the recycled materials in the constructions in the initial leaching phase were polluted compared to natural water and could have toxic properties. However, the initial leachates may not be environmentally significant since attenuation processes occurring close to the source may considerably decrease constituent concentrations. A more important consideration is the amounts of constituents released over time from the materials, which is also influenced by the construction design. Upon incorporation of materials in, or their placement under, low-permeability layers (*e.g.* landfill liners or asphalt pavements) the amounts released were minor and, hence, the cumulative environmental impact will be low as long as the construction remains intact. For uncovered utilisation scenarios, the release of readily mobile constituents such as Cl^- from ashes may, at least in the short term, become a concern in *e.g.* water catchment areas. As for the trace elements, the environmental impact caused by leaching will to a larger extent be dependent on the characteristics of the transport media.

The laboratory and field tests did not always identify the same critical constituents, indicating the deficiencies of the batch leaching test for simulating leaching conditions in the field. Batch tests are among the most simplified tests, in that the only release-controlling factor they consider is the amount of water. However, interactions of the tested material with other materials and environmental conditions in the field can substantially affect (positively or negatively) releases, causing release rates to be very different from those estimated using batch tests. For example, the leaching of metals such as Cu and Zn from the BFS was low in the batch tests, while elevated releases were observed in the field. Similarly, the leaching of these elements from the BA2 and SS was low in the laboratory tests, but elevated from the protective layer with a mixture of BA2 and SS. Conversely, the leaching of As from the CSR exceeded limits for non-hazardous waste landfills, but only occasionally reached the threshold value of freshwater toxicity in the field lysimeters. Thus, it is not possible to assess the significance of leaching emissions from a material based solely on results of compliance batch leaching tests and generic criteria. The effects of a specific location and methods of use must be considered.

4.2 Factors controlling the leaching of constituents

Many laboratory tests used to simulate field leaching are based on assumptions that conditions will be saturated and that changes in leaching conditions will be relatively minor. However, materials in field applications are often not continuously wetted but are subject to cyclic wetting and drying. During periods of unsaturated conditions, many processes may occur that change the chemical and physical properties of the materials (*e.g.* carbonation, oxidation/reduction and mineral precipitation). These processes can influence the potential and actual rates of constituent release and transport from the solid matrix.

Water-to-solid contact frequency

Physical properties of the materials used in field applications, such as the degree of compaction, and placement of granular materials under a low permeability cover affect the extent and rate of leaching. Solid-state diffusion is likely to be the major process mediating leaching from materials that are well compacted, *e.g.* in a landfill cover liner, or covered by asphalt, *e.g.* under the pavement of a road construction (Apul *et al.*, 2007; Kosson *et al.*, 1996). In porous layers, where water percolates through the material, *e.g.* in roadside slopes or the protective layer of a landfill top cover, solubility could be a key determinant of constituent release (Kosson *et al.*, 1996). Rates of release and transport of constituents are generally substantially lower of they are predominantly limited by diffusion rather than by solubility. For example, slope leachates collected from the BA road section contained about 0.02 g Cl$^-$ l^{-1} after three years and road leachate about 1 g Cl$^-$ l^{-1} (Figure 3; Paper I), indicating that there was ca. 50-fold difference in cumulative water infiltration between the asphalted parts of the road and the open roadside slopes. Other constituents, *e.g.* Cu, showed similar tendencies, since their concentrations were up to an order of magnitude higher in road than in slope leachates after three years. The leaching patterns of Cr substantially differed, since Cr concentrations were lower in road than in slope leachates. Possibly, the conditions were more oxidising at the edge of the construction than under the pavement, allowing Cr to occur in its more mobile hexavalent form in the slope leachates.

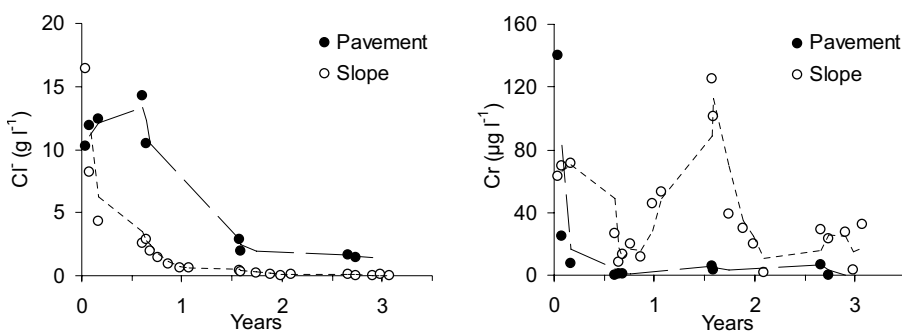Figure 3   Changes in concentrations of Cl$^-$ and Cr in leachates from the BA1 in the Dåva test road. Leachates were collected from below the asphalt pavement and the roadside slope, respectively. Trend lines represent moving averages over time.

pH

Upon prolonged exposure to CO_2 from the atmosphere or biological degradation, carbonation processes can decrease the pH of alkaline solutions towards the level of a calcite buffered system (~pH 8.3; Stumm and Morgan, 1996). The pH of leachates from the roadside slopes of the test sections with BA and RC decreased to about pH 8, irrespective of the initial pH (Figure 4). The pH in the BFS road section decreased even further (see *Redox potential* below). However, the pH values measured in leachate collected at the edge of the construction are not representative for the whole road body. Leachate collected from the middle of the BA road section had pH values of 8-11 during the sixth year, possibly indicating flow channelling.
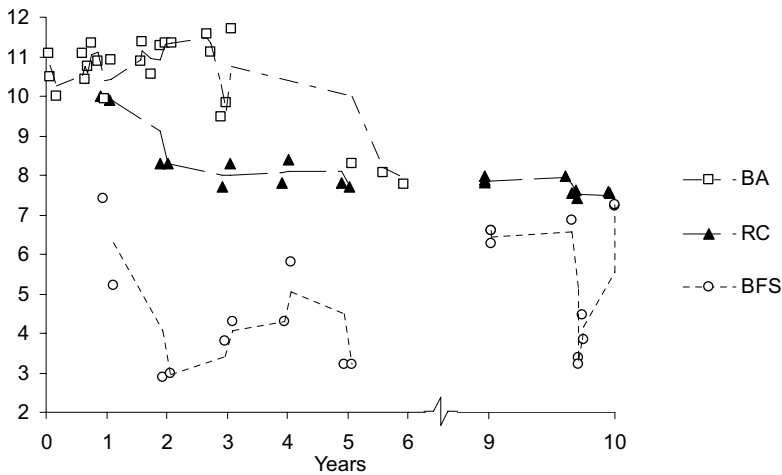

Figure 4   Changes of pH in the leachates from the roadside slopes of the road test sections with BA, RC and BFS over time. Trend lines represent moving averages over time.

Carbonation may induce important changes in the leachate composition. For example, in a laboratory assay the leaching of Pb and Zn was found to increase after moderate carbonation of the Dåva BA (Todorovic and Ecke, 2006). However, in leachates from the test road the concentrations of these elements remained low during the sixth year (~1 µg Pb l[-1] and <0.6 µg Zn l[-1]; Paper I), indicating that other processes outweighed the carbonation effect. The leaching of oxyanionic species from uncarbonated cement-based products could be expected to increase as the leachate pH decreases towards neutral to mildly alkaline (Van der Sloot, 2000). The release of some species, *e.g.* As and Cr, from RC in the test road increased markedly as the pH decreased (from 10 to ~8; Figure 4), but the increase was of short duration (Paper IV). In the presence of carbonation, Sanchez *et al.* (2002) found that the solubility of As increased due to As re-speciation, but decreased with decreasing solution pH. Hence, carbonation can also influence constituent speciation, the effects of which may outweigh pH effects for some constituents.

Despite the initial biodegradation of organic matter in the BA in the test road, the production of CO_2 was too low to influence the BA leachate pH (Paper I). In the landfill cover application (Paper III), CO_2 generated from degradation of the landfilled waste and sludge in the protective layer is likely to be a key determinant of the rate of ash car-

bonation. However, the pH of the ash leachate remained high (10-11) and relatively constant over the monitoring period, indicating that there were kinetic constraints. Future reductions in pH from >10 to 8-8.5 may, for instance, increase the leaching of Zn but reduce the leaching of Al, Mo and Pb from the ashes (Meima and Comans, 1997).

Redox potential

Reducing materials may remain reduced during short-term tests, but become oxidised upon prolonged contact with air under field conditions, which could alter the leaching conditions substantially. Evidence of such effects was seen in the comparison between the pH and redox potentials (pE) observed in laboratory and field tests performed on BFS (Figure 5). The analyses of the leachates indicted that BFS was exposed to significantly more reduced conditions in the laboratory tests than in field conditions, presumably because in the former saturated conditions are usually maintained and fine-grained (<4 mm) BFS was used, while the coarse-grained (<125 mm) materials in the lysimeters retain water poorly and provide greater exposure to atmospheric CO_2 and O_2. Although carbonation can be expected to reduce the leachate pH to 8-9, the pH in the field leachates decreased even further to (at its lowest point) <4, probably due to the oxidation of reduced sulphides in the BFS (Paper IV; Fällman, 1997). Similarly, Schwab *et al.* (2006) observed variations in pH between 4.8 and 11.5 in leachates from a highway embankment built with air-cooled BFS, which were attributed to the formation of BFS leachates under fluctuating oxidised and reduced conditions. As discussed previously, the decrease in pH significantly increased the solubility of many constituents (*e.g.* Al, Ca, Cr, Cu, Pb and Zn) from the BFS road section. It can be hypothesised that the use of well-graded BFS with a relatively high portion of fines would reduce the access of air and percolation of water and, hence, the risk of acidity developing, with associated trace metal releases.
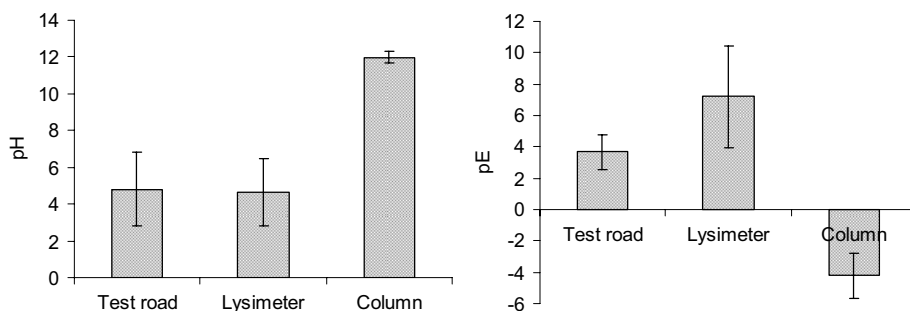
Figure 5   Average pH and pE (±SD) of BFS leachates from the test road, pilot-scale lysimeters and laboratory column leaching tests. Data for the lysimeters and the column tests are from Fällman (1997).

Redox conditions could also become more reducing under field conditions than in laboratory tests. For example, diffusion of landfill gas from the deposited waste is expected to create a redox gradient in landfill cover constructions, with more reducing conditions in the lower parts of the cap. This is illustrated in the Tveta case study by the higher proportions of oxidised nitrogen species in the drainage water than in the leachate, where nitrogen occurred mainly as NH_4-N (Paper III). The reducing conditions in the

liner resulted in higher releases of some species (*e.g.* As and Se) from the liner than from the protective layer. However, the geochemical equilibrium calculations indicated that the precipitation of metal sulphides in the liner might be possible if the conditions become even more reducing, which could contribute to the trapping of trace metals in the ashes.

Degradation of organic matter in soil over time could promote the development of reducing conditions if the soil system is not sufficiently aerated. Such conditions have been shown to increase As mobility in stabilised CSF and CSR by causing dissolution of iron oxides and the reduction of As(V) to the more toxic As(III) species (Maurice *et al.*, 2007). In the field lysimeters, the concentrations of Fe in pore water from the amended soils were low and the predominant As species was As(V), indicating that the soil conditions remained aerobic (Paper II). Hence, in this respect, recycling the stabilised soils as a cover material at landfills is a better management option than disposal in anaerobic landfills.

Presence of dissolved organic matter

The mobility of many constituents may be strongly impacted by the presence of dissolved organic matter. For example, the availability of organic ligands positively influences the mobility of Cu in ashes (Chandler *et al.*, 1997; Meima *et al.*, 1999).

A statistically significant correlation between releases of Cu and TOC from the road test section with BA has been reported by Ore *et al.* (2007). The release of these elements decreased in a wash-out manner, by about 90% over three years (Figure 6). The loss-on-ignition (LOI) of the BA was low (12 ± 0.8 g (kg TS)$^{-1}$; Paper I), indicating that it has a low content of organic matter. Hence, the content of TOC in the leachate from this material was expected to decline over time.
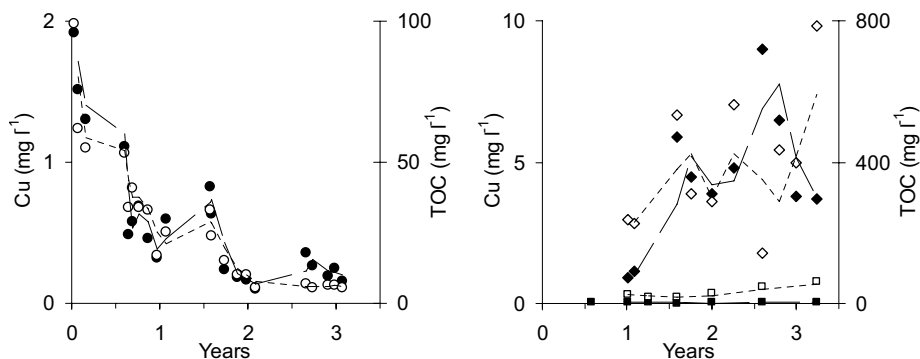
Figure 6   Changes in concentrations of Cu (filled symbols) and TOC (open symbols) in ash leachates from the roadside slopes of the Dåva test road (left) and the Tveta landfill cover (right) over time. Dåva, ● and ○ = BA1; Tveta, ■ and □ = BA4+FC, ◆ and ◇ = BA2+SS. Note the different scales of the figures.

In the Tveta landfill cover, the leaching of Cu was ten-fold higher from the protective layer with the mixture of BA and sludge (SS) than from the liner with the mixture of BA and Friedland clay (FC), which corresponds well with the higher concentrations of

TOC in leachate from the latter (Figure 6). The LOI of the BA/SS-mixture (~200 g (kg TS)$^{-1}$; Paper III) indicated a high content of organic matter and the release of TOC and, consequently, Cu showed no tendency to decline over the three-year period. Geochemical modelling indicated that the solubility of cuprite (Cu_2O) could be a major determinant of the release of Cu from the liner with BA and FC (Paper III), *i.e.* organic matter complexation probably had a minor influence. Binding of organic matter to the FC may explain this effect since clay minerals such as montmorillonite are known to sorb natural organic substances in soil strongly (Baham and Sposito, 1994; Kaiser and Zech, 2000).

Dissolved organic matter also has a high affinity for iron oxides, which may impair the efficiency of iron stabilisation treatments. The adsorption of some species, *e.g.* As, by iron oxides has been reported to decrease as a result of dissolved organic matter competing for sorption sites (Grafe *et al.*, 2001; Redman *et al.*, 2002). Such processes likely explain the lower treatment efficiency for As in the soil with the relatively high organic matter content (CSR) than in the soil with low organic matter content (CSF) (Paper II).

Particle size

For a soil treatment with iron to succeed, optimising the contact between the iron product and soil contaminants is essential. In the field experiment, the addition of SA to CSF and CSR reduced the leaching of As by (on average) 54-68% and 24-36%, respectively (Paper II). The effect of SA was weaker than expected; a similar iron product was found to reduce As leaching by 99% in previous laboratory tests (Kumpiene *et al.*, 2006). However, smaller particles (<0.1 mm instead of <1 mm) were used in the latter, which have greater reactivity due to their larger relative surface areas. The degree of mixing of the soil and iron product should also be considered. It can be hypothesised that better mixing may be achieved in laboratory-scale tests than in the field, and when using smaller particles, which increases the probability of chemical interactions.

The duration of contacts between particles and percolating water is also a key factor to consider in order to elucidate constituent release mechanisms. For example, if the weathering of minerals in the BFS that reduce acidity by binding protons (calcium hydroxide and silicate minerals) was more rapid than that of minerals that generate acidity (sulphate minerals), this will result in alkaline solutions. Hence, the observed reduction in leachate pH to <4 indicates that the acidifying weathering reactions outcompeted those that reduce acidity. In the BFS road test section, dissolution of calcite - which is formed when easily dissolved $Ca(OH)_2$ reacts with atmospheric CO_2 - was initially the most rapid reaction, as indicated by leachate equilibrium with respect to calcite, and abundant releases of Ca (Paper IV). This resulted in a leachate pH >7. Deviation from solubility equilibrium in the following leachate samples indicated depletion of available calcite, which could be due to slow diffusion of ions from the interior of particles to their surfaces. Studies of mining waste rock indicate that calcite within particles larger than 5-10 mm dissolves too slowly to neutralise acid production by sulphide oxidation (Strömberg and Banwart, 1999). As the pH decreases to 3-4, the dissolution rate of silicate minerals accelerates, which inhibits further reductions in pH, *i.e.* the effluent pH is controlled by relative rates of sulphide and primary silicate mineral dissolution (Strömberg and Banwart, 1994). Temporary neutralisation of the leachate pH may thus be due to remaining reservoirs of calcite in fine particles (indicating flow channelling) or ions diffusing from the interior of large particles during prolonged water retention.

Mineral transformations over time

When exposed to atmospheric conditions, the materials are subject to a number of weathering reactions which may cause alterations of metastable minerals and formation of new phases. Such processes can greatly affect the long-term environmental and technical performance of the materials by inducing changes in constituent solubility as well as structural properties of the material matrix.

For example, one of the incentives for using ashes in landfill liners is their capacity for mineralogical changes leading to the precipitation of clay-like structures (Zevenbergen *et al.*, 1999; Zevenbergen *et al.*, 1994) which may reduce the hydraulic conductivity of the liner over time. Geochemical equilibrium modelling indicated the potential formation of several clay minerals in the liner of two of the test areas after less than three years of weathering (Paper III). Clay and other secondary minerals, *e.g.* carbonates and amorphous Fe- and Al-(hydr)oxides, can also effectively retard several trace elements once formed in weathered ash (Meima and Comans, 1999; Piantone *et al.*, 2004; Zevenbergen *et al.*, 1999). Fe-(hydr)oxides which may sorb oxyanion-forming elements (*e.g.* As, Sb and Se), and carbonates which may trap heavy metals (*e.g.* Cd, Pb and Zn) are relatively stable under atmospheric conditions. Thus, they may constitute stable scavenging media in the long-term as the landfill cover system becomes increasingly aerated. In the long term (several hundred years), oxidising conditions are expected to develop in the ash liner due to depletion of the substrates for microbial degradation in the deposited waste. As indicated by the geochemical modelling, this might induce the precipitation of several Fe-(hydr)oxides (Paper III).

In smelter slags such as FS, trace metals are incorporated in metastable glass phases, which may take relatively long periods of time to alter and dissolve, but their contribution to the leaching processes may still be important (Yan and Neretnieks, 1995). Several studies have indicated that dumps with fayalitic smelter slags at abandoned mine sites could cause significant long-term releases of potentially toxic elements due to natural weathering (Kucha *et al.*, 1996; Parsons *et al.*, 2001; Piatak *et al.*, 2004). However, as for the ashes, the precipitation of secondary phases such as amorphous Fe-, Si- and Al-oxyhydroxides may contribute to the retention of species released upon glass phase dissolution.

Further studies should therefore be directed towards improving our understanding of the dissolution or alteration of the original minerals in the materials under various environmental conditions.

External contamination

Several factors may complicate the evaluation of constituent leaching data obtained from field tests. For example, air intruding during collection and sampling may affect the status of alkaline water samples. Care was taken to minimise atmospheric exposure of all of the fresh samples collected from the field, *e.g.* by completely filling the sampling bottles or flushing the headspace by inert gas. However, the sampled percolated water was at greater risk of exposure to external influences due to its storage prior to sampling, especially samples from the Björsbyn test road, where the drainage pipes from the lysimeters enter wells with open water surface (Paper IV). Initially (during 1998-2002), the water was stored in contact with the atmosphere for up to two weeks

prior to sampling, while samples collected during 2006-2007 were taken at the outlet of the drainage pipe. In the latter case, the only contact between the percolated water and atmosphere occurred during transportation through the 4 m long drainage pipe. However, the measured pH of leachates collected during the two time periods was in good agreement (Figure 4; Paper IV).

Samples collected in the field may also be influenced by contamination from other sources, *e.g.* surface runoff water and atmospheric deposition. Comparing results from tests performed at the same site may help to evaluate the possible significance of such possibilities. For example, the possibility of acid rain giving rise to the acid BFS leachate can be ruled out since no concurrent pH decrease was observed in leachates from the other road test sections (Figure 4; Paper IV).

To minimise the risk of external contamination, use of a closed lysimeter system (as for the Dåva test road; Paper I) or, even better, extraction of pore water (as for the CCA-contaminated soils; Paper II) is preferable.

Concluding remarks

In order to accurately predict the release of constituents from the materials under field conditions the following important factors were identified:
-   Water-to-solid contact frequency: As assesses by the difference between leachates collected under the road slopes and pavement, increased water-to-solid contact frequency increased the mobility of many constituents, especially readily soluble salts.
-   Carbonation: As indicated by changes in pH of the leachates, recycled concrete and ash in the open roadside slopes were carbonated within three to six years after construction, while less carbonation effects were observed for ashes used below the asphalt pavement and in the landfill liner. For example, carbonation led to a temporary increase in the leaching of oxyanions from the recycled concrete, indicating the impact of carbonation on both pH and constituent speciation.
-   Redox conditions: Oxidation of sulphidic slag exposed to the atmosphere in roadside slopes led to reductions in pH and subsequent increases in trace metal leaching. In landfill covers, a redox gradient with more reducing conditions in the liner than in the protective layer was established due to the diffusion of landfill gas from degradation of the deposited waste. This led to a higher leaching of oxyanions from ashes in the liner than from those in the protective layer.
-   The presence of organic matter: Increased availability of dissolved organic matter increased the mobility of several trace elements in ashes and soil due to complex binding or competitive sorption. As previously noted, the presence of biodegradable materials also indirectly affected the trace element mobility due to changes in redox conditions.
-   Particle size: There is a difference in reaction rates between fine materials tested in laboratory assays and coarse materials applied in field, which were indicated by the limited neutralisation reactions upon oxidation of the sulphidic slag.
-   Mineral transformations: In the long term, secondary phases formed upon mineral dissolution or alterations in the materials are expected to control constituent leaching.

4.3   Environmental assessment of the recycled materials

Given knowledge about a material and its placement, various methods could be applied to estimate the potential environmental impacts and to demonstrate the acceptability of an intended use. There are at least three different approaches to be noted (Lidelöw, 2004):
-    Source term assessment
-    Risk assessment
-    System analysis

An assessment can be performed with regard to one, two or all of these aspects. The aspects that should be considered, and to what extent, depend on the aim of the assessment. This is also largely contingent upon the values and attitudes of the stakeholders.

Source term assessment

The potential release of constituents from a given material can be estimated through measurements of fundamental properties that affect leaching, such as availability, solubility and mass-transfer rates of relevant species in appropriate laboratory leaching tests (Kosson *et al.*, 2002; Van der Sloot *et al.*, 1997). However, even if the leaching mechanisms can be reasonably well simulated in the laboratory, the predictability of leaching in field situations is limited due to the effects of reactions with slow kinetics (*e.g.* mineral transformation, carbonation and organic matter degradation) and external stresses (*e.g.* infiltration rates and design features) in the field. Leaching tests should not therefore be regarded as accurate simulations of field scenarios, but rather as a means to understand how factors that affect releases, such as pH, redox conditions and water contact may affect the tested material. Further, although a wide range of tests are available, appropriate tests to assess the impact of variations in redox conditions and degree of water saturation are needed.

To properly evaluate the source term, it is essential to define the relevant range of environmental conditions that the material may be exposed to in the long term. For example, constituent leaching from ashes at pH 4-6 is relevant for characterisation, but less important for the evaluation of environmental impacts since these pH values are unlikely to be reached during field exposure due to calcite buffer formation. The relevant range of conditions to consider for each specific application may be quantified using physical simulators (*e.g.* lysimeter tests), in which the influence of factors such as biological activity in the material and construction design can be studied (see section 4.2). In addition, geochemical modelling can provide useful insights into the role of sorption processes, solubility-influencing minerals and complexation with dissolved organic matter (Apul *et al.*, 2005; Meima and Comans, 1997). Such models can also be coupled with reactive transport codes to estimate quantitatively the importance of time-dependent processes (De Windt *et al.*, 2007; Dijkstra *et al.*, 2008).

The intense research on wastes as pollution source terms has led to the development of a methodological standard, EN12920 (CEN, 1997), which addresses a series of steps aiming to define the range of anticipated field conditions, determine fundamental leaching properties for the material using leaching tests, and estimate long-term releases based on mass-transfer models of the considered scenario. However, the standard does not provide any guidance about the experimental and modelling tools that could be used.

Risk assessment

In relation to leaching tests, risk assessment is a more comprehensive method for assessing the environmental effect of a material since it considers the entire causal pollution source-transfer-recipient chain. Simplified procedures for waste recycling scenarios based on ecological risk assessment methodology have been implemented (*inter alia*) in Denmark and the Netherlands (Danish MoE, 2007; VROM, 1999) and proposed (*inter alia*) in Finland, France, Norway and Sweden (ADEME, 2002; Hartlén *et al.*, 1999; Håkansson *et al.*, 2004; Mroueh *et al.*, 2000; Petkovic *et al.*, 2004). Of these, the proposed French ecocompatibility method comprises the most detailed evaluation, requiring case-specific data to characterise each of the three subsystems pollution source, pollution transport and impact on living organisms (ADEME, 2002). In most of the other models only the source term is assessed experimentally, while the transfer and impact on recipients are estimated from generic models. For example, the transfer of pollutants from the source to the recipient is often assessed by extrapolating leaching test results using generic dilution or retardation factors. Further, while models such as the French and Norwegian ones use the EN12920 methodology to assess the source term, standard leaching tests are specified in the Finish and Dutch models.

While the French model can identify and quantify impacts on specific targets (a population or individual species; ADEME, 2002), all other models evaluate the risk qualitatively by comparing leaching test results with generic criteria aiming to protect a predefined recipient (usually ground water or soil). Applying generic criteria facilitates the evaluation, but introduces a risk for inappropriate uses (*e.g.* if applied to recipients other than those intended). The case-specific assessment proposed in the French model requires more resources, but is likely to provide more accurate evaluations (*i.e.* it is less likely to over- or under-estimate risks) than the use of generic criteria. There have been few published case studies in which risk assessment methodologies was used to evaluate waste recycling scenarios and to verify the proposed assessment models. However, Tiruta-Barna *et al.* (2007) report some application cases (field studies) that were used for the development of the French model and work is ongoing (Hjelmar *et al.*, 2007) to validate the Danish model.

System analysis

While much focus has been placed on risks of constituent leaching, other environmental factors related to energy use and avoidance of landfilling have received relatively less attention. To address the environmental impacts of using recycled materials from a broader perspective, approaches based on life-cycle concepts may be useful (Roth and Eklund, 2003). Apart from identifying the most significant environmental impact to be expected from specific materials or their applications, such approaches can be used in comparative studies of the effects of different construction materials (Birgisdóttir *et al.*, 2006; Mroueh *et al.*, 2001; Olsson *et al.*, 2006) and management options, *e.g.* landfilling versus recycling, of a material (Birgisdóttir *et al.*, 2007).

Olsson *et al.* (2006) and Mroueh et al (2001) found that while the use of by-products as substitutes for natural aggregates would reduce energy use, higher leaching of metals could be expected. On the other hand, if leaching from the whole system (including environmental impacts from landfilling) and the total content available for leaching was considered, the difference in leaching between the alternatives was marginal (Birgisdót-

tir *et al.*, 2006; Olsson *et al.*, 2006). However, since system boundaries and case-specific data affect the outcome, the results cannot be generally applied and need to be complemented with local assessments. Data and knowledge obtained from risk assessments may therefore serve as inputs to evaluations such as life-cycle assessments (LCA), while LCAs can provide indications of the relative importance and relevance of potential impacts for risk assessments. However, the combination of global- and local-scale impact assessments is not straightforward since they may give different or even contradictory results.

Regulatory and economic aspects

From the legislative perspective, all industrial residues are wastes. Anyone who intends to recycle them has to apply for an environmental permit unless the potential environmental impact may be regarded as minor. In Sweden, no general procedure to evaluate the feasibility of using recycled materials in different applications has been formulated, and no criteria have been established to assess threshold loads that should be regarded as acceptable. This situation leads to lengthy and costly legal processes, which considerably reduces interest in using recycled materials among prospective users.

The problem of establishing environmental guidance for using recycled materials in construction arises from the conflicting interests of two Swedish Environmental Quality Objectives; a God bebyggd miljö (literally, Good Built Environment) and a Giftfri miljö (Non-Toxic Environment). The former objective emphasises the sustainable management of natural resources. The use of recycled materials in construction helps fulfil specific targets linked to this objective, such as reducing landfilling and exploitation of natural resources. The official formulation of the latter objective states that "The environment must be free from man-made substances and metals that represent a threat to human health or biological diversity". This may be interpreted as referring to the total element concentrations of a material. However, such an approach is not technically valid for judging the environmental impact because the release and transport of the constituents play a major role in determining risks and can be very different for each specific case (see chapters 4.1 and 4.2).

Risk assessment could provide indications of the relationships between the results of leaching tests and maximum acceptable loads for specific targets. Unfortunately, such assessments are resource- and time-consuming and need to be simplified, *e.g.* through the use of predefined scenarios, in order to be practical. However, such an approach was, for example, successfully adopted in Danish and Dutch legislation. A survey of Swedish road construction projects with recycled materials showed that little (and varying) information about the surrounding environment is taken into account in assessments of different materials' suitability for use in different applications (Visser, 2003; Östman, 2002). This also implies that the accuracy of the assessments varies. Hence, risk assessment approaches could be useful to improve the quality and consistency of environmental impact assessment (EIAs) of planned construction projects.

If not validated as secondary raw materials, large amounts of mineral waste will be disposed of in landfills, with considerable consumption of energy and natural raw material (and thus, simply reallocation of the problem). System analysis based on life-cycle concepts could be used to assess the relative merits of using natural resources versus the leachability of contaminants. Such analyses could be useful tools for strategic environ-

mental assessment (SEA), which is required for strategic decision-making in construction planning (EU Council, 2001).

From an economical perspective, it can be advantageous to substitute natural materials for recycled materials. For example, the Tveta landfill cover system is about half as expensive as the conventional solution with geomembranes and natural mineral materials if alternative costs for natural materials and landfilling fees are taken into account (Tham *et al.*, 2005). With respect to roads, industrial residues such as slags and ashes that are generated close to urban centres are becoming increasingly competitive as proximal sources of natural materials become depleted. However, the administrative costs involved in regulatory processes may be hindrances for waste recycling.

Extensive testing following the principles of risk assessment increases testing costs relative to the material-based approach, but these initial costs may be offset by alternative costs of, for instance, landfilling and extraction of conventional materials. Ideally, decisions on whether or not to use recycled materials should therefore be based on cost-benefit analyses that take into consideration the general benefits to society that result from waste recycling. Further, detailed characterisation of a material is only necessary initially to define its fundamental properties and interactions with various environments. Much less testing may be needed to verify that new samples of the material from the same source conform to the previously established properties. The same reasoning may apply to resource-demanding system analyses, which once conducted could form a basis for material management systems operated at a regional level.

Concluding remarks

By defining the relevant range of field conditions that the material may be exposed to in various applications, constituent leaching from an intended use can be estimated based on leaching tests and modelling efforts. However, the environmental impact of using a given material also is dependent on the characteristics of the transport media and recipient. Evaluations based on the principles of ecological risk assessment could be used to identify and quantify expected impacts on specific targets. Such an evaluation requires more resources than the use of generic criteria applied to the source term, but provides more accurate estimations of the risks and can also be simplified through the use of pre-defined scenarios outlining relevant factors to consider for various applications and environments. Any increased leaching caused by substituting natural materials for recycled materials in constructions must also be put in relation to the environmental impacts of the default alternative, *i.e.* landfilling of industrial residues and extraction, pre-processing and transport of natural material. Evaluations based on life-cycle concepts have good potential for use in planning of the strategic level of material management systems. A combination of system analyses and case-specific assessments would be the ideal option to account for impacts both at the global and local scale. If the utilisation of a material is judged to be environmentally preferable from a systems perspective, its environmental suitability could be further examined in a risk assessment. Results from the risk assessment could then be used as inputs for new, revised system analyses etc. The need to apply different methods to the same problem could lead to the development of a wide variety of tools for addressing different issues and generating different results. This calls for a focussed approach in which tools for system level and case-specific assessments are developed in consensus, which in its turn emphasises the need for inter-disciplinary research in this area.

5   CONCLUSIONS

Environmental significance of the leachates

The analyses of the examined road and landfill cover constructions indicated that leachates from recycled materials contained higher concentrations of several environmentally relevant constituents compared to natural water and leachates from conventional materials. However, these studies only considered emissions sampled at the boundary of the construction, and while mobile constituents such as salts released from the materials can affect the water recipients in the short term, many trace elements will be strongly retarded by sorption processes occurring close to the source, which may reduce their concentrations considerably. Further, both the volumes of the leachates, and their contents of various constituents, were sensitive to the construction design, showing that it is possible to limit the significance of leaching by using appropriate design measures. In road base applications, leachates from materials in uncovered roadside slopes posed greater concerns than leachates from materials under the pavement. In landfill cover applications, water percolating through the materials in the protective layer rather than leachates from materials used in the liner was the main environmental concern.

Factors controlling the leaching of constituents in a construction

Compaction and the presence of low-permeability covers both reduced the rates of water percolation and carbonation, and the mobility of many constituents. However, the carbonation of alkaline materials will either increase or decrease constituent leaching, depending on changes in pH and constituent speciation over time. Carbonation effects were observed in leachates sampled from the open roadside slopes within three to six years when recycled concrete and ash were used as sub-base in the road construction, while ashes used below the asphalt pavement or in the compacted landfill cover liners take longer time to carbonate. In addition, granular materials were found to be exposed to greater degrees of oxidation when they were uncovered than when they were under the pavement. The analyses of leachates sampled from the roadside slopes with coarse-grained sulphidic slag indicated that their acidity and elevated constituent concentrations were due to oxidation of reduced sulphides in the slag. Further, the presence of organic matter in the constructions increased the availability of dissolved organic matter in the leachates, and thus the mobility of several trace elements via complexation or competitive sorption. In landfill covers, a redox gradient with more reducing conditions in the liner than in the protective layer was established due to the diffusion of gas formed during degradation of the deposited waste. This increased the leaching of oxyanions from the liner, but might also induce the precipitation of metal sulphides, thereby decreasing the mobility of metals if reducing conditions persist. Hence, since the rate and extent of constituent leaching from a construction material is heavily dependent on the way it is used, defining the range of conditions that a material may be exposed in the field is essential in order to make reliable predictions of leaching parameters based on laboratory assays.

Environmental assessment of the recycled materials

Assessments of the likely environmental impacts of using recycled materials in construction are usually based on results of simplified laboratory leaching tests. However,

assessing the environmental impact of using such materials in specific applications solely on the basis of results of compliance leaching tests is not a valid approach because (i) the tests do not always reflect the leaching behaviour in the field, and (ii) the results only apply to the source term in its initial phase. Since the impact will be dependent on case-specific factors related to the construction design, transfer conditions and characteristics of the recipient, an evaluation based on ecological risk assessment principles is needed. The leaching emissions must also be considered in relation to the environmental impacts of the default alternative, *i.e.* landfilling of industrial residues and the extraction, pre-processing and transport of natural materials. Therefore, a combination of case-specific assessments and system analyses would be the ideal approach to evaluate impacts at both local and regional scales.

Outlook

In order to accurately assess the environmental impacts of substituting natural materials for recycled materials in construction, the present investigations need to be complemented with:

- Predictions of long-term leaching emissions from the materials using temporal monitoring of field releases in combination with geochemical and transport modelling and mineralogical analyses of weathered materials from the construction.
- Quantification of the environmental impacts of the studied leachates on the local recipients, *e.g.* soil, ground water and vegetation, according to risk assessment principles.
- Assessment of the relative importance of the case-specific environmental impacts caused by leaching from the materials and impact factors related to the default alternative, *i.e.* landfilling of industrial residues and exploitation of natural resources.
- Assessment of the potential leaching of constituents from the materials after the service life of the construction.

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APPENDICES

PAPER I-IV

CONTRIBUTION FROM THE AUTHOR

I actively contributed to the development of the concept for each paper. My further contributions are as follows:

Paper I   I planned and performed the laboratory tests on the crushed rock. I performed the statistical analyses of the data. I interpreted the results and wrote the paper with support from the co-author.

Paper II   I actively participated in designing, planning and performing the pilot-scale experiment. I took active part in the material characterisation and laboratory leaching tests. I did the statistical analyses, interpreted the data and wrote the paper with assistance from the co-authors.

Paper III   I performed the geochemical modelling. I actively participated in the analyses and interpretation of data as well as the writing.

Paper IV   I planned and performed the field samplings during 2006-2007. I performed the geochemical modelling and statistical analyses. I interpreted the data and wrote the paper with help of the co-author.

PAPER I

Lidelöw, S., Lagerkvist, A., 2007. Evaluation of leachate emissions from crushed rock and municipal solid waste incineration bottom ash used in road construction. *Waste Management* 27: 1356-1365.

ELSEVIER

Technical paper

Evaluation of leachate emissions from crushed rock and municipal solid waste incineration bottom ash used in road construction

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Abstract

Three years of leachate emissions from municipal solid waste incineration bottom ash and crushed rock in a full-scale test road were evaluated. The impact of time, construction design, and climate on the emissions was studied, and the predicted release from standard leaching tests was compared with the measured release from the road. The main pollutants and their respective concentrations in leachate from the roadside slope were Al (12.8–85.3 mg l^{-1}), Cr (2–125 µg l^{-1}), and Cu (0.15–1.9 mg l^{-1}) in ash leachate and Zn (1–780 µg l^{-1}) in crushed rock leachate. From the ash, the initial Cl$^-$ release was high ($\sim$20 g l^{-1}). After three years, the amount of Cu and Cl$^-$ was in the same range in both leachates, while that of Al and Cr still was more than one order of magnitude higher in ash leachate. Generally, the release was faster from material in the uncovered slopes than below the pavement. Whether the road was asphalted or not, however, had minor impacts on the leachate quality. During rain events, diluted leachates with respect to, e.g., salts were observed. The leaching tests failed to simulate field leaching from the crushed rock, whereas better agreement was observed for the ash. Comparisons of constituent release from bottom ash and conventional materials solely based on such tests should be avoided.
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1. Introduction

Bottom ash from municipal solid waste incineration (MSWI) is technically possible to use as a road construction material (Arm, 2003; Forteza et al., 2004). However, its relatively high content of trace constituents (Chandler et al., 1997) raises environmental concern due to the potential release of salts and metals to soil and groundwater. Several studies of bottom ash aiming to understand its pollution potential have been carried out using laboratory tests (Chandler et al., 1997; Johnson et al., 1995; Kirby and Rimstidt, 1994; Meima and Comans, 1997; van der Sloot et al., 2001). Meanwhile, relatively few large-scale field studies have been performed to verify the results, although Schreurs et al. (2000) and Bruder-Hubscher

et al. (2001) present some exceptions. Schreurs et al. report a reasonably good agreement between laboratory leaching data and field observations, although significant discrepancies occurred due to differences in the pH and the degree of water saturation. Bruder-Hubscher et al. studied water percolates from two roadbeds with natural gravel and bottom ash, respectively, and observed only minor differences between the percolates after one year. The pollution potential of conventional road construction materials such as natural gravel and crushed rock is poorly investigated and, hence, data that could serve as a reference for alternative materials leaching are sparse.

In this work, the quality differences of three years of leachates from municipal solid waste incineration (MSWI) bottom ash and crushed rock used in a full-scale test road are discussed. Specific objectives are: (i) to study the impact of factors such as time, construction design, and climate on the leachate quality and (ii) to verify the predicted release of pollutants based on total dissolution and batch leaching tests with the measured release from the test road.

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2. Methods and materials

2.1. Material characterisation

The crushed rock (CR) is a quartz-diorite crushed to a particle size of ⩽80 mm, which is composed mainly of quartz, plagioclase, biotite, and amphibole. About 200 kg of CR was sampled at the road construction site in 2001 and stored in a metal container with lid. Prior to laboratory experiments, about 20 kg of CR was taken from the container and air-dried at 20 °C. Incremental sampling (Pitard, 1993) was applied to obtain a laboratory sample of about 3 kg, which was used for elemental composition analysis and for two batch tests, viz. an availability and a compliance leaching test.

Total elemental composition was determined according to the modified EPA methods 200.7 (ICP-AES) and 200.8 (ICP-SFMS) at Analytica AB, Luleå, Sweden. Total solids (TS) were determined by drying at 105 °C for 24 h according to the Swedish standard SS 028113 (SIS, 1981) and loss on ignition (LOI) after ignition at 1000 °C for 2 h.

The availability test was performed according to the Nordtest method NT ENVIR 003 (Nordtest, 1995). The test is conducted on finely ground material (95 wt% <125 μm) in two steps at a liquid-to-solid (L/S) ratio of 100 l (kg TS)$^{-1}$ each. The first step is performed at pH 7 for 3 h and the second at pH 4 for 18 h. Distilled water acidified with HNO$_3$ is used as a leachant. The two eluates are combined prior to analyses. The compliance test was performed as a two-stage batch test at L/S 2 for 6 h and subsequently L/S 8 for 18 h according to the European standard EN 12457-3 (CEN, 2002). Prior to the test, the samples were crushed and sieved to a particle size 95 wt% <4 mm. Distilled water is used as a leachant, i.e., the leaching pH is dictated by the material itself. The two eluates are analysed separately. pH and electrical conductivity (EC) were measured in unfiltered eluates using pH meter 340/SET-1 with a combined electrode Sen-Tix 41 (WTW, Wielheim, Germany) respective a CDM210 conductivity meter (Radiometer, Copenhagen, Denmark). Before further analysis, eluates were filtered with 0.45 μm nitrocellulose membrane filters and stored frozen. Elements were analysed by ICP-OES (Perkin Elmer Optima 2000 DV), and Cl$^-$ and SO$_4^{2-}$ by spectrophotometry (AACE Quaatro, Bran+Luebbe, Germany).

The MSWI bottom ash (BA) originates from the Dåva power plant in Umeå, Sweden. The plant is mainly fueled with MSW and small fractions of sorted industrial wastes such as wood, rubber and plastic. Prior to utilisation, the BA was screened to remove magnetic material and particles >50 mm, and then stored outdoors for ~6 months. The BA was characterised by SGI (2002) and Ecke and Åberg (2006).

2.2. Description of the field site, sampling and sample analyses

The test road was built during the summer of 2001 at the Dåva power plant in Umeå, Sweden, and is used mainly by
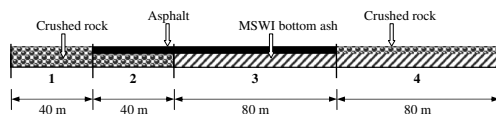

Fig. 1. The test road divided into sections 1–4.

trucks for transport of incineration residues. In this region, the ground is frozen and covered by up to 0.5 m of snow for about 5–7 months of the year. The average yearly precipitation in the area is about 600 mm (Alexandersson et al., 1991), of which 40–50% falls as snow (Hernebring, 1996). The test road is divided into four sections (Fig. 1). Two sections (3 and 4) contain a 0.4 m thick layer of BA. One is covered with asphalt and the other with compacted CR. Sections 1 and 2 are reference sections built with CR.

For leachate collection, each section is equipped with two high density polyethylene (HDPE) geomembrane lysimeters (2 × 15 m): one below the cover and one positioned mainly under the roadside slope outside of the cover (Fig. 2). The leachate is sampled in wells on the side of the road. The water flow from the lysimeters is measured by tipping buckets. Precipitation data are collected from a nearby weather station.

On 21 occasions from October 2001 to October 2004, leachate was sampled regularly except during the winter months when the water was frozen. At the site, pH and temperature were measured using pH meter 340/SET-1 as above and total alkalinity (Alk) was determined using Merck Alkalinity Test. After transport, EC was measured as soon as possible in the laboratory using the CDM210 conductivity meter. Most samples were stored frozen prior to further analyses, which included:

- Elements analysed by ICP-OES as above. Samples with Cl$^-$ concentrations >10^5 ppm were analysed using the modified EPA methods 200.7 (ICP-AES) and 200.8 (ICP-SFMS) at Analytica AB in Luleå, Sweden.
- Cl$^-$ determined using an ion selective electrode (ISE glass membrane electrode) or by titration with AgNO$_3$ according to the Swedish standard (SS) 028120 (SIS, 1974).
- SO$_4^{2-}$ determined using ion chromatography according to the standard ISO 10304-2 (ISO, 1995).
- Total solids (TS) and volatile solids (VS) determined according to SS 028113 (SIS, 1981).
- Total organic carbon (TOC) determined as the difference between total carbon and inorganic carbon according to the European standard EN 1484 (CEN, 1997).
- Chemical oxygen demand (COD) determined according to SS 028142 (SIS, 1991) or using Merck Spectroquant Test Kit, and biological oxygen demand (BOD) determined according to SS 028143 (SIS, 1998).
- Total nitrogen (N$_{tot}$), ammonia nitrogen (NH$_4$–N), nitrite nitrogen (NO$_2$–N), and nitrate nitrogen (NO$_3$–N) analysed by TRAACS 800 autoanalyzer (Bran and Luebbe, Norderstedt, Germany). NO$_2$–N and NO$_3$–N
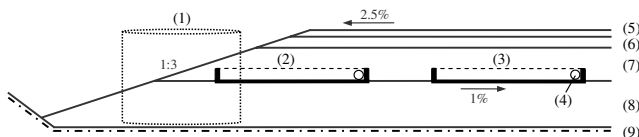
Fig. 2. Cross section of the test road with lysimeters: (1) Position of sampling well; (2) slope lysimeter; (3) road lysimeter; (4) drainage pipe; (5) pavement: asphalt or crushed rock; (6) base: crushed rock; (7) sub-base: bottom ash or crushed rock; (8) subgrade: sand; (9) geotextile.

were analysed using TRAACS method J-002-88 B (Bran+Luebbe, 1993b). N_{tot} was analysed using method J-002-88 B after digestion according to SS 028131 (SIS, 1976). NH_4–N was analysed using TRAACS method J-001-88 B (Bran+Luebbe, 1993a).

All analyses, except the ICP analyses, were performed on unfiltered samples.

2.3. Statistical analyses

Multivariate data analyses were performed using principle component analysis (PCA) and partial least squares (PLS) projection to latent structures (Eriksson et al., 2001). The aim of these methods is to explain the variation within the original multivariate data set by a minimum number of dimensions, i.e., of principal components. PCA was used to investigate how the laboratory and the field data relate to each other. PLS, which is a regression extension of PCA, was applied to the field data to find out how different factors (X) influence the response variables (Y) (Table 1), and how the responses correlate with each other. The analyses were performed at 5% significance level using the software Simca-P 10.5 (Umetrics, Umeå, Sweden).

Prior to modelling, data were pre-processed using mean-centering and unit-variance (UV) scaling. Logarithmic transformation of variables was applied to achieve approximate normality. Variables with $R^2 < 0.4$ were excluded from the models and so were variables and observations with more than 80% missing data. Data below detection limit were replaced by a value representing 50% of the detection limit.

3. Results and discussion

3.1. Laboratory assessment

On the average, the BA has a higher content of trace elements than the CR (Table 2). Compared with composition ranges of MSWI bottom ash reported by Kosson et al. (1996), the BA contains relatively large amounts of Cu and Zn, but small amounts of Al and Na. Data variability for Cr and Ni is high, probably due to the small pieces of metal found in the ash. The LOI indicates a low level of unburned material in the BA. The CR is, compared with the average composition of Swedish rock materials used in road building (Tossavainen and Forssberg, 1999), rich in Ba, Zn, and S. The high S content indicates a potential existence of sulphide minerals, increasing the risk for release of commonly associated elements, e.g., As, Cu, and Zn, under aerobic conditions.

Available amounts of all constituents except As are higher in the BA than in the CR (Table 3). The high availability of dissolved salts such as Cl^-, Na, and SO_4^{2-} in the BA was expected because of their abundant existence in ashes and their high water solubility (Chandler et al., 1997). Regarding metals, the availability of Al, Pb, and Zn is more than two and that of Cu and Cr more than one order of magnitude higher in the BA. From the total contents, the large difference in Al availability was unexpected. Probably, while Al in the CR is bound in stable

Table 1
Variables included in the factor matrix X and the response matrix Y of the PLS model

Matrix	Variable	Type	Setting
X	Sub-base material	Qualitative	BA
			CR
	Time	Quantitative	Number of days since the first sampling
	Precipitation	Quantitative	Accumulated amount (mm) between samplings[a]
	Temperature	Quantitative	Temperature of leachate (°C) at sampling
	Pavement	Qualitative	CR pavement
			Asphalt
	Lysimeter position	Qualitative	Slope
			Road
Y	Flow	Quantitative	Accumulated amount (l) between samplings[a]
	pH, EC, Alk	Quantitative	Leachate pH, electrical conductivity (mS cm^{-1}), and alkalinity (mmol l^{-1})
	Constituents	Quantitative	Leachate concentrations (μg or mg l^{-1}) of Al, As, Ba, Ca, Cd, Cl$^-$, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Zn, NH$_4$–N, NO$_2$–N, NO$_3$–N, N$_{tot}$, SO$_4^{2-}$, BOD, COD, and TOC
	TS, VS	Quantitative	Amount of total and volatile solids (g kg^{-1}) in the leachate

[a] Values for the first sample of a sampling year (after the winter) cannot be provided.

Table 2
Total content of oxides and elements, total solids (TS) and loss on ignition (LOI) in the MSWI bottom ash (Ecke and Åberg, 2006) and the crushed rock (±SD)

	MSWI bottom ash[a]	Crushed rock[b]
Total solids (g (kg material)$^{-1}$)		
TS	830 ± 3	999 ± 0.7
Major constituents (g (kg TS)$^{-1}$)		
SiO_2	370 ± 9	533 ± 11
Al_2O_3	130 ± 3	148 ± 2.1
CaO	150 ± 2	52.6 ± 2.6
Fe_2O_3	150 ± 5	113 ± 14
K_2O	14 ± 0.2	38.7 ± 1.4
MgO	25 ± 1	35.9 ± 1.8
MnO_2	3 ± 0.2	1.32 ± 0.13
Na_2O	28 ± 1	28.2 ± 1.4
P_2O_5	10 ± 1	14.4 ± 1.1
TiO_2	16 ± 1	26.3 ± 0.71
LOI	12 ± 0.8[c]	7.50 ± 2.1
Minor constituents (mg (kg TS)$^{-1}$)		
As	33 ± 3.2	3.90 ± 2.3
Ba	n.a.	1460 ± 0.0
Cd	6 ± 1.1	0.21 ± 0.042
Co	34 ± 6.0	19.7 ± 1.8
Cr	568 ± 435	118 ± 9.9
Cu	11570 ± 3261	76.7 ± 23
Hg	n.a.	0.050 ± 0.014
Mo	24 ± 2.6	<6.0
Ni	567 ± 446	34.3 ± 4.0
Pb	2260 ± 983	10.3 ± 0.28
S	5103 ± 38	984 ± 51
Zn	9117 ± 1198	193 ± 22

n.a. – data not available.
[a] $n = 3$ for oxides and elements and $n = 12$ for TS and LOI.
[b] $n = 2$.
[c] Determined after ignition at 550 °C.

Table 3
Results of the availability and the two-stage batch leaching test on MSWI bottom ash (SGI, 2002) and crushed rock presented as mean values

	Availability test		Compliance test			
			L/S 2		L/S 10	
	BA[a]	CR[b]	BA[c]	CR[b]	BA[c]	CR[b]
pH	4.6	5.4	9.4	9.8	10.4	10.0
Constituent (mg (kg TS)$^{-1}$)						
Al	2200	0.82	40.9	1.4	274	5.8
As	0.49	1.2	0.0086	0.23	0.014	0.52
Ba	180	77.9	0.20	0.065	0.73	0.59
Ca	30200	2550	955	12.5	1410	36.0
Cd	4.5	0.032	0.0015	0.00078	0.0020	0.0016
Cl^-	2540	756	1870	7.3	1850	26.9
Cr	4.0	<0.16	0.13	0.0023	0.17	0.0085
Cu	620	11.8	0.67	0.015	0.97	0.019
K	1470	1220	272	26.5	325	70.6
Mg	1840	177	3.1	2.2	3.68	9.7
Mn	195	34.5	3.4×10^{-6}	0.011	$<7.9 \times 10^{-6}$	0.030
Mo	1.6	n.a.	0.61	n.a.	0.85	n.a.
Na	2200	36.9	1050	14.4	1100	22.6
Ni	17.1	0.76	0.024	<0.00025	0.039	<0.0012
Pb	190	<0.47	0.0037	0.018	0.018	0.034
Sb	3.5	0.22	0.14	0.024	0.49	0.055
SO_4^{2-}	8560	<412	2060	15.7	2760	29.7
Zn	1960	14.1	0.0097	0.012	0.040	0.020

n.a. – data not available.
[a] $n = 10$.
[b] $n = 6$.
[c] $n = 5$.

minerals such as plagioclase, Al in BA is present in Al(OH)$_3$ with high solubility at the low pH used in the availability test (pH 4).

The trend of considerably higher leaching of dissolved salts, Cr, and Cu from the BA is shown also in the batch test (Table 3). Pb and Zn leaching, however, are in the same range for both materials, likely due to their low solubility at pH 9–10 (Chandler et al., 1997) established during the test. One criterion suggested for acceptance of waste materials in construction is compliance with the leaching criteria for landfilling as inert waste stipulated by the EU Council (2002). The leaching of four constituents from the BA exceeds these criteria, viz. Sb (by one order of magnitude), Cl$^-$ and SO$_4^{2-}$ (by ~3 times), and Mo (by ~2 times), while As leaching from the CR is about twice the criteria at L/S 2. Hence, none of the materials meet the requirements for acceptance at landfills for inert waste.

3.2. Field assessment

The impact of the factors sub-base material, time, precipitation, temperature, pavement, and lysimeter position on the leachate from the road was investigated by means of PLS. The model is interpreted using the PLS weight plot

(Fig. 3) and the multiple regression coefficients (Table 4). Fig. 3 gives information about influential variables and how they correlate. The further away from the plot origin a variable lays, the more influential it is. Grouping of factors and/or responses indicate that they are correlated. Table 4 are used to distinguish whether the impact of the different factors on the responses is statistically significant ($p < 0.05$) or not. Strongly correlated responses will demonstrate similar coefficient profiles, indicating their similarity in leaching behaviour.

The largest variation in the data (about 50%) is explained by the sub-base material used, while the second largest primarily reflects changes in sample properties over time and differences between road and slope leachates (Fig. 3). On the average, the BA leached more Al, Cl$^-$, Cr, Cu, K, Na, TOC, COD, BOD, N$_{tot}$, NH$_4$–N, NO$_2$–N, TS, and VS than the CR, while the leaching of Ba, Mg, Mn, Zn, and NO$_3$–N was lower (Table 4). In slope leachate, the metal concentrations ranged between 12.8 and 85.3 mg l^{-1} for Al, 2–125 µg l^{-1} for Cr, and 0.15–1.9 mg l^{-1} for Cu for section 3, and between 1 and 780 µg l^{-1} for Zn for section 2.

The leaching of many constituents decreased significantly over time (Table 4). The concentrations in slope leachate of section 3 decreased, e.g., by 95% for Cl$^-$, 90% for Cu, 93% for TOC, and 97% for NH$_4$–N over the three years and approached those of section 2 (cf. Ore et al., in press). After three years, the content of Ba, Cl$^-$, Cu, K, Na, N$_{tot}$, TOC, and TS in the leachate was in the same
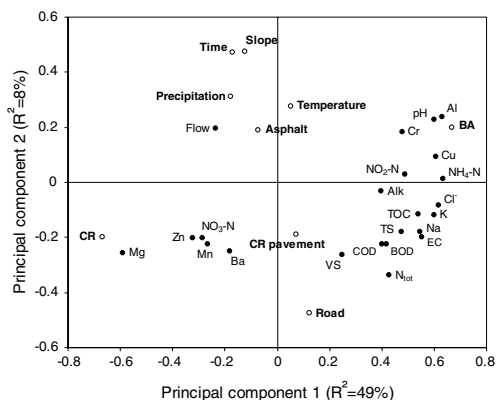
Fig. 3. PLS weight plot of the test road samples collected during three years showing how material, time, field conditions, and sampling point (empty circles) are correlated and affect the leachate quality (filled circles).

range as that of section 2, while the amount of Al and Cr still was more than one order of magnitude higher in the BA leachate. BA leachate generated below the pavement was changing less drastically than the slope leachate, the last samples having similar properties as the 2002 slope leachate.

Nitrogen in BA leachate occurred mainly as NH_4–N or NO_2–N, while NO_3–N was the predominant species in CR leachate (Fig. 3). A large proportion of reduced

nitrogen species indicates a relatively low redox potential and a high degradability of organic material in the leachate. Elevated release of BOD and other variables related to the organic content (COD, TOC, VS) was observed from BA during the first year, after which it declined considerably (Fig. 4). Consequently, a shift towards more oxidised nitrogen species occurred, especially in the slopes, indicating oxidation of the ash upon prolonged contact with air.

The pH of BA leachate (ranging from 8.5 to 12.3) was higher than CR leachate pH (ranging from 6.9 to 9.1), and showed no clear time trend (Fig. 5). Ageing effects such as carbonation was expected to decrease BA leachate pH towards calcite equilibrium (8.3) (Meima and Comans, 1997) through uptake of carbon dioxide from the atmosphere or from biological degradation. However, carbonation was probably hampered by the limited infiltration and gas exchange through the compacted BA and its overlaying layers and the biological activity too low to influence pH in the longer term.

Al release from the BA, being strongly correlated to pH (Fig. 3), did not decrease significantly over time and neither did Mg and Zn leaching from the CR nor Cr leaching from the BA (Table 4). Assuming that Zn is bound to sulphides, oxidising conditions prevailing in the CR layer would explain its high mobility from the CR. The large fluctuations in the Zn leaching (Fig. 5) might be due to fluctuating redox conditions within the road body. During the snow melting period in 2003, a peak occurred in the release of several constituents (Figs. 4 and 5), especially for Cr from

Table 4
Significance of multiple regression coefficients ($p < 0.05$) for the PLS model of samples from the test road

	Lysimeter		Pavement		Sub-base		Time	Precipitation	Temperature
	Road	Slope	Asphalt	Crushed rock	Bottom ash	Crushed rock			
pH	0	0	0	0	+	−	0	0	+
EC	+	−	0	0	+	−	−	−	0
Alkalinity	0	0	0	0	+	−	−	−	0
Flow	−	+	0	0	0	0	+	+	0
Al	0	0	0	0	+	−	0	0	+
Ba	+	−	0	0	−	+	−	0	−
Cl⁻	+	−	0	0	+	−	−	−	0
Cr	0	0	0	0	+	−	0	0	0
Cu	0	0	0	0	+	−	−	0	0
K	+	−	0	0	+	−	−	−	0
Mg	0	0	0	0	−	+	0	0	−
Mn	+	−	0	0	−	+	−	0	−
Na	+	−	0	0	+	−	−	−	0
Zn	0	0	0	0	−	+	0	0	−
TOC	+	−	0	0	+	−	−	−	0
COD	+	−	0	0	+	−	−	−	0
BOD	+	−	0	0	+	−	−	−	0
NH_4–N	0	0	0	0	+	−	−	−	0
NO_2–N	0	0	0	0	+	−	−	0	+
NO_3–N	0	0	0	0	−	+	0	0	−
N_{tot}	+	−	0	0	+	−	−	−	−
TS	+	−	0	0	+	−	−	−	0
VS	+	−	−	+	+	−	−	−	−

+, Positive correlation between variables; −, negative correlation and 0, non-significant correlation.
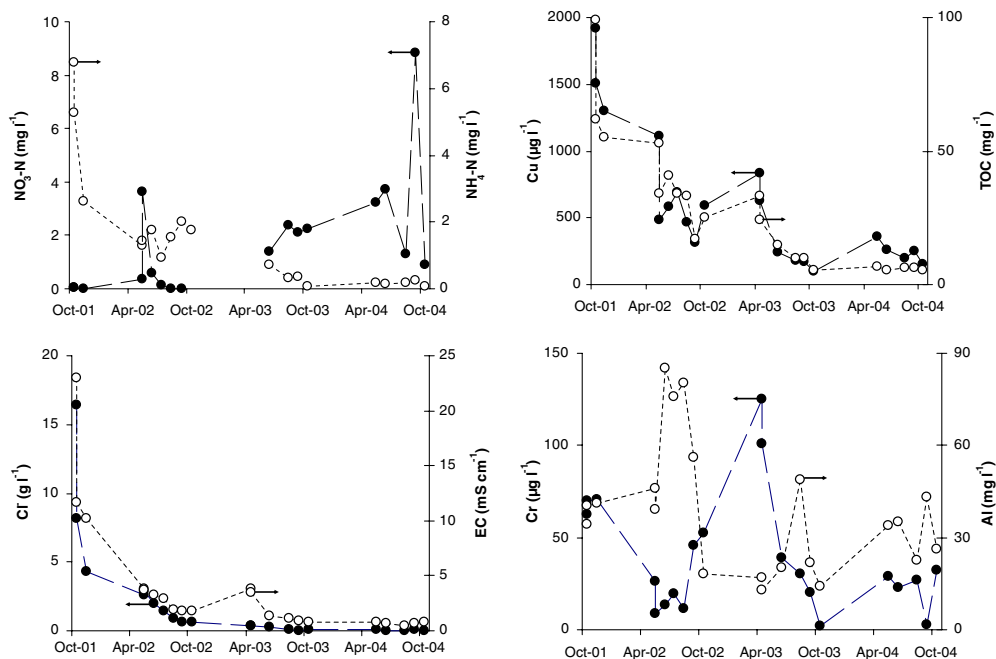
Fig. 4. Concentrations of constituents in bottom ash leachate collected from the slope lysimeter of section 3 during three years of sampling.

the BA. Zn mobility from BA increased during the last few months, possibly due to increasingly oxidising conditions in the ash (see discussion above). Cu mobility from the BA over time is likely controlled by mineral precipitation or complex formation with organic material (Åberg et al., 2006). Ore et al. (in press) established a close linear relationship between the release of Cu and TOC, also indicated in Fig. 4.

The flow meters were frequently malfunctioning due to their frost-susceptibility, making quantitative estimations of flows or released amounts of leachate constituents difficult. Nevertheless, the strong correlation between the flow and the precipitation (Fig. 3) motivates a qualitative assessment of the response. A higher flow through the CR sections than the BA sections was indicated, probably due to higher permeability of CR. The majority of leachate was generated in the roadside slopes where the road surface runoff infiltrates (Table 4). Here, the leaching of organic material, nitrogen, and dissolved salts also was significantly faster than below the pavement (Table 4). While covering BA with a relatively impermeable layer lowers the L/S ratio and thus the release rate of these constituents, not covering leads to a higher L/S ratio and a more rapid release (washout). For example, slope leachate from section 3 contained about $0.02 \text{ g Cl}^- \text{ l}^{-1}$ after three years and road leachate about $1 \text{ g Cl}^- \text{ l}^{-1}$. Other constituents, e.g., Cu showed sim-

ilar tendencies with up to one order of magnitude higher concentrations in road than in slope leachate after three years. Cr behaved differently, having lower concentrations in road than in slope leachates throughout the sampling period, i.e., increased material wetting seemed to enhance the amount of Cr in the leachate. In the slopes, a higher leachate production was indicated in sections 2 and 3 compared with sections 1 and 4, likely due to a higher runoff coefficient of the asphalted surface. This had minor impacts on the leachate quality, but Cl^- leaching from the slopes was considerably slower in section 4 than in section 3 as leachate from the former contained about 10 times more Cl^- (0.5 g l^{-1}) after three years.

The initial amount of Cl^- in slope leachates was very high (~16 and 20 g l^{-1} for section 3 and 4, respectively). Kosson et al. (1996) and Bruder-Hubscher et al. (2001) reported initial concentrations of $\sim2 \text{ g Cl}^- \text{ l}^{-1}$ in BA leachate from a monofill and an experimental road, respectively. In road runoff water, Cl^- concentrations of up to $\sim13 \text{ g l}^{-1}$ were found after application of de-icing salts (Bjelkås and Lindmark, 1994). In a mung bean assay, Ore et al. (in press) showed that the first leachate from the slope of section 3 can be toxic to plants, partly due to its high Cl^- content. In the long-term, however, the cumulative Cl^- load caused by the BA will be negligible compared with that caused by road salting. Compared with an average use of
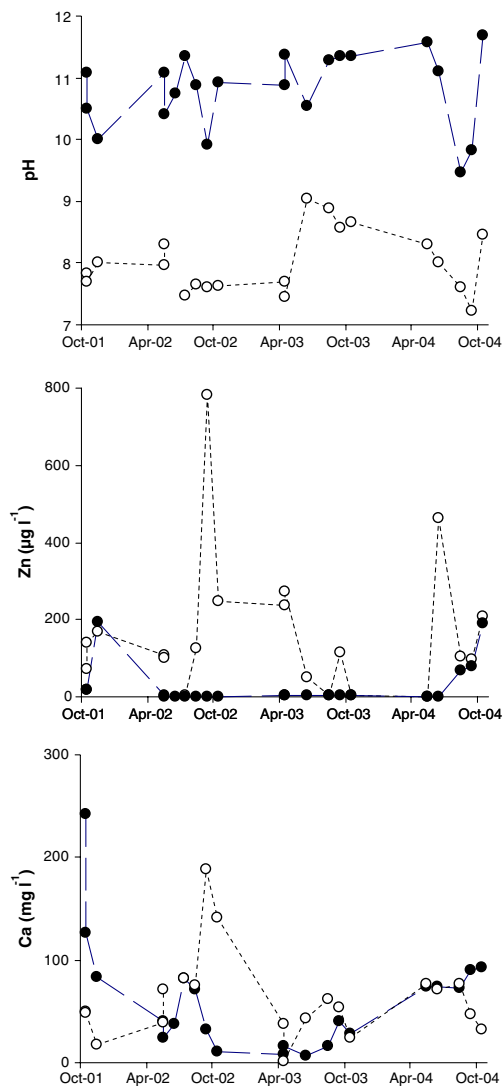
Fig. 5. pH and concentrations of Zn and Ca in crushed rock leachate (empty circles) and bottom ash leachate (filled circles) collected from the slope lysimeters of sections 2 and 3 during three years of sampling.

6 kg of salt per meter road and year in Sweden (Bjelkås and Lindmark, 1994), the amount of Cl^- available for leaching in BA per meter of the test road corresponds to 4.5 years of road salting. Considering its rapid release from the road, Cl^- will be leached up to its availability before an L/S of 1 is achieved, which, however, might take several years. In a high-infiltration-scenario with an annual infiltration of 300 mm, an L/S of 1 may be obtained within 2 years, whereas in a low-infiltration-scenario with less than 50 mm infiltration per year (e.g., below an asphalt pavement) it might take more than one decade.

The asphalt layer was expected to reduce constituent leaching due to its low permeability, limiting water infiltration and gas exchange with the atmosphere. The leachate quality was, however, not significantly affected by the type of pavement (Table 4), except the VS content being lower in leachate from asphalted sections. Compaction of the CR over time might have caused the formation of a tight and firm surface layer resembling asphalt. Ocular examinations of the test road support this hypothesis.

During rain events, diluted leachates with significantly lowered amounts of dissolved salts, organic material, N_{tot}, and NH_4–N were formed (Table 4). Probably, the decreased amount of organic material partially account for the lowered NH_4–N concentration. The lowered N_{tot} release during the warmest periods (Table 4) might be due to increased nitrogen reduction, a process favoured by higher temperatures. The increased pH and the shift towards more reduced nitrogen species during such periods support this hypothesis. As pH increased, leaching of Al increased while that of Ba, Mg, Mn, and Zn decreased, possibly due to solubility controlling processes. Zn, for example, might precipitate with carbonates (Freyssinet et al., 2002), having lower solubility in warm than in cold water. Åberg et al. (2006) showed carbonate precipitations to be possible in BA leachate from the road.

The variables As, Ca, Cd, Co, Fe, Hg, Ni, Pb, and SO_4^{2-} were poorly explained by the PLS model and therefore excluded from the statistical analysis. Data on SO_4^{2-} for the first few samples are missing, but during the rest of the sampling period the leached amount was of the same order for the CR and the BA (on average 370 and 250 mg l^{-1}, respectively) and showed no tendency to decline. Ca leaching was also in the same range for BA and CR (Fig. 5). The lowered Ca mobility from the BA during 2002–2003 could be due to carbonation or, more likely, to low-flow conditions in the road. The two years were unusually dry as the precipitation in the area amounted to about 65% of the normal average given in Alexandersson et al. (1991). During periods of drought, the buffering capacity of BA leachate can thus be expected to decline. This might imply an increased risk of decreasing the pH and, subsequently, increasing the heavy metal leaching, although no such effects were noted here. Leached amounts of As, Cd, Hg, and Pb were generally below the detection limit of the analysis. The amounts of Co and Fe were also low (mainly <0.01 and 0.2 mg l^{-1}, respectively) and fell after one year of leaching below the detection limit in both BA and CR leachate. Ni leaching was of the same order for the CR (on average 42 mg l^{-1}) as for the BA (on average 17 mg l^{-1}), except during the first few months when leached amounts were higher from the BA (maximum 42 mg l^{-1} below pavement).

Highly polluted leachates were occasionally generated below the pavement of the road. For example, in samples collected below the asphalt cover during the snow melting period in 2003, concentrations of up to 120 µg Pb l^{-1} and 4 mg Cu l^{-1} appeared in BA leachate, while peaks of 710 µg Ni l^{-1} and 2 SO$_4^{2-}$ g l^{-1} were found in CR leachate. In view of the low L/S ratio below the pavement, this might be attributed to flow heterogeneities, e.g., channelling, and to the displacement of the initial water content rather than infiltration seeping through the entire road body. It might also be influenced by external contamination, i.e., presence of pollutants in road runoff water.

Based on the field study, we can conclude that Cu, Cr, and Al are the most important pollutants from the BA, while Zn is the main pollutant from the CR. The high initial release of Cl^{-} from the BA might also be critical, although the cumulative load will be negligible compared to that caused by road salting. However, this study only considered emissions from the boundary of the construction. Attenuation processes may occur close to the source, especially for metals, reducing concentrations downstream to acceptable levels.

3.3. Laboratory versus field assessment

The correlation between data from the test road and the two-stage batch test was investigated using PCA (Fig. 6). Batch test data of the BA most resembles BA leachate from the last two sampling years, while those of the CR are closer to early samples of CR leachate. At L/S 2, the test overestimated the SO$_4^{2-}$ leaching and the buffering capacity of BA leachate, but underestimated the release of, e.g., Cl^{-} and Cu. For SO$_4^{2-}$, the missing data on initial

concentrations is a possible explanation, while dry weather might explain the relatively low buffering capacity of BA leachate from the road. At the accumulated L/S 10, the eluate had lower average concentrations of dissolved salts, Al, Cr, and Cu than most leachate samples from the road. These discrepancies can be attributed to dilution effects (higher L/S in the laboratory test than in field). In general, field leaching from the BA could be reasonably well predicted from the laboratory assay. A high release of Al, Cr, Cu, and dissolved salts was previewed, whereas the leaching of Zn and Pb from the road was lower than expected due to the high BA leachate pH. Since road leachate was not analysed for Sb and Mo, their field leaching behaviour cannot be verified. Especially Sb leaching was, however, relatively high in the laboratory tests. Hence, it is recommended to include Sb together with Al, Cr, Cu, and Cl^{-} in future studies of BA used in roads.

The two eluates from the batch test on CR are outliers and, thus, do not show similar properties as the field samples (Fig. 6). The test largely underestimated the release of Ba, Ca, Mg, SO$_4^{2-}$ and Zn from the CR in the road. This might be explained by the presence of sulphide minerals, which upon oxidation in the field caused leaching of SO$_4^{2-}$ and associated metals. Tossavainen and Forssberg (1999) showed elements associated to sulphides to be the most leachable ones in rock materials. Test methods to assess the impact of stable oxidising conditions on elemental release from such materials may therefore be suggested.

We can conclude that to compare constituent release from BA and CR solely based on standard batch leaching tests such as the availability and the compliance leaching test is not a viable approach. Firstly, the results need to be interpreted with the aid of more detailed characterisation data (e.g., leaching vs. pH) to be applicable to the field situation in question. Secondly, the potential release of constituents from conventional materials such as CR is not possible to assess from these tests. Further studies are therefore recommended to develop a procedure suitable for evaluating leaching from rock materials under various conditions.

4. Conclusions

The main pollutants in the bottom ash leachate from the test road were Al, Cr, and Cu, while Zn was the most important pollutant in the crushed rock leachate. The initial Cl^{-} release from the ash was high ($\sim$20 g l^{-1}), but the cumulative amount released will be negligible compared to that caused by road salting. After three years, the amount of, e.g., Cl^{-} and Cu in the ash leachate was of the same order as in leachate from the crushed rock, while that of Al and Cr still was more than one order of magnitude higher in the ash leachate. No ageing effects due to carbonation of the ash could be detected.
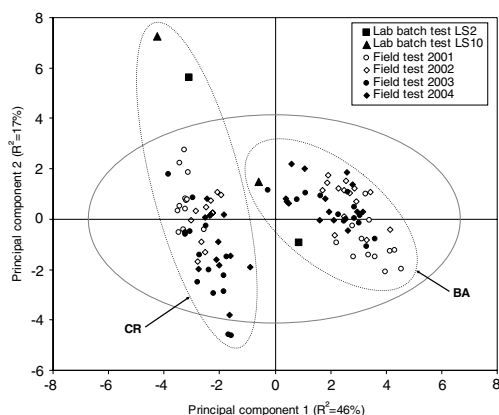

Fig. 6. PCA score plot of samples from the test road and the two-stage batch tests. Each sample is represented by one point. CR and BA denote samples from road sections with crushed rock and bottom ash, respectively. The ellipse defines the 95% confidence region of the model.

The release of relatively easily leachable constituents such as dissolved salts, organic material, and nitrogen was significantly ($p < 0.05$) faster from material in the uncovered roadside slopes than below the pavement. Whether the road was asphalted or not, however, had minor impacts on the leachate quality. Rain events led to diluted leachates with respect to, e.g., dissolved salts and organic material. During the warmest periods, the Al leaching increased together with the pH of the leachates.

Standard batch leaching tests such as the availability and the compliance leaching test poorly predicted constituent release from the crushed rock in the road, while a better agreement was found for the bottom ash. To compare the release of constituents from bottom ash and conventional materials solely based on such tests is therefore not recommended. For rock materials, test methods to assess the impact of stable oxidising conditions on the release are suggested. Follow-up studies in the field to assess constituent leaching and changes in, e.g., pH and redox conditions within the road body after longer exposure times are also recommended.

Acknowledgements

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PAPER II

Lidelöw, S., Ragnvaldsson, D., Leffler, P., Tesfalidet, S., Maurice, C., 2007. Field trials to assess the use of iron-bearing industrial by-products for stabilisation of chromated copper arsenate-contaminated soil. *The Science of the Total Environment* 387, 68-78.

Field trials to assess the use of iron-bearing industrial by-products for stabilisation of chromated copper arsenate-contaminated soil

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Abstract

Two industrial by-products with high iron contents were tested for their effectiveness in the stabilisation of arsenic and trace metals in chromated copper arsenate (CCA)-contaminated soil. Steel abrasive (SA; 97% Fe^0) and oxygen scarfing granulate (OSG; 69% Fe_3O_4) were applied at levels of 1% and 8% (w/w) respectively to two soils with different organic matter contents. Field lysimeter measurements indicated that SA and OSG treatments decreased the arsenic concentration in pore water by 68% and 92%, respectively, for the soil with low organic matter content, and by about 30% in pore water of soil with high organic matter content. At pH ≤ 6, the amended soil with low organic content contained elevated levels of manganese and nickel in their pore water, which were sufficient to induce cytotoxic effects in L-929 mouse fibroblast cells. The industrial by-products have significant potential for soil amendment at field-scale, but caution is required because of the potential release of their chemical contaminants and their reduced capacity for sorption of arsenic in organic-rich soils.
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Keywords: Remediation; Iron oxides; CCA; Arsenic; Leaching; Toxicity

1. Introduction

Chemical stabilisation is a remediation technique whereby an additive ('ameliorant') is incorporated and mixed with a contaminated soil. The objective is to induce chemical reactions such as sorption, co-precipitation, or complex formation, all of which reduce the mobility and bioavailability of the targeted soil contaminants.

Iron oxides can effectively sorb many trace elements in soil and have thus been considered for the remediation of soils contaminated with mixtures of metals and arsenic (As) resulting from industrial activities such as mining, wood impregnation, or pesticide use (Hartley et al., 2004; Kumpiene et al., 2006; Mench et al., 2003; Moore et al., 2000; Warren et al., 2003). The efficiency of remediation treatments depends on the intrinsic properties of the soil, the sorption capacity of the iron ameliorant, and the environmental conditions to which the treated soil is exposed. For example, the occurrence of reducing conditions induced by flooding or the

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degradation of organic matter could reduce the efficiency of remediation by causing dissolution of iron oxides and the reduction of As(V) to the more toxic As(III) species (Masscheleyn et al., 1991; McGeehan and Naylor, 1994). Furthermore, under oxidising conditions, a rise of the pH of the soil leads to greater solubility of As(V), but the risk of As(III) and trace metal releases could then be considerably reduced (Masscheleyn et al., 1991; Pierce and Moore, 1982; Raven et al., 1998).

In this study, we evaluated the capacity of two iron-rich industrial by-products to stabilise soils contaminated by chromated copper arsenate (CCA) resulting from the previous use of the wood impregnation chemical, CCA. One of the by-products tested consisted mainly of metallic iron (Fe^0), which corrodes and oxidises to produce iron oxides *in situ*, and the other contained mainly crystallised iron oxide, *i.e.* magnetite. The aim of the study was to investigate the effects of the ameliorants on As and trace metal mobility over time in CCA-contaminated soils with different organic matter contents. The assessment was based on the soil solution concentration, cytotoxicity, and As speciation observed in field lysimeters before and after soil amendment at an industrial scale.

2. Materials and methods

2.1. Soils

Soils were collected from two former industrial sites in Northern Sweden, at Forsmo (soil F) and Robertsfors (soil R). The sites were previously used for wood impregnation with the CCA chemical K33 containing (w/w) 17% CuO, 27% CrO_3, and 34% As_2O_5. Subsamples of the soils were obtained using fractional shovelling and were air-dried, homogenised, and sieved to <2 mm before characterisation (Table 1). Soil pH and

Table 1
Principal characteristics of the unamended soils (±SD, $n=3$)

	Unit	Soil F	Soil R
pH (1:2 ddH_2O)	–	6.02±0.01	5.75±0.03
Electrical conductivity (EC)	mS cm^{-1}	439±26	721±3
Total solids (TS)	wt.%	88.1±1.8	87.4±0.1
Loss on ignition (LOI)	wt.%	1.2±0.0	4.8±0.1
Organic carbon (OC)	wt.%	0.95±0.18	3.13±0.05
Water holding capacity (WHC)	wt.%	39.8	53.1±0.2
Cation exchange capacity (CEC)	cmol kg^{-1}	5.04±0.26	11.6±0.3
Texture		Sandy loam	Loamy sand
Sand	%	69.5	77.6
Silt	%	28.5	21.4
Clay	%	2.0	1.0

electrical conductivity (EC) were measured in suspensions comprising soil-doubly distilled water (ddH_2O) in the ratio 1:2. Total solids (TS) were determined after drying at 105°C and loss on ignition (LOI) was determined after ignition at 550°C (SIS, 1981). Organic carbon (OC) contents were determined according to the European standard method EN 13137 (CEN, 2001). Water holding capacity (WHC) was estimated from the content of water remaining in drained soil after saturation. Total cation exchange capacity (CEC) was determined by the ammonium acetate method (Lavkulich, 1993) and soil texture was determined by the hydrometer method (SIS, 1992).

2.2. Soil amendment

The capacity of two by-products from the steel industry to stabilise the soils was evaluated: (a) spent steel abrasive (SA), 98 wt.% <1 mm particles, containing 97% Fe^0 with Mn (0.91%), Cr (0.24%), and Ni (0.11%) as the major impurities and (b) oxygen scarfing granulate (OSG), 89 wt.% <1 mm particles, containing 79% Fe_{tot} (28% Fe^0 and 69% Fe_3O_4 (magnetite)) with Cr (0.97%), Mn (0.42%), Ni (0.17%), and Cu (0.14%) as the major impurities.

For each soil, ameliorants were applied at concentrations of 0 (control), 1% SA, and 8% OSG (w/w). OSG was added at a higher rate than SA since the sorption capacity of iron oxides decreases with increasing crystallinity (Bowell, 1994; Fuller et al., 1993). Soils F and R were mixed in batches of 10 and 3 tonnes, respectively. Soil F was mixed using first a screener–crusher attached to a wheel loader, then a rotating single skin trommel, while soil R was mixed using only a screener–crusher.

2.3. Lysimeter tests

About 1.3 tonnes of each soil mixture (with or without ameliorant) was placed in separate polyethylene (PE-HD) lysimeters (∼0.9 m^3) (Fig. 1). A drainage layer of 5–7 cm of coarse gravel was placed in the bottom and covered with geotextile to prevent wash-out of small particles. Three MacroRhizon soil moisture samplers (Eijkelkamp, the Netherlands) were then installed in each lysimeter at depths of 0.1, 0.4, and 0.7 m respectively. Nine equally-sized soil samples were collected from each depth and pooled into separate composite samples of ∼1 kg each. The soil was mixed and subsampled for batch leaching tests and total composition analyses using a stainless steel riffle splitter.

The lysimeters were left to equilibrate for 1–3 weeks at field moisture (about 50% and 30% of the soil WHC
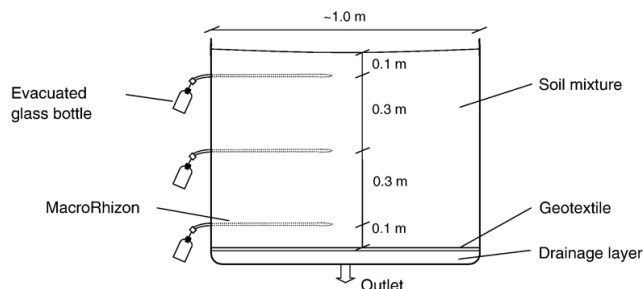
Fig. 1. Experimental lay-out of lysimeters.

for soils F and R, respectively), after which they were irrigated with 5–6l day^{-1} of ordinary drinking water to reach the natural average annual precipitation ($\sim$600 mm y^{-1} in Northern Sweden) in one sampling season. The lysimeters were exposed to the prevailing temperature but were sheltered from rain. The experiments started in 2005 for soil F and experiments with soil R commenced the following sampling season. Samples of soil pore water were collected on seven occasions over a 15-month period (July 2005–October 2006) for soil F and on three occasions over a 4-month period (July 2006–October 2006) for soil R. The samples were stored frozen at −20°C prior to analysis of pH, EC, redox potential, total elemental composition (for all samples), DOC (dissolved organic carbon), As speciation and cytotoxicity (for samples collected after 2 and 4 months).

2.4. Leaching tests and extraction

Batch leaching tests were performed in two stages at an accumulated L/S (liquid-to-solid ratio) of 2 for 6h and 8 for 18h according to the European standard method EN 12457-3 (CEN, 2002). Soil samples for these tests were prepared without sieving (>95 wt.% <4 mm).

Pseudo-total concentrations of elements in soil samples were determined by digesting 2g of soil in 10 ml of a mixture of 3:1 hydrochloric acid (HCl)/nitric acid (HNO$_3$) (v/v) using a microwave digestion system (Mars 5, CEM, USA) according to EPA method 3051 (USEPA, 1994).

2.5. Chemical analyses

Soil leachates and extracts were filtered through 0.45 µm syringe filters, acidified with HNO$_3$, and stored at 4°C prior to elemental analysis.

Element concentrations were analysed using ICP-OES (Optima 2000 DV, Perkin Elmer, USA), except for pore water sampled in 2005, which was analysed by the accredited laboratory of ALcontrol (Linköping, Sweden) using ICP-MS and ICP-AES for the determination of trace elements and Fe, respectively. DOC was determined according to the European standard method EN 1484 (CEN, 1997).

As(III) and As(V) were separated and identified using ion chromatography coupled to inductively coupled plasma mass spectrometry (ICP-MS). The samples were injected using a Rheodyne 7010 6-port injection valve fitted with a 100µl sample loop. A Hamilton PRP X-100 (125 mm × 4.0 mm, 10 µm) was used as an ion exchange column and the eluent, 12.5 mM H$_3$PO$_4$ adjusted to pH 8.5 with NH$_3$, was pumped isocratically at a rate of 1.0 ml min^{-1} using a Jasco PU-1580 HPLC-pump. The ICP-MS (SCIEX ELAN 6000, Perkin-Elmer, USA) was equipped with a cross-flow nebulizer combined with a double-pass spray chamber for sample introduction.

Redox potential and pH were measured using InLab 502 and 405 glass electrodes (Mettler Toledo, Sweden), respectively, connected to a PHM95 pH/ion meter (Radiometer, Denmark). EC was measured using a 2-pole conductivity cell (CDC641T, Radiometer, Denmark) connected to a CDM210 conductivity meter (Radiometer, Denmark).

2.6. Toxicity measurements

Basal cytotoxicity of the pore water of the soils was assessed using the growth inhibition of L-929 mouse fibroblast cells monitored by a neutral red incorporation assay (Borenfreund and Puerner, 1985) adapted for L-929 cells (Sauvant et al., 1995). Cells were incubated in a humidified atmosphere at 37°C, 5% CO$_2$, and pH 7.2 in 96-well microplates (Falcon, Becton Dickinson Labware, USA) seeded with 2500 cells per well and grown in EMEM (Gibco, Sweden) complemented with 10% fetal calf serum (Gibco), 1% L-glutamine (Gibco), 1% non-essential amino acids (Gibco) and gentamicin (50 mg l^{-1}, Merck, Sweden) for 24h prior to exposure. Six replicates

Table 2
Pseudo-total concentrations of elements (mg kg^{-1} dw for all except Fe; g kg^{-1} dw) in soils F and R before and after treatment ($\pm$SD, $n=6$)

Element	Soil F			Soil R		
	Control	1% SA	8% OSG	Control	1% SA	8% OSG
As	222±13	247±16	235±26	89±11	100±11	91±7
Cr	45±2	89±64	585±25	42±4	75±9	620±104
Cu	8±2	18±7	113±13	29±4	43±4	129±20
Mn	364±44	527±176	561±34	289±13	383±31	521±67
Ni	11±1	26±18	128±21	7±1	16±2	132±12
Zn	80±7	83±5	71±6	58±6	68±10	63±23
Fe	18±3	26±6	81±7	16±1	30±4	79±17

of pore water from each soil were sterilised by filtration (0.22 μm, Millipore) and were tested in 12.5, 25, and 50% (v/v) dilution series with growth medium (200 μl/well) for 72h. Cell survival was determined by reference to the linear uptake of neutral red over a 3h exposure period, detected spectrophotometerically at 540 nm (EMax, Molecular Devices, USA). Data are presented as percentages relative to the survival of unexposed control cultures.

2.7. Statistical analyses

The statistical significance of differences in means was determined (where appropriate) using the two-sample t-test ($p<0.05$).

3. Results

3.1. Total elemental concentrations in field lysimeters

Compared with the normal concentration range of As in uncontaminated topsoils (0.1–40 mg kg^{-1} dw;

Bowen, 1979), total As concentrations in the unamended soils (Table 2) were high and exceeded the generic guideline value for contaminated land designated for "less sensitive use" (e.g. industrial areas) in Sweden (40 mg kg^{-1} dw; SEPA, 1996). For the unamended soils, the metal concentrations were within normal ranges, but the metal concentrations increased following soil amendment. In soil with added OSG, the concentration of Cr exceeded the Swedish guideline value for contaminated land designated for less sensitive use (250 mg kg^{-1} dw), while the contents of Cu and Ni exceeded the guideline levels for land with sensitive use (100 and 35 mg kg^{-1} dw, respectively).

3.2. Elemental leaching in batch leaching tests

Depending on the soil type, amendment with OSG reduced the leaching of As by 28–94% and the leaching of Cr, Cu and Zn by 82–85%, 66–79% and 94–96%, respectively. However, the leaching of Ni increased by 1300–1500% at a cumulative L/S ratio of 10. The

Table 3
Results of batch leaching tests (in mg kg^{-1} dw) on unamended and amended soils ($\pm$the range of values; $n=2$) compared with the European limit values for waste acceptable at landfills for inert waste (EU Council, 2003)

L/S	Element	Soil F			Soil R			Limit value
		Control	1% SA	8% OSG	Control	1% SA	8% OSG	
2	As	**0.17±0.006**	0.018±0.01	<0.004	**0.15±0.007**	**0.11±0.03**	0.032±0.00001	**0.1**
	Cr	0.0025±0.0002	0.00046±0.0001	<0.0004	0.005±0.001	0.0060±0.004	0.0030±0.001	0.2
	Cu	0.0050±0.001	0.0005±0.001	0.0014±0.002	0.032±0.002	0.025±0.005	0.016±0.002	0.9
	Ni	0.022±0.0007	0.033±0.003	**0.30±0.08**	0.005 0±0.001	0.0070±0.001	0.063±0.003	**0.2**
	Zn	**2.24±0.007**	0.21±0.04	0.022±0.01	0.69±0.08	0.52±0.1	0.050±0.01	**2**
	Fe	0.052±0.007	0.038±0.01	0.024±0.02	0.21±0.001	0.17±0.02	0.18±0.04	n.a.
10	As	**3.07±0.8**	**2.34±0.4**	0.18±0.3	**2.78±0.1**	**1.28±0.2**	**1.99±0.1**	**0.5**
	Cr	0.070±0.02	0.076±0.02	0.011±0.007	0.012±0.0007	0.039±0.03	0.002±0.0007	0.5
	Cu	0.027±0.003	0.015±0.005	0.006±0.01	0.18±0.005	0.13±0.02	0.062±0.001	2
	Ni	0.035±0.0006	0.051±0.01	**0.56±0.1**	0.016±0.005	0.039±0.009	0.22±0.002	**0.4**
	Zn	2.66±0.09	0.27±0.06	0.12±0.02	1.74±0.2	0.65±0.001	0.11±0.003	4
	Fe	11.6±4.2	18.1±1.3	4.78±3.6	5.7±0.2	11.3±0.1	17.1±0.4	n.a

Values written in bold were over the limit given by the EU Council.
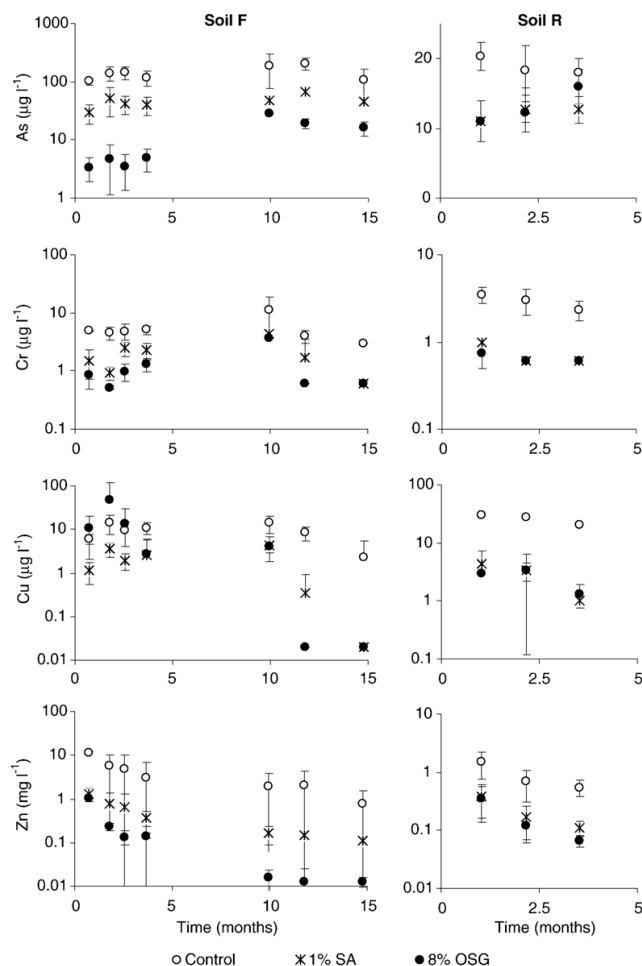< below instrument detection limit.
n.a. not available.

Fig. 2. Changes in pore water concentrations of As, Cr, Cu, and Zn over time in the lysimeters. Error bars represent the standard deviations of mean values ($n=3$).

addition of SA reduced leaching of As, Cu and Zn by 24–54%, 26–45% and 63–90%, respectively. However, the leaching of Cr and Ni increased by 8–200% and 50–140%, respectively. According to the waste acceptance criteria for landfills set by the Council of the European Union (EU Council, 2003), none of the soil mixtures complied with the limit values for inert waste landfills (Table 3). For the controls and soils amended with 1% SA, As exceeded control limits, and Ni leaching from soil F amended with 8% OSG also exceeded control levels. Further, the concentrations of Zn at L/S 2 from the unamended soil F exceeded the limit value. After

treatment of soil R with 8% OSG, As leaching still exceeded critical limits and exceeded the concentration leached from soil F by an order of magnitude. Both the controls and soil F amended with 1% SA would require landfill for hazardous waste (>2 mg As kg^{-1} dw at the cumulative L/S 10), while the other soil mixtures would be acceptable at landfills for non-hazardous waste.

3.3. Elemental leaching in field lysimeters

On average, treatment with SA reduced the leaching of As by 68% for soil F and by 36% for soil R, while the
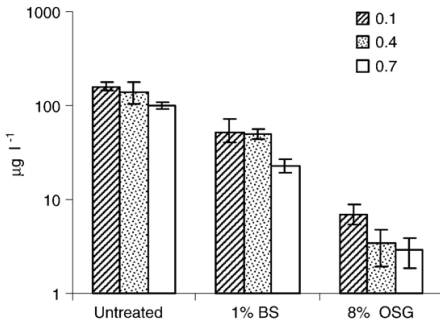
Fig. 3. Average concentrations of As in lysimeter pore water at depths of 0.1, 0.4 and 0.7 m in unamended and amended soil during the first year of the experiment. Error bars represent the standard deviations of mean values ($n=4$).

addition of OSG reduced As leaching by 92 and 31%, respectively. Over time, the mobility of As increased in both soils after amendment with OSG (Fig. 2). As concentrations in soil solution from soil F increased from about 4 to 28 $\mu g \, l^{-1}$ after the first winter. Leached concentrations from the control and this soil amended with SA varied between 101–208 and 30–67 μg As l^{-1}, respectively, during the observation period. The release of As decreased with soil depth, with the most pronounced differences being observed during the first sampling year (Fig. 3). In soil R, no significant ($p < 0.05$)

difference in As leaching from the control and the OSG mixture was found after 3 months, but the concentrations in solution were low ($\leq 20 \, \mu g \, l^{-1}$ As).

Soil treatment with SA and OSG reduced Cr and Zn leaching by (on average) 80–90%. In soil F, the efficiency of OSG was slightly higher than that of SA in this respect. The Zn concentration in the pore water decreased over time and increased with soil depth, causing the large standard deviations presented in Fig. 2. The leaching of Cu decreased by (on average) 80–90% after treatment of either soil with SA and after amendment of soil R with OSG. Initially, Cu leaching increased after treatment of soil F with OSG, but towards the end of the observation period the leached Cu concentrations fell below the detection limit of 0.02 $\mu g \, l^{-1}$.

Soil treatment with OSG increased the leaching of Mn by (on average) 20–40%, whereas the addition of SA caused 3–4 times greater Mn leaching (Fig. 4). The leaching of Ni increased by 93–94% after the addition of OSG, while pore water from soil amended with SA contained twice the amount leached from the control. The levels of Mn and Ni leached from soil decreased considerably over time and, as for Zn, they increased with soil depth.

Treatment of soil R reduced the concentration of DOC (dissolved organic carbon) in the pore water by (on average) 65% (from 35 to 12 mg l^{-1}), while treatment of soil F by SA and OSG gave average reductions
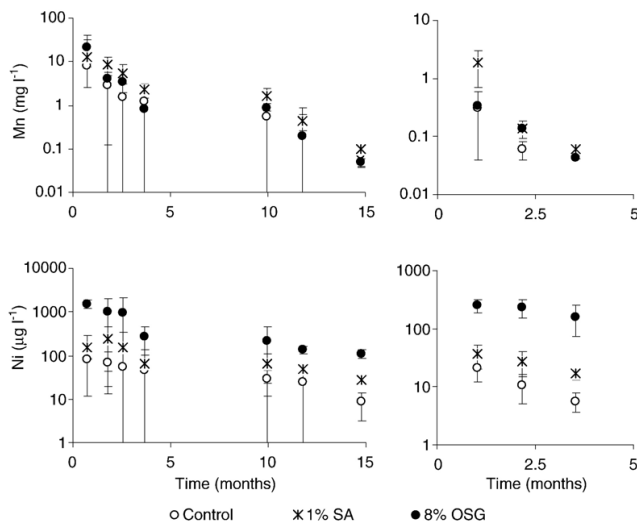

Fig. 4. Changes in pore water concentrations of Mn and Ni over time in the lysimeters. Error bars represent the standard deviations of mean values ($n=3$).
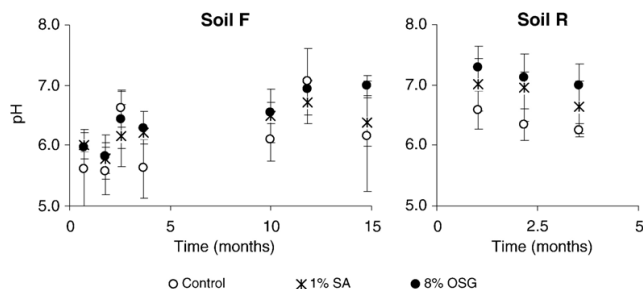
Fig. 5. Changes of pH in the pore water from the lysimeters over time. Error bars represent the standard deviations of mean values ($n=3$).

of 13% and 54%, respectively (from 11 to 9.5 and 5 mg l^{-1}). Compared to the controls, the concentrations of Fe in the first two pore water samples from soils amended with OSG were slightly elevated (<1 mg l^{-1}), but they rapidly decreased to levels below the detection limit (0.05 mg l^{-1}).

The treatments led to increases in pore water pH in both soils (Fig. 5). Initially, the pore water pH was lower in soil F than soil R, but the difference decreased over time as the pH increased in soil F and decreased in soil R.

The redox potentials of soils F and R were not significantly different and the treatments had no significant effect on the redox potentials either. During the last sampling occasion in 2006, the redox potential varied from 138mV to 164mV in the soil solutions.

3.4. Arsenic speciation in soil pore water

As(V) was the predominant As species measured in soil solutions from both the unamended and amended soils F and R. The concentration of As(III) was below the detection limit of 0.4 μg l^{-1} in all samples except for a few samples from soil F collected after 2 months. In these samples, no clear effect of the iron treatment on the speciation of As was discerned.

3.5. Toxicity of soil pore water

SA and OSG treatment of soil F induced cytotoxicity of the pore water in a dose-dependent manner (Fig. 6). The toxicity increased with soil depth and, at 50% dilution, the pore water collected after 2 months from 0.7m depth in SA- and OSG-amended soil reduced the survival rates of L-929 cells by (on average) 7 and 31%, respectively. However, after 4 months, only the pore water from 0.7m depth in SA-amended soil was cytotoxic. Pore waters from unamended and amended
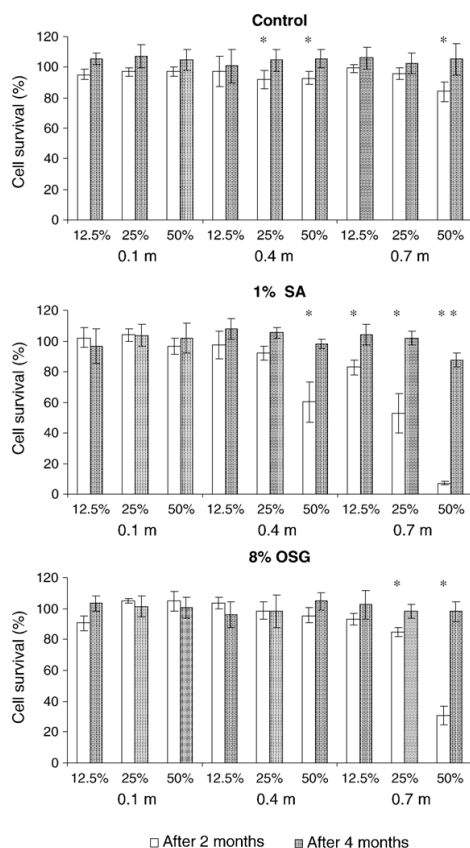

Fig. 6. Cytotoxic effects at 12.5, 25, and 50% (v/v) dilution of lysimeter pore water collected from unamended and amended soil F after 2 and 4 months of the experiment. Each column represents one sample from a depth of 0.1, 0.4, or 0.7 m. Error bars represent the standard deviations of mean values ($n=6$). *Cell survival statistically different from control ($p<0.05$).

soil R did not induce detectable cytotoxic effects in the L-929 cells.

4. Discussion

4.1. SA and OSG as stabilising additives

Soil stabilisation with 1% SA decreased the mobility of As, Cr, Cu, and Zn without causing substantial increases in Fe leaching, thus confirming the effectiveness of Fe^0 for stabilising As and trace metals in contaminated soil (Kumpiene et al., 2006; Mench et al., 2003). The treatment could be considered effective for both studied soils, although it had a greater effect on As mobility in the soil with the lower organic matter content. In addition, some Mn and Ni were released upon oxidation of the SA in the soil.

Although the effect of SA was significant, it was lower than reported in laboratory studies (Kumpiene et al., 2006), where As leaching was reduced by 99% after addition of 1% Fe^0 with <0.1 mm particles. The poorer stabilisation in the field experiment could be due to an uneven distribution of the ameliorant in the soil body caused by insufficient mixing. It can be hypothesised that better mixing of the soil and ameliorant would increase the probability of chemical interactions, leading to increased sorption of As to iron oxide surfaces. Moreover, use of smaller particles generally leads to increased reactivity due to increases in their relative surface area and more even distribution of the particles at a micro scale.

Kumpiene et al. assessed the effects of soil amendment using a similar batch leaching test to that in our study but a different filtration procedure, *i.e.* an open-air system (vacuum filtration). Such a procedure increases the probability of iron oxide precipitation in the filter and the subsequent sorption of As. This would lead to underestimation of the As content of the leachate. However, the authors also observed a 99% reduction of As concentration in the soil pore water. Hence, to enhance the effect of SA treatment higher addition rates and/or smaller particles could be used, but these changes would increase the potential risks of Mn and Ni leaching. Alternatively, a more efficient mixing procedure could be developed that would improve the efficiency of the remediation.

In the soil with the low organic matter content (soil F), 8% OSG was more effective than 1% SA in scavenging As, Cr, and Zn, but was less effective for Cu retention. However, in the soil with the higher organic matter content (soil R) the efficiencies of OSG and SA treatment were similar. The effect of OSG treatment on As mobility in soil R became insignificant after about 3 months. The low iron content of soil pore water indicated that As desorption occurred without dissolution of the iron oxide host. Thus, in soils with low organic contents, OSG can be an effective ameliorant, but addition rates should be minimised to reduce soil enrichment with Cr, Cu, and Ni and to minimise potentially high releases of Mn and Ni. The occurrence of such negative side-effects is a drawback of the use of industrial by-products. However, the effects should be weighed against the benefits of re-using material that would otherwise be landfilled.

4.2. Elemental leaching and toxicity of soil pore water

The concentrations of Fe in pore water from the amended soils were low and the predominant As species was As(V), indicating that the soil conditions were aerobic and the iron oxides were stable. The observed redox potentials were also in the range of moderately oxidising conditions. Thus, the depletion of As(III) in pore water from soil F over time was probably due to the oxidation of As(III) to As(V) since the total As concentration remained constant.

In aerobic environments, organic matter and pH play significant roles in controlling the mobility of As in soil (Bowell, 1994; Dobran and Zagury, 2006). Under aerobic conditions, soil organic matter can mediate the reduction of As(V) to As (III) in soil solutions (Redman et al., 2002). However, in the present study, no As(III) was detected in aqueous extracts of soil R, which had a high organic matter content. The As concentration in unamended soil F was more than double the concentration in soil R, but the As concentration in pore water of soil F was ten times greater than that of soil R. The increased retention of As in soil R may be due to its high organic matter content, since organic matter–metal complexes that form in soil can bind As anions strongly (Redman et al., 2002).

As(V) adsorption by iron oxides has been reported to decrease with increasing pH (Pierce and Moore, 1982; Raven et al., 1998) and also as a result of dissolved organic matter competing for sorption sites (Grafe et al., 2001; Redman et al., 2002). Such processes could explain the lower treatment efficiency for As in soil R than in soil F (Fig. 2). However, even though the pore water pH became similar in the soils over time (Fig. 5), the retention of As remained markedly higher in soil F. The increase in pore water pH in soil F amended with OSG (Fig. 5) could explain the increased mobility of As over time in this soil (Fig. 2). The sorption of DOC on iron oxides in soil R is suggested by the reduced DOC

concentration in pore water after treatment and probably explains the lower efficiency of As sorption in this soil. Consequently, iron treatment is not recommended for As-polluted soils with high organic matter contents. Minimising the addition of new organic matter to the soil could lead to a considerable decrease in the concentration of DOC in the pore water. However, Gu et al. (1994) found adsorbed organic matter to be difficult to desorb from iron oxides and Kalbitz et al. (2000) reported that adsorption reactions can protect DOC against degradation. These findings await verification under field conditions.

Because air penetrates the soil surface, the decreasing concentrations of As in pore water from greater soil depths were unexpected. However, this trend might be due to increased interactions with iron oxide as the water percolates through the soil. Other elements (Mn, Ni, and Zn) showed increasing concentrations in pore water with soil depth, possibly due to initial wash-out of the loosely-bound fraction in the top soil layers. Of these elements, Mn and Ni showed increased mobility after soil amendment and, hence, their concentrations correlated with the observed toxic responses (Fig. 6).

Ni leaching was higher after OSG treatment than after SA treatment, while Mn showed the opposite trends. Sauvant et al. (1997) determined the IC_{50} (50% inhibitory concentration) value for Mn to be 28 mg l^{-1} for the neutral red assay. Hence, the high Mn concentration (13 mg l^{-1}) in the pore water sample from 0.7m depth in SA-amended soil could possibly explain the induced cytotoxicity. The corresponding sample from OSG-amended soil, showing the next highest cytotoxicity, had high concentrations of both Mn and Ni (7.8 and 2.2 mg l^{-1}) whereas the concentrations of other elements were in the same range as for non-cytotoxic samples. However, the mixture of metals may have exerted additive or synergistic effects on cytotoxicity. The low initial pH of soil F pore water (pH ≤ 6, Fig. 5) could explain the greater release of metals from this soil than from soil R, and hence the difference in cytotoxicity values for pore waters from the two soils. The incorporation of lime to increase solution pH could reduce the risk of high trace metal leaching, but it would reduce the adsorption of As by iron oxides.

Leaching of Cr and Cu was low and was not considered to be environmentally significant. For example, the maximum concentrations measured in soil pore water were below the World Health Organization (WHO) threshold values for drinking water, (50 µg l^{-1} for Cr and 2 mg l^{-1} for Cu; WHO, 2006). Despite the high soil concentrations of these elements after OSG addition, their mobility decreased after soil amendment. One exception

was the initial increase of Cu leaching observed after OSG amendment of soil F (Fig. 2). This was probably associated with low pH (≤ 6) resulting from the addition of OSG, which outweighed the effects of adsorption. As pH declines, Cu adsorption by iron oxides decreases markedly (Schwertmann and Taylor, 1989). The increased leaching of Cu from the unamended soil R was probably due to higher complexation to DOC in this soil.

4.3. Assessment and management of iron-amended soil

Iron treatment could be applied in situ or ex situ, i.e. prior to landfilling or re-using excavated soil. Swedish guidelines for contaminated soils comprise generic clean-up values for trace elements depending on proposed future uses of the remediated sites, e.g. residential or industrial areas (SEPA, 1996). The ideal target would be to meet the guideline limit, but iron treatment in situ is not suited for this purpose. The incorporation of OSG increased the total contaminant levels in the soil. However, soil treatment with both SA and OSG decreased the leaching of As and several trace metals without causing formation of the highly toxic As(III) species. Treatment with Fe^0 or iron oxides has also been shown to decrease the mobility and bioavailability of trace elements, to reduce microbial toxicity and to increase plant growth in metal-As contaminated soil (Hartley et al., 2004; Kumpiene et al., 2006; Mench et al., 2003; Mench et al., 2006). Since the use of industrial by-products could entail the release of chemical impurities, their application in sensitive environments should be avoided. Soil stockpiling at a treatment plant for aging prior to ex situ applications or the addition of pH-regulating substances could reduce this problem.

If iron stabilisation is used as pre-treatment before landfilling, the soil is assessed following the criteria and procedures for acceptance of waste at landfills. Applying the batch leaching test (CEN, 2002) and criteria set by the EU Council (2003), treatment with SA or OSG can result in the "re-classification" of soil to a different landfill class. However, the CEN batch test does not consider redox conditions and thus underestimates the risk of As release upon disposal of the amended soil at a traditional anaerobic landfill (Maurice et al., in press). Anaerobic conditions can be avoided by re-using amended soil in constructions such as noise barriers or landfill cover, thereby reducing the risk of significant releases of As. However, the acceptability of soil as a construction material in several countries, e.g. Germany, Italy, and the Netherlands, depends upon several factors, including chemical contamination levels.

5. Conclusions

Stabilisation of CCA-contaminated soil with steel abrasive (SA) or oxygen scarfing granulate (OSG) decreased the concentrations of As, Cr, Cu, and Zn in leachates and soil pore water. The effect on the mobility of As was lower in the soil with higher organic matter content, probably due to dissolved organic matter competing for sorption sites on the iron oxides. Because of its lower pore water pH, the release of metals was generally greater from the soil with lower organic matter content, but the treatment efficiency was similar for both soils. Oxidation of SA and OSG in the soils caused high initial releases of Mn and Ni that induced cytotoxicity of the soil pore water. SA and OSG may be effective amendments for CCA-contaminated soil at field-scale, but further measures are needed to reduce the release of their chemical contaminants.

Acknowledgements

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Assessing the environmental impact of ashes used in a landfill cover construction

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Abstract

Large amounts of construction materials will be needed in Europe in anticipation for capping landfills that will be closed due to the tightening up of landfill legislation. This study was conducted to assess the potential environmental impacts of using refuse derived fuel (RDF) and municipal solid waste incineration (MSWI) ashes as substitutes for natural materials in landfill cover designs. The leaching of substances from a full-scale landfill cover test area built with different fly and bottom ashes was evaluated based on laboratory tests and field monitoring. The water that drained off above the liner (drainage) and the water that percolated through the liner into the landfill (leachate) were contaminated with Cl^-, nitrogen and several trace elements (*e.g.* As, Cu, Mo, Ni and Se). The drainage from ash containing layers will probably require pretreatment before discharge. The leachate quality from the ash cover is expected to have a minor influence on overall landfill leachate quality because the amounts generated from the ash covers were low, $<3\text{-}30$ l $(m^2 \, yr)^{-1}$. Geochemical modelling indicated that precipitation of clay minerals and other secondary compounds in the ash liner was possible within 3 years after construction which could contribute to the retention of trace elements in the liner in the long term. Hence, from an environmental view point, the placement of ashes in layers above the liner is more critical than within the liner.

Keywords: landfill capping; construction material; ash; leaching; geochemical modelling; clay formation

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Introduction

Recent EU legislation (EU Council, 1999) prescribes stricter rules for landfilling which leads to the closure of many old landfills. According to Swedish legislation, the landfill operator must install a top cover after closure for both municipal solid waste and hazardous waste landfills. A landfill cover is a multilayer system that serves to reduce the emission of landfill gas into the atmosphere and the infiltration of water into the waste. The only legal requirement is that the amount of water that percolates through the cover must not exceed $5\,l\,(m^2\,yr)^{-1}$ for hazardous waste landfills and $50\,l\,(m^2\,yr)^{-1}$ for non-hazardous waste landfills (SFS, 2001), which corresponds to a hydraulic conductivity of about 10^{-10} and 10^{-9} m s^{-1}, respectively.

The landfill cover is usually built using a combination of natural mineral materials (*e.g.* gravel, sand, till and clay) and synthetic materials (*e.g.* geomembranes). An estimated 50 000 t ha^{-1} of such materials are needed to fulfil the legal requirement (Lagerkvist, 2000) which raises costs of about 2 million Euros ha^{-1} and puts strain on the environment through the exploitation of natural resources. An alternative can be to use wastes such as ashes from the incineration of municipal solid waste or bio fuels provided that they can meet the same functional requirements as the materials they replace. For example, compacted fly ash can have a hydraulic conductivity similar to that of clay, *i.e.* $<10^{-9}$ m s^{-1} (Chandler *et al.*, 1997; Muhunthan *et al.*, 2004). Another prerequisite for using wastes is their available quantities on the market. In Sweden, over 1 million tonnes of ashes are generated annually (Ribbing, 2007) and the production is increasing with the efforts to minimise the landfilling of waste and to increase the use of bio fuels. However, because ashes are enriched in trace elements such as Cd, Cu, Pb and Zn as compared to natural materials (Chandler *et al.*, 1997), their management raises serious environmental concerns due to the potential leaching and release of these contaminants. A thorough characterisation of the ashes to be used and an investigation of their behaviour under the expected exposure conditions are compulsory.

Studies by Zevenbergen *et al.* (1994; 1999) indicated that the weathering products of incineration ashes are analogues to those of volcanic ashes, though the kinetics of incineration ash weathering is considerably more rapid. Other studies (*e.g.* Lin and His, 1995; Miyake *et al.*, 2002; Kasture *et al.*, 2005; Penilla *et al.*, 2003) describe the conversion of fly and bottom ashes into zeolithes. Zevenbergen *et al.* (1994; 1999) identified the neoformation of well-ordered clay minerals such as illite and non-crystalline clay (allophanes) in incineration ashes after about 10 years of weathering. The precipitation of clay and other secondary compounds such as Fe/Al-hydroxides can significantly contribute to the retention of trace elements in the ashes (Zevenbergen *et al.*, 1999; Meima and Comans, 1999) and, hence, could affect the long-term leaching behaviour.

In this study, the leaching of substances from a landfill cover test area built with different ashes was evaluated based on laboratory tests and a 3-year field study. Processes controlling the short- and long-term release of substances from the ashes were discussed based on geochemical equilibrium calculations. The overall aim was to assess the potential environmental impacts of using ashes in landfill covers.

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Material and methods

Field tests

From 2003 to 2005 a four hectares landfill cover test area was established at the Tveta landfill, southwest of Stockholm, Sweden. The area was divided into six sub-areas with different recycled materials used in different layers of the construction. Three of the areas, A1, A2 and A4, were considered in this paper (Figure 1). The construction of A1 and A2 was finalised in September 2003 and A4 was completed in March 2005.

	A4	A2	A1
Vegetation layer ≈ 0.3 m	Compost		
Protection layer ≥ 1.5 m	Sludge/Fine BA fraction (40/60)		Sludge/FA (40/60)
Drainage layer ≈ 0.3 m	Coarse BA fraction		
Liner ≥ 1.0 m	FA/BA (50/50)	BA/FC (90/10)	FA
Gas drainage layer ≈ 0.3 m	FBI sand	BA	

Figure 1   Design of the sub-areas A1, A2 and A4 of the landfill cover test area at the Tveta landfill. BA = Bottom ash; FA = Fly ash; FC = Friedland clay; FBI = Fluid bed incineration.

A layer of sand from fluid bed incineration or bottom ash (BA) was placed on the waste as a foundation for the landfill cover and to enable the drainage of landfill gas. This layer is connected to the gas collection system. BA in the liner (barrier layer) was mixed with either fly ash (FA) or Friedland clay (FC) to reduce its hydraulic conductivity, while FA was tested separately. A drainage layer consisting of coarse BA was placed above the liner to collect and discharge percolating water. In the protection layer, which protects the liner from freezing, desiccation and root penetration, two ash-sludge mixtures were tested. A layer of compost was placed on top of the landfill cover to enhance the establishment of vegetation.

Material

Four different ashes from two incinerator plants were used in the test areas (Table 1). Since the test areas were built during three years, the composition of the materials may vary though the ashes originate from the same source. For example, the mixture of FA and BA in A4 does not correspond to a mixture of the BA in A2 and the FA in A1.

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Table 1   Origins and types of ashes used in the landfill cover test areas A1, A2 and A4.

Abbreviation	Origin	Ash type	Position in the landfill cover
BA-L	Grate type incinerator	Bottom ash	Liner (A2; A4)
FA	Grate type incinerator	Fly ash	Liner (A1; A4)
			Protection layer (A1)
BA-P	Stoker grate type incinerator	Bottom ash (sieved to <10 mm)	Protection layer (A2; A4)
BA-D	Stoker grate type incinerator	Bottom ash (sieved to >10 mm)	Drainage layer (A1; A2; A4)

The grate type incinerator is supplied with RDF composed mainly of sorted construction and demolition waste like paper, cardboard, plastic, wood, railway ties and wood chips. The bottom ash used in the liner (BA-L) was screened to remove magnetic material. Prior to mixing with FC, the BA-L was stored outdoors for about one year for ageing in order to reduce the risk of deteriorating the swelling properties of the FC (Brundin *et al.*, 2001). The FA consists of a mixture of electrostatic precipitator and hose filter ash. It was stored in silos at the power plant and moistened prior to transport to the landfill. After arrival at the landfill, the FA was used immediately with no ageing period. If this was not possible, the ash was stored outside covered with tarpaulins for a maximum of six months. The FA used in area 1 was not a pure fly ash, but the fine fraction of a BA-FA mixture containing predominantly FA. At that time FA and BA were not separated at the incineration plant. After arrival at the landfill it was sieved to <10 mm particle size. The FA mixed with BA for A4 was not sieved.

The stoker grate type incinerator mainly receives municipal solid waste. Immediately after incineration, the bottom ash was quenched in a water tank. After arrival at the landfill the BA was air dried for several months. Afterwards coarse components and magnetic material were removed and the remainder was separated into two fractions using a 10 mm mesh sieve. The larger particle size (>10 mm) was used in the drainage layer (BA-D) and the smaller fraction (<10 mm) was used in the protection layer (BA-P).

The grain size distribution of the used ashes is given in Figure 2. The ashes for areas A1 and A2 were sieved after removing the fraction > 10 mm while the FA/BA mixture for area A4 was sieved in its original state (< 35 mm). The particle size distribution shows that all ashes used in the liner were well graded, *i.e.* the ratio d_{60}/d_{10} was higher than 6. Both BA-P and BA-D were uniformly graded, *i.e.* BA-P was fine gravel and BA-D was fine to medium gravel size.

The sludge used in the protection layer consists of anaerobically digested and dewatered municipal sewage sludge. After transport to the landfill the sludge was stored for several weeks up to months (as long as possible) before it was mixed with the BA-P.
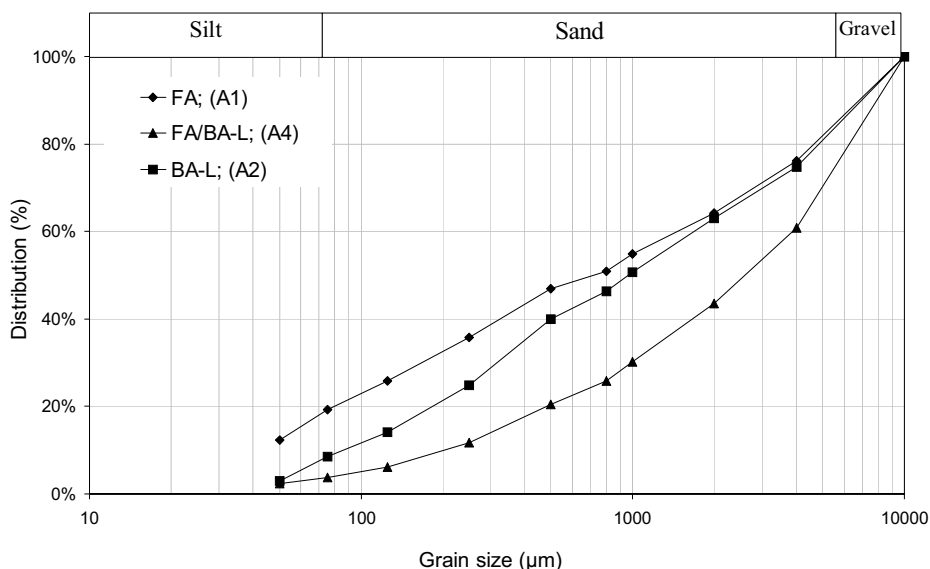
Figure 2   Particle size distribution of ashes used in the liner of the test areas A1, A2 and A4.

Material characterisation

Before and during the installation, several sub-samples of the materials used in the test areas were taken and pooled into composite samples of about 500 kg of BA, 400 kg of FA and 30 kg of sludge. The ash samples were sieved to <10 mm for BA and to <4 mm for FA. The samples were homogenized and then characterised with regard to their total composition and leaching behaviour. Prior to total composition analyses, the samples were ground in a vibratory disc mill to a particle size of 95% <125 µm.

A one-step batch leaching test was used to estimate the water soluble fraction of elements. Solid material was mixed with doubly-distilled water (ddH$_2$O) at a liquid to solid ratio (L/S) of 10 l kg^{-1} and agitated for 24 h using an end-over-end tumbler. The pH and the electrical conductivity (EC) of the suspensions were measured in unfiltered samples. Eluates were then separated from the solid phase samples by filtration through 0.45 µm membrane filters.

Instrumentation and sampling at the field site

In order to simulate a worst case scenario for the hydraulic conductivity of the liner, a part of the slope was levelled and with a bund to retard runoff. For leachate collection, ten lysimeters (1×1m²) made of glass-reinforced epoxy were placed randomly below the liner at the plateau in each area. The ten lysimeters were distributed over an area of about 100 m^2. In some cases, leachate was also sampled via hoses (semi-rigid nylon, 4x6 mm in diameter) for gas sampling installed below the liner. The gas sampling hoses are attached to the horizontal temperature probes below the liner. The samples were taken using a peristaltic pump placed in an enclosure on top of the cover. Drainage was

sampled from wells installed in covered ditches at the bottom of the landfill slope (Figure 3). The wells collected drainage from an area of about 2300 m^2 in A1, 2500 m^2 in A2 and 1900 m^2 in A4.
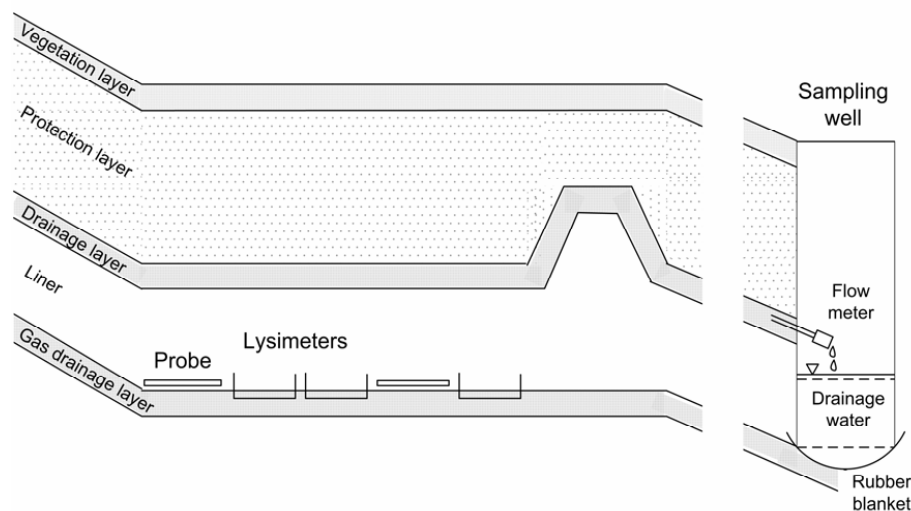

Figure 3   Cross section of the landfill cover test area at the plateau of the slope.

In A1 and A2, leachate and drainage were sampled on ten and eleven occasions, respectively, during 31 months (from April 2004 to December 2006). Samples from A4 were taken on five occasions during 14 months (from September 2005 to December 2006). The samples were stored frozen (-20ºC) until analysis.

Analyses

Total concentrations of elements in the ash samples were determined by the accredited laboratory of ALS Scandinavia (Luleå, Sweden) using ICP-AES (EPA method 200.7; modified) and ICP-SFMS (EPA method 200.8; modified) after digestion according to the ASTM methods D3683 and D3682. Loss on ignition (LOI) was determined after ignition at 1000 ºC for 2 h.

Aqueous samples were acidified with HNO$_3$ (suprapure) and analysed for elemental concentrations using the same methods as above but without prior digestion. Cl$^-$ in leaching test eluates and field samples taken before April 2005 was determined by titration with AgNO$_3$ according to the Swedish standard method SS 028120 (SIS, 1974). SO$_4^{2-}$ in these samples was determined using ion chromatography according to the standard method ISO 10304-2 (ISO, 1995). From April 2005 and onwards Cl$^-$ and SO$_4^{2-}$ were analysed spectrophotometrically (AACE Quaatro, Bran+Luebbe, Germany). Total organic carbon (TOC) and dissolved organic carbon (DOC) were determined according to EN 1484 (CEN, 1997). Total nitrogen (N$_{tot}$) and ammonia nitrogen (NH$_4$-N) were analysed using TRAACS 800 autoanalyzer and from April 2005 using AACE Quaatro (Bran+Luebbe, Germany). N$_{tot}$ was analysed after digestion according to the Swedish standard method SS 028131 (SIS, 1976). In leaching test eluates, pH was measured us-

ing a 340/SET-1 pH meter with a SenTix 41 combined electrode (WTW, Germany) and EC was determined using an inoLab Cond Level 1 meter equipped with a TetraCon 325 standard-conductivity cell (WTW, Germany). In field samples, pH and EC were measured on site using a MX-300 X-mate (Mettler-Toledo, Switzerland). Analysis of most of the elements was accurate within 20% analytical error.

Geochemical modelling

Geochemical equilibrium modelling using PHREEQC-2 (Parkhurst and Appelo, 1999) was applied to the leachates from the test areas in order to (i) identify potential solubility controlling minerals and (ii) to evaluate the possible formation of clay minerals in the ashes. The calculations were performed with the Minteq v4 database modified to include allophone-1.26 (log K_{sp} = 11.27; Su and Harsh, 1998), calcium antimonate (log K_{sp} = -12.55; Johnson *et al.*, 2005), ettringite (log K_{sp} = 62.54; Lawrence Livermore National Library (LLNL) database), halloysite (log K_{sp} = 9.57; USEPA, 1999), illite (log K_{sp} = 9.03; LLNL database), imogolite (log K_{sp} = 13.04; Su and Harsh, 1994) and kaolinite (log K_{sp} = 7.43; USEPA, 1999).

The discussed minerals were selected based on (i) their likeness to be present or formed in MSWI ashes (*e.g.* Dijkstra *et al.*, 2006; Johnson *et al.*, 1999; Zevenbergen *et al.*, 1996) and/or (ii) calculated saturation indices (SI) that approach zero (-1 < log SI < 1). The SI does not confirm whether or not a solid phase is actually present, but it can indicate whether a given solid phase would have a tendency to precipitate (SI > 0) or dissolve (SI < 0). The input files were composed of measured elemental concentrations, pH, alkalinity and temperature of leachates from one selected lysimeter per area in April 2006 (*i.e.* 31 months after construction of A1 and A2 and 13 months after construction of A4). Redox potential (pE) was not measured but reducing conditions corresponding to the pE for methane formation (pE = -4) were assumed in the calculations since methane gas was detected right below the liner (results not shown). Supplementary calculations using pE values between -6 and 6 were performed in order to determine the sensitivity of solid phases to changes of the redox potential.

Results

Total elemental concentrations

The most abundant elements in the ashes are Ca and Si (Table 2). The ashes are also relatively rich in trace elements such as Zn, Cu, Pb, Cr and As. Most trace elements in the sludge/BA-P-mixture likely originate from the BA-P, while the sludge contributes to the elevated content of organic matter in the mixture (as indicated by the LOI; Table 2).

Table 2   Total composition of the ashes and the sludge used in the landfill cover.

	BA-D[a]	BA-P[a]	Sludge/BA-P[a]	FA[b]	BA-L[c]	FA/BA-L[a]
Major constituents (g (kg TS))$^{-1}$)						
LOI	45	132	195	163±30	163±50	190
Al	25	33	29	10±3	33±5	22
Ca	77	120	91	260±50	162±20	214
Cl⁻	n.a.	n.a.	n.a.	66±10	18±20	n.a.
Fe	60	43	33	12±1	17±3	14
K	6	6	7	5±1	6±1	8
Mg	11	12	10	11±2	14±1	10
Mn	1	1	1	1±0.1	1±0.1	1
Na	20	16	13	4±1	6±3	8
P	2	4	6	1±0.1	1±0.2	0.8
S	7	12	13	0.02±0.002	24±20	30
Si	210	140	153	112±30	142±30	102
Ti	4	7	6	5±2	9±4	12
Minor constituents (mg (kg TS)$^{-1}$)						
As	54	31	17	139±29	124±50	135
Ba	1400	1290	947	1910±225	1800±390	2030
Cd	7	8	7	13±2	27±20	25
Co	27	26	20	17±10	33±7	19
Cr	484	455	367	320±120	525±340	433
Cu	2020	3190	2130	475±110	3910±4160	2940
Hg	0.02	0.4	0.4	15±1	1.4±1	1.4
Mo	15	15	8	10±2	27±10	13
Ni	181	180	127	41±9	157±100	123
Pb	1630	883	615	1800±260	1810±1620	2130
V	24	25	28	33±5	98±50	40
Zn	3040	9480	4140	3230±450	5070±4300	6710

[a] n=1.
[b] Average value (±SD); n=3.
[c] Average value (±SD); n=21.
LOI - loss on ignition
n.a. – data not available

Leaching of constituents in batch leaching tests

The results from the leaching test were compared with the European waste acceptance criteria for inert waste landfills, since materials that meet these criteria should also be acceptable in landfill construction applications. BA-P is the only material tested that complies with the criteria for inert waste (Table 3), while the Cl⁻ leaching from other ashes exceeds them. Further, the leaching of SO_4^{2-} exceeds the criteria for all ashes apart from FA and BA-P. Pb leaching from FA exceeds the limit values for inert waste landfills 3-5 times as does Cu leaching from BA-P. The release of Mo from FA also exceeds the criteria. The FA/BA-L mixture shows almost two orders of magnitude higher Pb leaching than the limit value. From BA-D, the leaching of organic matter (as indicated by DOC) is relatively high. The sewage sludge shows elevated SO_4^{2-} release compared to the limit value but also high leaching of nitrogen (N_{tot}).

Table 3   Results of batch leaching tests (L/S 10) for the materials used in the landfill cover compared with the European limit values for acceptance of waste to landfills for inert waste (EC, 2002).

	BA-P[a]	Sludge[b]	Sludge/BA-P[a]	BA-D[c]	FA[c]	BA-L[d]	FA/BA-L[b]	Limit value (L/S 10)
pH	10.4 ±0.3	8.4	10.7±1.2	10.2	12.3±0.2	10.7±1.1	12.3	n.a.
EC (mS/cm)	1.3±1.3	1.3	5.6±2.0	2.3	17.3±12.6	3.8±1.9	18.9	n.a.
Component (mg (kg TS)$^{-1}$)								
N_{tot}	23±20	160	2300±730	35	57±70	31±30	33	n.a.
NH_4-N	0.30±0.2	2.7	1380±640	0.05	5.8±3	4.5±6	23	n.a.
DOC	190±180	250	3940±2600	320	28	n.a.	42	500
Cl^-	3460	690	34600	3460	43400±46000	7360±5500	46100	800
SO_4^{2-}	3140±3100	4980	3780	5290	4010±4300	6630±5300	4370	1000
As	0.1±0.04	0.04	0.24±0.2	<0.07	0.16±0.2	0.04±0.02	<0.16	0.5
Ba	0.18±0.1	0.38	1.1±0.5	0.27	29±40	2.2±4	8.5	20
Cd	0.004±0.003	0.005	0.005±0.001	0.002	0.0019±0.001	0.003±0.001	0.002	0.04
Cr (total)	0.13±0.06	0.02	0.07±0.09	0.17	0.25±0.05	0.29±0.2	0.14	0.5
Cu	3.6±5	1.4	110±100	7.0	0.18±0.2	0.16±0.3	0.23	2
Hg	<0.0002	0.006	<0.0002	0.0003	<0.0002	<0.0002	<0.0002	0.01
Mo	n.a.	n.a.	n.a	n.a.	0.68	n.a.	n.a.	0.5
Ni	0.04±0.02	0.33	3.6±1	0.06	0.013±0.02	0.01±0.01	<0.005	0.4
Pb	0.01±0.01	0.05	0.08±0.09	0.02	12.8±19	0.10±0.2	28.3	0.5
Sb	n.a.	n.a.	n.a.	n.a.	0.033	n.a.	0.002	0.06
Zn	0.05±0.01	1.1	0.57±0.5	<0.04	0.38±0.3	0.08±0.1	4.0	4

n.a. – data not available
[a] Average value (±SD); n=2.
[b] n=1
[c] Average value (±SD); n=3.
[d] Average value (±SD); n=21.

Amounts of drainage and leachate collected in the field tests

The amount of drainage could not be properly assessed due to measurement problems. Based on Swedish climate conditions, about one third each of the yearly precipitation evaporates, runs off at the surface and infiltrates into the ground, respectively (Raab and Vedin, 1995). Given a yearly precipitation of 550 to 650 mm (Alexandersson *et al.*, 1991), the infiltration can be assumed to be 180 to 220 mm. After saturation of the protection layer and vegetation uptake an average of about 150 l (m² yr)$^{-1}$ of drainage water can be expected.

The amounts of collected leachate varied between the test areas and also between the lysimeters within one area. The highest amount of leachate, about 30 l (m^2 yr)$^{-1}$, was collected in A1. In A2, all lysimeters were dry, but leachate samples could be taken through the gas sampling hoses. The lysimeters in A4 collected about 134 l of leachate during the observation period corresponding to about 3 l (m^2 yr)$^{-1}$.

Leaching of constituents in field tests

The quality of leachate and drainage collected from the field test is summarised in Table 4. The pH varied between 6.6 and 8.3 in the drainage and between 8.8 and 12.4 in the leachate without any clear temporal trends.

Table 4   Average quality of all leachate and drainage samples collected from the landfill cover test areas during 31 months for A1 and A2 and during 14 months for A4 (±SD).

	Unit	Drainage			Leachate		
		A1 [a]	A2 [b]	A4 [c]	A1 [d]	A2 [e]	A4 [f]
pH		7.4 ±0.5	7.8 ±0.2	7.1 ±0.5	10.7 ±0.8	9.9 ±0.5	9.7 ±0.4
EC	mS cm^{-1}	18.2 ±2	52.6 ±13	23.5 ±10	57.6 ±12	35.2 ±13	154 ±62
N_{tot}	mg l^{-1}	390 ±450	820 ±430	350 ±180	310 ±82	66.8 ±22	260 ±92
NH_4-N	”	180 ±190	3.1 ±2	110 ±120	220 ±80	31.2 ±12	230 ±100
TOC	”	130 ±51	390 ±190	220 ±100	364 ±100	48.3 ±32	240 ±52
Cl^-	g l^{-1}	7.8 ±6	15.9 ±7	7.0 ±3	21.4 ±5	13.2 ±5	76.9 ±29
S	”	0.56 ±0.2	1.8 ±0.6	n.a.	0.48 ±0.3	0.84 ±0.3	0.34 ±0.07
As	µg l^{-1}	24.1 ±16	85.0 ±39	47.7 ±7	110 ±72	55.4 ±33	210 ±160
Cd	”	1.3 ±1	6.3 ±4	8.2 ±6	12.7 ±28	13.9 ±19	17.1 ±19
Cr (total)	”	7.1 ±10	17.4 ±11	28.3 ±21	12.1 ±15	5.7 ±5	25.1 ±18
Cu	mg l^{-1}	0.51 ±0.5	4.4 ±2	2.3 ±2	2.2 ±2	0.074 ±0.1	5.6 ±6
Hg	µg l^{-1}	0.081 ±0.06	0.17 ±0.07	0.24 ±0.08	0.32 ±0.4	0.090 ±0.05	<0.13
Mo	”	210 ±210	2350 ±870	320 ±120	3850 ±1920	12600 ±8490	1600 ±640
Ni	”	320 ±170	300 ±117	400 ±23	78.7 ±53	13.8 ±12	180 ±250
Pb	”	11.0 ±13	150 ±230	71.7 ±30	13.4 ±25	13.5 ±17	33.4 ±29
Sb	”	35.1 ±75	100 ±89	74.5 ±50	64.4 ±96	32.6 ±66	110 ±48
Se	”	330 ±380	730 ±740	350 ±300	1110 ±1030	200 ±310	2380 ±3390
Zn	”	1460 ±1910	5560 ±2380	2800 ±820	620 ±2450	32.7 ±29	1150 ±2190

n.a. – data not available
[a] n = 11 (1 sampling spot)
[b] n = 10 (1 sampling spot)
[c] n = 3 (1 sampling spot)
[d] n = 33 (7 sampling spots)
[e] n = 13 (4 sampling spots)
[f] n = 11 (4 sampling spots)

Concentration of Cl^- in leachate from A4 decreased by ~50% in nine months, but it appeared relatively constant in the other areas (Figure 4). In agreement with the batch leaching test results (Table 3), leachate from A4 had at least two times higher Cl^- concentration than leachate from the other areas. The EC of both drainage and leachate showed followed the same time trends as the Cl^- leaching.

The N_{tot} in drainage varied greatly, but had decreased by 70% in A1 after two years and in A4 after one year compared to the initial concentrations, *i.e.* ~710 mg l^{-1} for A1 and 450 mg l^{-1} for A4. The concentrations of N_{tot} in leachate were relatively constant over time except for A4 where they decreased by 60% in 14 months (from 310 to 130 mg l^{-1}). NH_4-N accounted for about 45%, <1% and 30% of the total nitrogen content in the drainages from A1, A2 and A4, respectively, and for about 70%, 50% and 90% in leachates from the same areas.
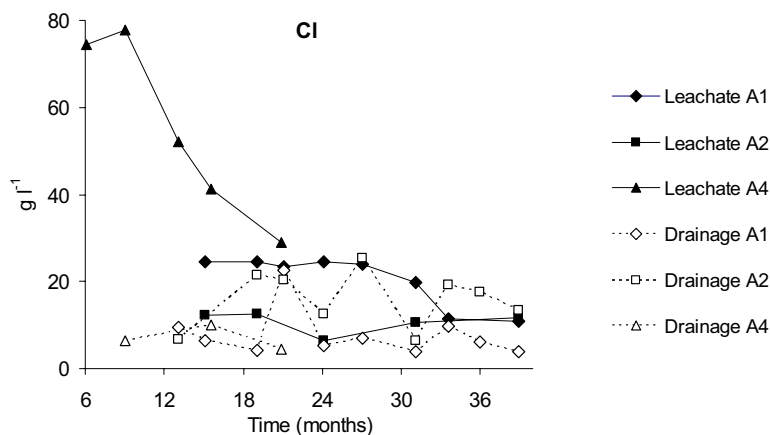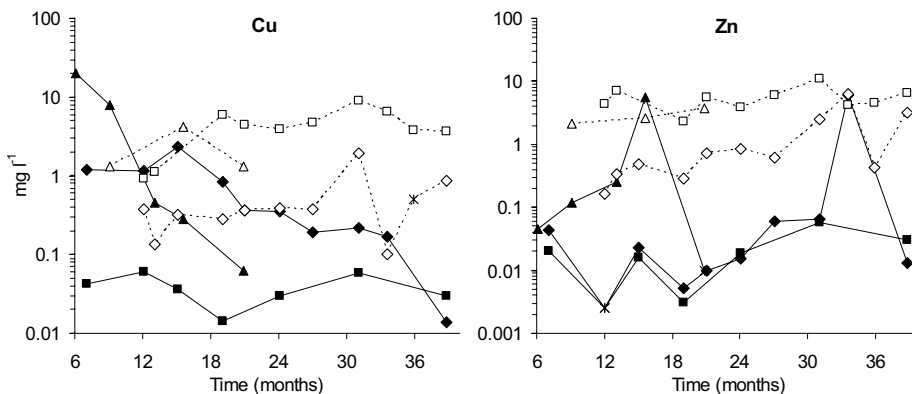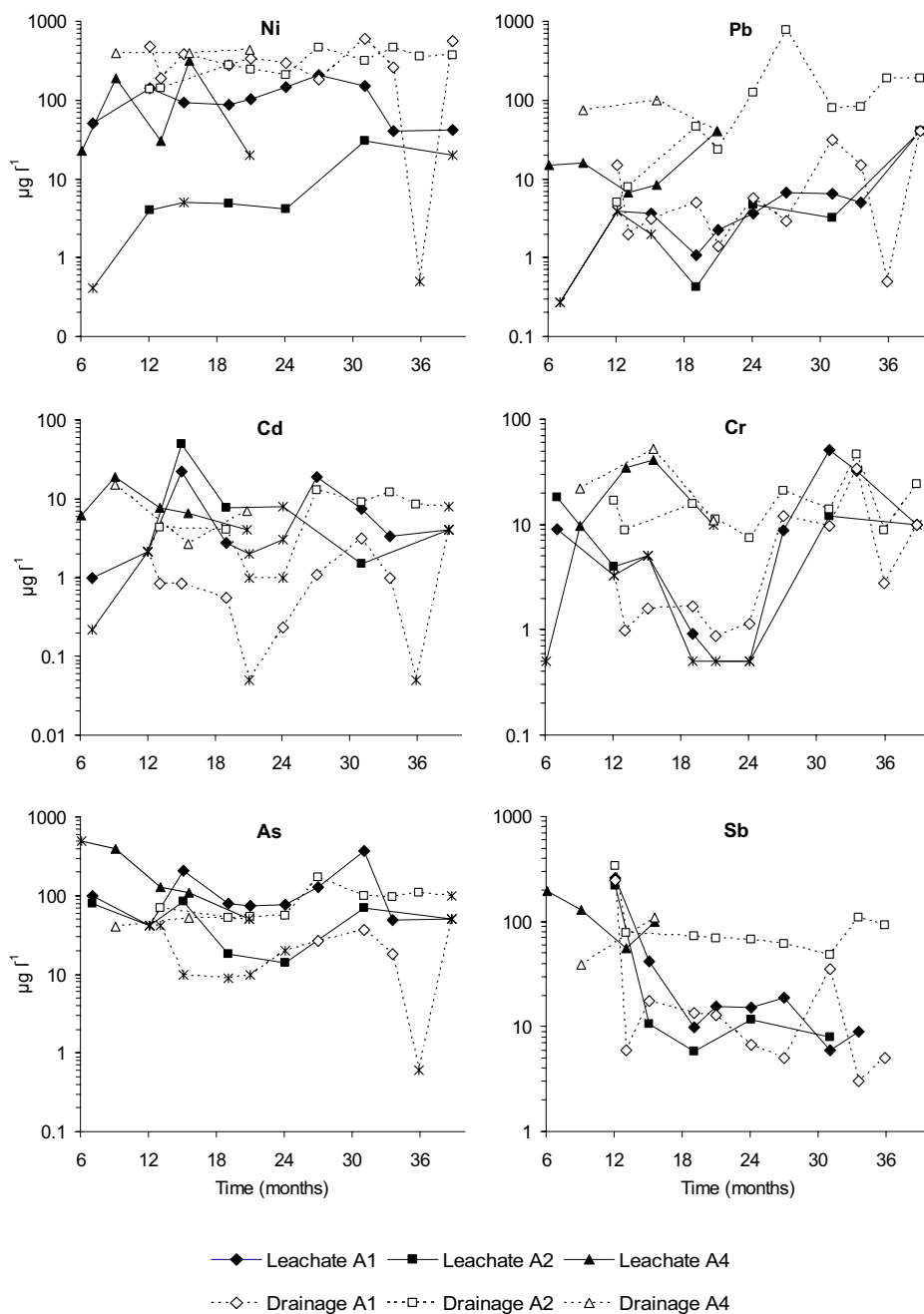
Figure 4   Changes in concentrations of Cl⁻ over time in leachate (average of 2-5 sam-
            ples depending on sampling occasion) and drainage from the test areas A1,
            A2 and A4. Time refers to the period elapsed after construction of the cover.

Generally, the concentrations of dissolved salts and trace elements decreased in the or-
der of A1<A4<A2 for drainage and A2<A1<A4 for leachate (Table 4), with deviations
for some elements. Concentrations of trace elements in the drainage and leachate did
not show any clear tendency to decline over time, except for Sb in all leachates and As
and Cu in leachate from A4 (Figure 5). On the contrary, the leaching of *e.g.* As, Cr, Pb
and Zn tended to increase after about two years. The release of Mo was constant over
time and was about one order of magnitude higher in leachate than in drainage (Table
4).

Figure 5   Changes in concentrations of trace elements over time in leachate (average
of 2-5 samples depending on sampling occasion) and drainage from the test
areas A1, A2 and A4. Time refers to the period elapsed after construction of
the cover. * Concentration below the detection limit of the analysis.

In order to assess the pollution potential of the leachate and the drainage their compositions (presented in Table 4) were compared with different reference values for water quality (Table 5). The limit values for discharge of leachate at the Tveta landfill were assigned by the local authorities based on a classification of the environmental status for lakes and rivers provided by the Swedish Environmental Protection Agency (SEPA, 2000). Also, some limit values used in different European countries for discharge of landfill leachate to surface waters are included in the table. One is the limit values for the percolation test eluate at L/S 0.1 set by the EU Council (2003) for waste acceptance at landfills for inert wastes.

Table 5   Reference values for water quality used for comparison with leachate and drainage from the landfill cover test areas.

Constituent	Unit	Limit values for discharge of leachate into local recipient at Tveta landfill	European limit values for discharge of leachate to surface water recipients [a]	Leaching limit values for inert waste in percolation test at L/S 0.1 [b]
N_{tot}	mg l^{-1}	50	8-70	n.a.
NH_4-N	"	5	n.a.	n.a.
TOC	"	n.a.	70	160 [c]
Cl^-	"	n.a.	n.a.	460
SO_4^{2-}	"	n.a.	300-1000	1500
As	µg l^{-1}	15	50-100	60
Cd	"	0.3	2.5-200	20
Cr	"	5	2100-2200	100
Cu	"	15	50-1000	600
Hg	"	n.a.	0.5-50	2
Mo	"	n.a.	n.a.	200
Ni	"	45	100-2000	120
Pb	"	3	50-1000	150
Sb	"	n.a.	n.a.	100
Se	"	n.a.	30	40
Zn	"	6	200-3000	1200

n.a. – data not available
[a] Based on data from Doedens and Theilen (1992) and Hjelmar *et al.* (1994).
[b] EU Council (2003).
[c] Valid for DOC.

Compared to the Tveta discharge limits, the concentrations of the considered constituents are higher in both leachate and drainage, with the exception of Ni in the leachate from A2. Compared to the European limit values, both leachate and drainage comply with the upper limits except N_{tot}, TOC and Se in both leachate and drainage with the addition of As, Cu and Zn in leachate from A1 and A4 and As (A2), Cu (A2 and A4), S (A2) and Zn in drainage. Compared with the waste acceptance criteria for inert waste landfills, Cl^-, Mo and Se in both leachate and drainage had higher concentrations. In addition, the leachate concentrations of As (all areas) and TOC, Ba, Cu, Ni, Sb and Zn (A1 and A4) and the drainage concentrations of TOC (A2 and A4), As (A2), Cu, Ni, S (A2), Pb (A2), Sb and Zn were higher than the limit values. The concentrations of Cd in leachate and Sb in both leachate and drainage only occasionally exceeded these values.

Geochemical modelling

The calculated SI indicated that gypsum ($CaSO_4: 2H_2O$), bunsenite (NiO), $Ni(OH)_2$ and $PbOH_2$ (for all areas), $CrOH_3$, $SbOH_3$, $Zn(OH)_2$, and zincite (ZnO; for A2 and A4), cuprite (Cu_2O), chalcocite (Cu_2S) and wulfenite ($PbMoO_4$; for A2), powellite ($CaMoO_4$; for A1) and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}:26H_2O$; for A4) could be in equilibrium with the leachates (Table 6). All leachates were undersaturated with respect to carbonates, sulphides and sulphates of the trace elements. Simulations indicated that calcite ($CaCO_3$) and several Fe/Al-(hydr)oxides could precipitate in all leachates. The leachates were supersaturated with respect to allophone in A4 and imogolite, halloysite, kaolinite and illite in A2 and A4.

Table 6   Saturation indices (SI) for minerals and solids in leachates from the landfill cover test areas A1, A2 and A4 collected in April 2006.

Element	Mineral	Log SI		
		A1	A2	A4
Major elements				
Al	$Al(OH)_3$, gibbsite	-0.77	0.29	0.56
	AlOOH, diaspore	0.61	1.68	1.97
	$Al_2O_3(SiO_2)_{1.59}:2.63H_2O$, allophane-1.26	-3.64	-0.28	1.84
	$Al_2SiO_3(OH)_4$, imogolite	-2.27	0.59	2.04
	$Al_2Si_2O_5(OH)_4:2H_2O$, halloysite	-3.45	0.19	2.58
	$Al_2Si_2O_5(OH)_4$, kaolinite	-1.48	2.17	4.65
	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$, illite	-0.09	3.64	9.19
Ca	$CaCO_3$, calcite	3.10	2.30	3.00
	$CaSO_4: 2H_2O$, gypsum	-0.90	-0.17	-0.06
	$Ca_6Al_2(SO_4)_3(OH)_{12}:26H_2O$, ettringite	-2.35	-6.97	-0.25
Fe	$Fe(OH)_3$, ferrihydrite	0.97	1.04	1.05
	FeOOH, goethite	3.75	3.81	3.82
Trace elements				
Cd	$Cd(OH)_2$	-2.15	-4.29	-4.65
Cr	$Cr(OH)_3$	-1.81	-0.87	-1.01
Cu	CuO, tenorite	-2.20	-5.10	-5.67
	Cu_2O, cuprite	2.61	-0.17	-1.84
	Cu_2S, chalcocite	-12.91	-0.25	-6.78
Mo	$CaMoO_4$, powellite	1.09	1.97	3.04
	$PbMoO_4$, wulfenite	-4.14	0.77	-1.24
Ni	NiO, bunsenite	-0,43	-0.60	-0.52
	$Ni(OH)_2$	-0.76	-0.93	-0.88
Pb	$Pb(OH)_2$	-0.70	0.35	-0.59
Sb	SbO_2	-1.59	1.45	1.50
	$Sb(OH)_3$	-5.24	-0.72	-1.02
	$Ca(SbO_3)_2$	-4.65	-4.62	-1.93
Zn	ZnO, zincite	-1.92	-0.43	-0.24
	$Zn(OH)_2$	-2.30	-0.87	-0.81

The major result from varying the pE was that sulphides, *e.g.* chalcocite, greenockite (CdS) and NiS, tended to exhibit supersaturation at lower pE-levels, especially in A2 and A4. (Hydr)oxides of Cu and Fe (*e.g.* tenorite (CuO), Cu(OH)2, malachite (Cu2(OH)2CO3), ferrihydrite (Fe(OH)3) and maghemite (Fe2O3)) might precipitate or equilibrate with the leachates at higher pE-levels. Results indicated that the (hydr)oxides of Cr and Sb (e,g, Cr(OH)3, SbO2 and Sb(OH)3) remained dissolved. Changes of the pE did not affect the SI of the clay minerals.

Discussion

Critical elements as identified from laboratory and field tests

All leachates from the test areas were mainly contaminated with Cl^- and Mo. In particular, A1 and A4 were further contaminated with As, Cu, Se, TOC and nitrogen. The drainage contained elevated concentrations of Cl^-, Mo, Ni, Se, Zn and nitrogen with the addition of As, Cu, Pb, S and TOC in A2 and A4. Overall, the least concentrated leachate, except with regard to Mo and S, was observed in A2 and the least concentrated drainage, apart from NH_4-N, in A1. The relatively low release of constituents from the liner in A2 into the leachate can be explained by the use of only BA and a possible sorption of trace elements to the Friedland clay. Using fly ash in the protection layer (area A1) seems to lower the concentration of TOC in drainage. The high pH of the ash is one factor to consider, and also the high specific surface of the fly ash. In combination these factors may yield less bioactivity in the sludge and retention of organic degradation products. The wide variation of TOC concentrations in the drainage from A2 and A4 could indicate a stronger biological activity and less retention of degradation products in the sludge/BA-mixtures. This might also explain the lower mobilisation of trace elements from the mixture with FA than from that with BA.

The high leaching of easily leachable species such as Cl^- and SO_4^{2-} were predicted from the batch leaching test, while, for example, the leaching of Pb in the field was considerably lower than the laboratory test predicted. This discrepancy is likely an effect of the lower pH (10-11) observed in field than in lab (~12). Leachability of Pb is at its minimum at pH 9-10 and increases sharply at higher pH levels. The use of batch leaching tests at lower L/S (*e.g.* 2 l kg^{-1}) and percolation tests (L/S 0.1-10), could be suggested to better assess elemental leaching from ashes above the liner in the short term (up to 30 years). Leaching from well compacted ashes in the liner is assumed to be diffusion-controlled and, hence, could be better studied using diffusion leaching tests (Kosson *et al.*, 1996).

Processes controlling the release of constituents from the landfill cover

Ash leachate pH is mainly controlled by Ca minerals (Johnson *et al.*, 1995). Based on equilibrium calculations (Table 6), calcite is the predominant buffering constituent in the Tveta ash leachates. Meima and Comans (1997) recognised ettringite as the main pH controlling mineral in ash leachate at pH 10-11. In our study, ettringite was undersaturated in leachates from A1 and A2, but close to equilibrium in A4 and, hence, could control leachate pH in this area. In A1 and A2, the solubility of Ca could be controlled by gypsum. The precipitation of calcite and the undersaturation of ettringite might be explained by carbonation of ash in the liner. However, the high and constant pH of the ash leachate indicates that equilibrium between the ash and the CO_2 from landfill gas has not been reached. Over time, the absorption of CO_2 by the ash is expected to result in less alkaline conditions. The near-neutral pH of the drainages is likely related to the degradation of sludge in the protection layer and also landfill gas diffusion from the interior of the landfill.

Salt-forming anions such as Cl^- and SO_4^{2-} in ashes could be washed out already at an L/S of 1-2 (Sabbas *et al.*, 2003). However, to reach L/S 1 might take up to one decade above the liner and about one 30-50 years in the liner. The rapid drop of Cl^- leaching in

the liner of A4 was consistent with the extreme release of Cl^- from the FA/BA-L-mixture in the laboratory test (Table 3). The leaching of nitrogen from the ashes is also expected to decline considerably over time. The high nitrogen content (N_{tot}) of drainage is likely related to the use of sludge in the protection layer since the leaching of N_{tot} from the ashes is comparatively low (Table 3). The nitrogen content of leachate was unexpectedly high, possibly due to drainage percolating the liner. Nitrogen in leachate occurred mainly as NH_4-N, while a higher portion of oxidised species were present in the drainage. This illustrates the gradient towards more reducing conditions in the lower parts of the cap.

Complex formation with organic matter positively influences the mobility of Cu (Chandler *et al.*, 1997; Meima *et al.*, 1999). Thus, the higher content of Cu in drainage from A2 and A4 than A1 is likely an effect of their higher content of TOC (Table 4). It might also be influenced by the higher solubility of Cu in BA-P of A2 and A4 than in the FA of A1 (Table 3). Similarly, the elevated concentration of Cu in drainage compared to leachate in A2 is probably due to the higher content of TOC in the drainage (Table 4), but it could also be affected by the higher solubility of Cu in BA-D than the BA-L (Table 3). Geochemical modelling indicated that solubility-control by cuprite was possible in the liner of A2.

The concentrations of Ni, Pb and Zn were generally higher in drainage than in leachate, probably due to the lower pH of drainage (Table 4). In addition, similar to Cu, complexation of Ni and Pb with organic matter could enhance their mobility from ashes (Chandler *et al.*, 1997; Dijkstra *et al.*, 2006). Thus, in A2 and A4, easily leachable organic matter may contribute to the elevated release of Ni and Pb from the drainage layer. Bunsenite probably controlled the release of Ni from the liner (Table 6) but due to ash hydration $Ni(OH)_2$ is foreseen to control the release in the near future. The release of Pb might be controlled by $Pb(OH)_2$. Zincite could control the release of Zn from A2 and A4 but is too soluble to control the leaching of Zn at pH > 10 (Dijkstra *et al.*, 2006), which might explain its undersaturation in A1. The formation of *e.g.* calcite ($CaCO_3$), gibbsite ($Al(OH)_3$), ferrihydrite ($Fe(OH)_3$) and goethite (FeOOH) in the liner was possible according to the geochemical modelling (Table 6). Thus, a reduced mobility of Pb and Zn in the liner was probably achieved by trapping them in carbonates (Freyssinet *et al.*, 2002) and by sorption to Fe/Al-hydroxides (Kersten *et al.*, 1997; Meima and Comans, 1999).

The leaching of Cd at pH>7 is closely related to the Cl^- content of the ash (van der Sloot *et al.*, 2001). Hence, Cd will probably be leached from the layers above the liner and from the liner surface as long as Cl^- is present in sufficient concentrations to mobilise Cd. The equilibrium calculations did not lead to the identification of any minerals controlling the release of Cd from the liner, which indicates that other processes, *e.g.* complexation, were important.

The concentrations of Cr in leachate and drainage water were relatively low, probably due to that the redox was sufficiently low for Cr to occur in its more stable trivalent state. The increased leaching of Cr during the first year in A4 and during the third year in A1 and A2 (Figure 5) can not be explained at present, but increased material wetting was observed to increase the mobility of Cr in BA (Johnson *et al.*, 1999; Lidelow and Lagerkvist, 2006). According to the equilibrium calculations, $Cr(OH)_3$ could control the solubility of Cr in the liner of A2 (Table 6). However, the pH-independent behaviour of

Cr indicates the occurrence of sorption mechanisms rather than solubility-control by a pure mineral phase (Kersten *et al.*, 1997).

Typical for oxyanion-forming elements, the decreasing leaching of Sb (Figure 5) was probably an effect of wash-out. The low and constant release of Sb after one year could be explained by a depletion of available Sb in the ash matrix. According to Dijkstra *et al.* (2006), the solubility of Sb in BA at pH 10-12 may be controlled by Ca antimonate ($CaSbO_3$) but the equilibrium calculations indicated that this mineral was undersaturated in the liner of all areas (Table 6). However, solubility control by $Sb(OH)_3$ was possible in A2 and A4. At alkaline pH, Sb could be immobilised by substituting sulphate in ettringite (Meima and Comans, 1998), but this mineral was undersaturated in all areas except A4 where it was close to equilibrium.

The higher concentration of Mo in leachate than drainage (Table 4) was probably due to increased adsorption of Mo towards lower pH values (Goldberg *et al.*, 1996). The higher release of Mo from the liner in A2 than the other areas is consistent with the high content of Mo in BA-L used in A2 (Table 2). Solubility-control by wulfenite was possible in A2 (Table 6), while the leaching of Mo from A1 and A4 probably was availability controlled. Because Mo in ashes can be almost completely released within an L/S of 2 (van der Sloot *et al.*, 2001), the concentration of Mo in both leachate and drainage is expected to decrease over time.

The higher release of As and Se from the liner than the protection layer in A1 and A4 was probably caused by the alkaline leachate pH and the reducing environment in the liner. Both elements were undersaturated with respect to all mineral phases in Minteq, indicating sorption control. Fe-(hydr)oxides are, for example, known to sorb oxyanions strongly, but the sorption decreases with increasing pH and decreasing redox potential (Hingston, 1981). In the liner, the lower leaching of As and Se from A2 than A1 and A4 could be due to a more oxidising environment in this area than the other areas, as indicated by the lower fraction of the reduced nitrogen species (NH_4-N) present in A2.

Redox conditions can influence the leaching of several elements. For example, according to the equilibrium calculations metal sulphides, which have a low solubility, could be formed in the ashes at strongly reducing conditions (pE = -6). Such conditions might occur on the lower side of the liner as a result of microbial degradation of deposited waste and contribute to the trapping of trace metals in the ashes.

Prediction of leaching development in the landfill cover

The release of most constituents showed no clear tendency to decline over time. However, it is expected that easily leachable species such as Cl^-, SO_4^{2-}, Mo and nitrogen, will be depleted when an L/S of 2 is reached, *i.e.* after about 15-20 years above the liner and 50-100 years within the liner.

Most of the organic matter in the ash/sludge-mixtures will be probably be degraded within a few decades. Thus, the release of Cu from the layers above the liner might decline considerably over time. The release of Ni, Pb and Zn will continue at a similar rate as long as they are available for leaching since the drainages are expected to maintain a near-neutral pH. Hence, during the first few decades after installation of the cover drainage will need treatment before it is discharged. However, when evaluating the en-

vironmental impact of drainage discharge the characteristics of the recipient and not just the concentration of substances released from the source should be accounted for.

The expected decrease of the leachate pH might lead to an increased leaching of *e.g.* Ni and Zn from the ashes in the future. However, ageing of the ashes will result in mineralogical changes that could considerably contribute to the trapping of trace elements in the liner. The leachates from A2 and A4 were supersaturated with respect to several clay minerals (Table 6), indicating their potential formation in the liner of these areas within 31 and 13 months, respectively. Clay formation in the ashes could be accelerated by the alkaline pH of the leachates (Zevenbergen et al, 1999) and by the heat released from the degradation of deposited waste (Andrews *et al.*, 1996). Apart from immobilising leachate constituents, the precipitation of clay may also lead to a decreased hydraulic conductivity of the liner over time. Formation of clay minerals in A1 was not possible according to the geochemical modelling which indicates that the kinetics of FA weathering were slower than those of BA.

In the long term (several hundred years), the substrates for heterotrophic microbial degradation and energy sources for lithotrophs may be depleted in the deposited waste. Consequently, the redox potential of the landfill body will increase. As indicated by the equilibrium calculations, a shift towards oxidising conditions in the liner might lead to the dissolution of (hydr)oxides of Cr and Sb in the ashes, leading to an increased release of Cr and Sb. On the other hand, it might induce the precipitation of several (hydr)oxides of Cu and Fe, thereby decreasing the solubility of Cu and increasing the potential for sorption of trace elements to Fe-(hydr)oxides.

Leachate from the landfill cover liner will percolate through the deposited waste before being discharged to a treatment plant. This can impose changes in its composition due to, for example, the retention of trace metals by organic matter or metal sulphides in the waste. In the short term, the amount of leachate generated from the initial water content of the deposited waste will be considerably larger than that released from the liner. In the longer term, peculation of moisture through the cover will contribute to the generation of leachate. However, as stated above, it is expected that easily leachable species will then be depleted and that the secondary phases formed in the ashes will considerably contribute to the retention of trace elements therein. Hence, the leaching of constituents from the ash liner into the landfill might only have a minor impact on the leachate quality. This must be verified through long term studies.

Conclusions

The ashes and other materials investigated in this study showed a potential to be used in landfill cover constructions. The amounts of water that percolated through the cover construction were below the legal requirements of $<50 \, l \, (m^2 \, yr)^{-1}$ for non hazardous waste landfills and, in some areas, of $<5 \, l \, (m^2 \, yr)^{-1}$ for hazardous waste landfills. Water that drains off the landfill cover was contaminated with easily leachable species such as Cl^- and nitrogen, and several trace elements, *e.g.* Mo, Ni, Se and Zn. It will probably need treatment for one to two decades before being discharged. The use of a sludge/FA mixture instead of a sludge/BA mixture in the protection layer resulted in a less contaminated drainage, possibly due to the higher pH and sorption processes. Leachate, *i.e.* water that percolates through the liner into the landfill body, contained elevated concen-

trations of As, Cl⁻, Cu, Mo, TOC and nitrogen. The ashes in the liner might release salt forming elements and trace elements for up to one hundred years. Chemical equilibrium calculations indicated that the formation of clays and other secondary compounds, *e.g.* Fe-(hydr)oxides, was possible in BA and BA/FA-mixtures within three years after construction. This is expected to contribute to a considerable retention of trace elements in the liner in the long term. Moreover, the amounts of leachate generated are very low. Considering this, the design of the layers above the liner is more critical with regard to the environmental impact than that of the liner. Further research will focus on treatment needs for the drainage. The possible formation of clay minerals in the ashes also indicates that further research should be directed towards long term changes of their material properties.

Acknowledgements

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PAPER IV

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Leaching behaviour of copper slag, blast-furnace slag and recycled concrete used in a full-scale road construction

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Abstract

A road construction with fayalitic copper slag, air cooled blast-furnace slag, recycled concrete and crushed rock as sub-base material was monitored over ten years. The leaching behaviour of these aggregates is evaluated in this paper. The leachates from the recycled materials contained higher concentrations of several constituents than registered in leachate from the reference section with crushed bedrock and in natural water. The high concentrations of trace metals and the small particle size of the copper slag caused at least tenfold higher leaching of *e.g.* Cd (0.2-0.8 µg l^{-1}), Cu (110-1300 µg l^{-1}), Ni (90-460 µg l^{-1}) and Zn (190-3300 µg l^{-1}) from this material than the other materials. Oxidation of reduced sulphur compounds in the blast-furnace slag led to the generation of acid leachates (pH<4) at several occasions, probably due to the slower kinetics of the buffering reactions. Acidic conditions also accelerated the leaching of both major and minor elements such as Al (up to 16 mg l^{-1}), Cu (up to 560 µg l^{-1}) and Zn (up to 1500 µg l^{-1}) from the slag. Carbonation of the concrete aggregates caused a substantial but short-term increase in the leaching of oxyanions such as Cr (up to 340 µg l^{-1}). Comparisons between predicted releases from laboratory leaching tests and the observed field releases showed fairly good agreement for the copper slag but less agreement for the blast-furnace slag and the crushed concrete. This was most likely due to differences in redox potential, particle size distribution and degree of carbonation between laboratory and field conditions.

Keywords: Waste; Recycling; Roads; Recycled aggregates; Leachate quality; Geochemical modelling

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Introduction

The majority of granular materials (aggregates) used in constructions are obtained from natural bedrock, sand and gravel resources. Across Europe an estimated 3 Bt aggregates are produced each year, of which primary aggregates constitute over 90% (UEPG, 2006). Concerns about the depletion of natural resources and increased costs due to taxing of virgin materials as well as increasing landfilling fees have focussed attention on the potential use of alternative aggregates, especially for road construction (OECD, 1997). Available alternative aggregates include *e.g.* recycled concrete from construction and demolition waste, incineration ash, tyre shreds, metallurgical slags such as blast-furnace, steel and nonferrous slags, and mine waste rock. Many of these, *e.g.* blast-furnace slag and recycled concrete from sorted demolition waste, have physical properties that make them suitable as unbound road materials (Sherwood, 1995; Arm, 2003). The main barrier restricting their valorisation to aggregates is the potential leachability of substances that could contaminate adjacent soil and water systems.

Measurements of total chemical content and leachability are therefore a key in any environmental assessment of materials considered for recycling. However, feedback from experience with field applications is scarce, which constitutes a major drawback to understanding and verifying the leaching behaviour of the materials under field conditions. For example, copper slag and blast-furnace slag have been used extensively in road construction in Sweden for over 30 years, but until the 1990s little attention was paid to environmental issues. Based on laboratory testing, Tossavainen and Forssberg (2000) concluded that both slags could be used without any risk of excessive trace metal leaching since the high concentrations of metals in the copper slag are efficiently immobilised in a glass phase and the soluble amounts of metals in blast-furnace slag are smaller than in natural rock materials. To date, only a few pilot-scale lysimeter tests were reported on blast-furnace slags (Mulder, 1991; Fällman and Hartlén, 1994). Results from these studies indicated that laboratory tests can be useful for prediction of field leaching if adequately designed. However, size reduction prior to laboratory testing and carbonation upon field exposure, for example, may substantially alter controlling factors such as pH and redox causing more than tenfold difference in constituent leaching between laboratory and field studies. Since laboratory leaching tests are commonly used to support decision-making on the management (*e.g.* recycling as road aggregate) of recycled materials, improved knowledge of their leaching behaviour under real conditions is crucial for the development of accurate methods for environmental impact assessments.

In this study, the leaching behaviour of copper slag, air cooled blast-furnace slag, recycled concrete and crushed rock used as aggregates in test sections of a full-scale road construction is evaluated. The test sections were built and monitored for leachate emissions during four years by the Swedish Road Administration (Anonymous, 2002). Recently, supplementary samples were collected to create a ten year long time series of leachate data. While the use of recycled concrete still is limited, the copper slag and the blast-furnace slag have been used extensively in road-making in Sweden for over 30 years. However, until the 1990s little attention was paid to environmental issues.

The aims of this work are to (i) assess the environmental significance of leachates from the test sections and (ii) to explore the mechanisms and conditions controlling the leaching of constituents in the field application.

2. Material and methods

Description of the field site

Four separate 100 m sections with respectively copper slag, air cooled blast-furnace slag, recycled concrete and crushed rock (reference) in the sub-base was built outside the city of Luleå in Northern Sweden during rehabilitation of a public country road in 1997 (Anonymous, 2002). The road has an annual average daily traffic (ADT) of 800 vehicles (~5% heavy vehicles). The sub-base is built on a subgrade containing sulphide soil (silty clay to clay) with the exception of the test section with BFS. The groundwater surface lies 1-2 m below the road surface.

The road is asphalted with open road slopes. Lysimeters of LDPE (low density polyethylene) plastic sheets were installed below the sub base in each test section in order to collect the percolating water (Fig. 1). Each lysimeter covers a 4.4 m * 6.8 m area from the middle of the road to about 1 m outside the asphalted surface. The collected water is transported by gravity to 80 L PP (polypropen) sampling wells on the side of the road.
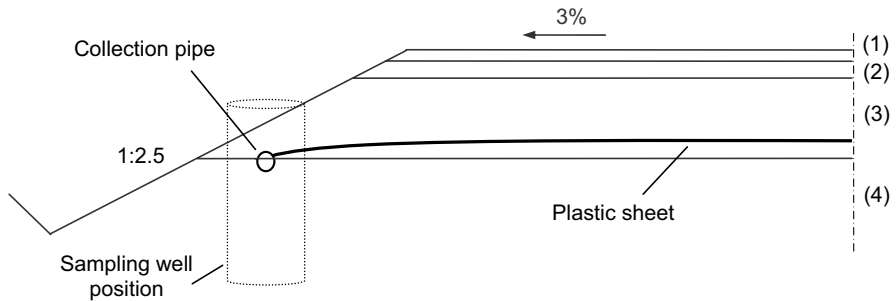
Figure 1   Cross section of the test road with leachate collection devices: (1) Wearing course: 70 mm asphalt; (2) base: 80 mm crushed rock; (3) sub-base: 500 mm fayalite slag, 500 mm blast-furnace slag, 420 mm recycled concrete or 420 mm crushed rock aggregates; (4) subgrade: silty clay-clay.

Description of the tested materials

The copper slag consists of fayalite slag (FS) from copper production at Boliden's Rönnskär smelter in Skellefteå, Sweden. The slag arises in the electrical smelting furnace as silica sand is added and reacts with the iron bound in the copper minerals. During slag fuming and subsequent settling the slag is stripped from zinc, lead, copper and other precious metals. The cleaned slag is rapidly cooled by water granulation which results in an almost completely amorphous (glassy) material (Mooseberg *et al.*, 2003) with a particle size of 0-5 mm (95% < 2 mm). Fe and Si are major elements in the slag (Table 1), which has a chemical composition similar to that of fayalite (Fe_2SiO_4).

The blast-furnace slag (BFS) originates from iron ore based production at the integrated steel plant SSAB Tunnplåt in Luleå, Sweden. The slag is formed in the blast-furnace as fluxing agents, mainly limestone, combine with *e.g.* silica and alumina compounds that would otherwise be incorporated into the molten iron. After tapping, the slag is slowly

cooled in air which results in the precipitation of crystallised phases such as melilite, a series of solid solutions from gehlinite ($Ca_2Al_2SiO_7$) to akermanite ($Ca_2MgSi_2O_7$). Ca, Si, Mg and Al are major elements in the slag (Table 1) and the primary mineral phases best match akermanite, monticellite ($CaMgSiO_4$) and spinel ($MgAl_2O_4$) (Tossavainen and Forssberg, 2000). Prior to road application, the slag was crushed to a particle size of 0-125 mm (10% < 8 mm).

The recycled concrete (RC) consists of sorted buildings demolition waste crushed to a particle size of 0-100 mm (50% <8 mm). Yet, pieces of *e.g.* wood, gypsum boards and plastics were identified during filling. The crushed rock (CR) is composed of biotite gneiss-granite crushed to a particle size of 0-30 mm (50% <8 mm). Major elements are Si, Ca and Al in the RC and Si, Al and Fe in the CR (Table 1). The mineral composition of the RC and the CR used in the road is unknown.

Table 1   Total chemical composition of the FS, BFS, RC and CR.

	FS [a]	BFS [b]	RC [c]	CR [c]
Major elements (g (kg TS)$^{-1}$)				
Al	26	64-72	60	77
Ca	15	210-240	110	21
Fe	370	1-3	33	51
K	5	4-6	20	30
Mg	8	100-120	17	19
Mn	3	3-6	1	0.7
Na	6	4-5	19	20
S	6	11-18	n.a.	n.a.
Si	180	140-160	230	290
Ti	1	15-21	5	6
LOI	0	<1	82	16
Minor elements (mg (kg TS)$^{-1}$)				
As	17	<0.7	5	0.6
Ba	3100	400-770	730	670
Cd	<1	<0.01-0.4	0.07	0.1
Cr	1600	32-63	65	120
Cu	4800	<1-7	11	31
Hg	0.7	<0.04-0.4	<0.04	<0.04
Mo	2800	<6	<6	<6
Ni	130	<1-8	12	31
Pb	140	<0.1-13	17	10
Sb	90 [d]	n.a.	n.a.	n.a.
Se	<5 [d]	n.a.	n.a.	n.a.
V	55	1-7	130	110
Zn	13200	350-460	72	99

[a] Fällman and Carling (1998), n=2.
[b] Based on data from Fällman and Hartlén (1994), n=2; Lindgren (1998), n=1; Kanschat (1996), n=1.
[c] Jacobsson and Mácsik (1997), n=1.
[d] SP (2003), n=1.
n.a. – data not available

Sampling and sample handling

From August 1998 to October 2002, water in the wells was sampled twice every autumn and two months apart (Anonymous, 2002). Two weeks prior to each sampling occasion, the wells were emptied and cleaned. From October 2006 to August 2007, samples were

taken on 6 occasions, twice every autumn and spring. These samples were taken directly from the outlet of the collection pipe to minimise the contact with air and the risk of contamination by road runoff or rain water seeping through the lid of the well. All samples collected had a volume of at least 1 L and were collected in acid-washed polyethylene bottles. Separate aliquots were collected for determinations of pH, electrical conductivity (EC), alkalinity and anions. The bottles were filled up to their maximum to avoid contact with air and immediately transported to the laboratory.

Chemical analyses

During 1998-2002, the samples taken were analysed for pH, EC, alkalinity, anions (Cl^-, SO_4^{2-}) and elements by the accredited laboratory of ALS Scandinavia (Luleå, Sweden). Alkalinity as HCO_3^- was determined by potentiometric titration with HCl. Sulphate (SO_4^{2-}) was determined by ion chromatography according to the standard method ISO 10304-1 (ISO, 1992). Element analysis was carried out on filtered (0.45 μm, syringe filters) and acidified (HNO_3, suprapure) samples using ICP-AES and ICP-SFMS according to modified EPA methods 200.7 and 200.8.

For the supplementary samples (2006-2007), pH and EC were measured on site using a MX-300 X-mate meter (Mettler-Toledo, Switzerland) with automatic temperature compensation to 25°C. The redox potential was measured as soon as possible in the lab using an InLab 502 glass electrode (Mettler Toledo, Sweden) connected to a PHM 95 pH/ion meter (Radiometer, Denmark). Alkalinity was determined by titration with HCl using the Aquamerck test kit (Merck, Germany). The samples were then frozen prior to analyses of anions and elements. SO_4^{2-} was determined spectrophotometrically using an AACE Quaatro (Bran+Luebbe, Germany). Element analysis was carried out on filtered (0.45 μm syringe filters) and acidified (HNO_3; suprapure) samples using ICP-OES (Optima 2000 DV, Perkin Elmer, USA).

Statistical analyses

Tukey's multiple comparison test was used to determine the statistical significance of differences in means between test sections. Pearson correlation coefficients were used to assess the linear correlations between leachate quality variables. $p < 0.05$ was considered statistically significant.

Geochemical modelling

Geochemical equilibrium modelling using Visual MINTEQ (Gustafsson, 2007) was applied to the leachates in order to identify potential solubility controlling minerals. The input files were composed of measured elemental concentrations, pH, alkalinity, redox potential and temperature of the leachates. The discussed minerals were selected based on (i) their likeness to be present or formed at the given conditions and/or (ii) calculated saturation indices (SI) that approach zero ($-1 < \log SI < 1$). The SI does not confirm whether or not a solid phase is actually present but it can indicate whether a given solid phase would have a tendency to precipitate ($SI > 0$) or, if present, dissolve ($SI < 0$).

Results

Leaching from the test sections over time

Leachates from the CR and the RC sections were alkaline (pH>7) throughout the observation period, while that of FS remained circum-neutral (Fig. 2). On average, the pH was found to be significantly higher in leachate from the RC section than in leachate from the FS section, whereas it was significantly lower in leachate from the BFS section than in leachate from any other section. The pH of leachate from the BFS section varied between 2.9-7.4 over time and acidic pH-values (<4) were observed after around two, five and ten years.
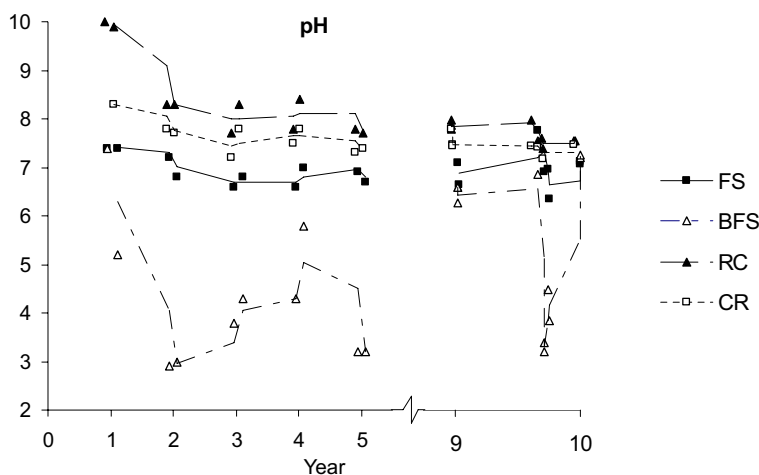
Figure 2   Changes of pH in the leachates from the test sections over time. The lines represent moving averages.

On average, the highest EC was measured in leachate from the BFS section (Table 2), though it decreased by about 60% over the ten years (Fig. 3). The release of main components such as Al, Ca, Fe, K, Mg, Mn and sulphur (expressed as SO_4^{2-}) was also significantly higher from this section than from the other sections (Table 2). The correlation coefficients showed significant negative correlations between the pH and the concentrations of Al, Fe, Mn, Si and SO_4^{2-} leachate from the BFS section (r = -0.8 to -0.6). Elevated concentrations of *e.g.* Ca, Mn and SO_4^{2-} were observed in leachate from the CR section after about two years, while elevated concentrations of K, Na and SO_4^{2-} occurred in leachate from the RC section during the second year. The EC of leachates from the RC and the CR sections decreased by about 90% from the maximum values reached during the second year, whereas the EC of the FS leachate remained low throughout the ten years (Fig. 3).

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Table 2   Average (± SD), minimum and maximum values of variables in leachate from the road sections.

	Av ± SD	Min-max	Av ± SD	Min-max	Av ± SD	Min-max	Av ± SD	Min-max
pH	6.9±0.4	6.3-7.8	**4.8±2**[A]	2.9-7.4	**8.2±0.8**[C]	7.4-10	7.6±0.4	7.2-8.3
EC	**0.1±0.04**[B]	0.06-0.2	**3±1**[A]	2-6	1±0.7	0.3-3	0.7±0.5	0.2-2
Al	0.2±0.1	0.02-0.5	**4±5**[A]	0.3-16	0.3±0.4	0.02-1	0.2±0.4	0.02-2
Ca	15±5	5-23	**520±170**[A]	190-850	32±40	4-170	110±89	14-370
Fe	0.4±0.5	0.02-2	**5±7**[A]	0.03-26	0.09±0.1	0.02-0.3	0.3±0.8	0.01-3
K[a]	5±1	4-7	**280±240**[A]	88-820	87±48	13-180	20±13	11-51
Mg	2±0.4	1-3	**40±19**[A]	6-71	3±4	0.4-15	**18±25**[C]	2-100
Mn	0.05±0.03	0.02-0.2	**1.2±1.2**[A]	0.01-4.7	0.004±0.004	0.0008-0.02	0.009±0.02	0.0009-0.06
Na[a]	5±5	2-14	96±65	31-240	**190±190**[B]	12-540	16±17	4-59
Si[a]	4±1	3-6	**19±10**[B]	5-36	**22±14**[B]	6-55	7±3	5-14
SO$_4^{2-}$	26±13	8-56	**1600±640**[A]	140-2700	140±120	17-460	280±300	21-1200
As	3±3	<0.9-9	2±4	<0.9-10	**16±12**[A]	<0.9-46	5±5	<0.9-18
Ba	**170±54**[A]	66-230	60±48	19-180	26±29	3-110	**90±55**[C]	17-230
Cd[a]	**0.5±0.2**[A]	0.2-0.8	**0.2±0.1**[B]	0.01-0.5	0.03±0.04	<0.005-0.1	0.03±0.05	<0.005-0.2
Cr	2±2	0.1-6	21±35	0.5-120	**87±93**[A]	0.4-340	4±14	0.2-53
Cu	**610±330**[A]	110-1300	100±170	<0.2-560	50±73	<0.5-240	5±4	<0.5-14
Hg[a]	0.003±0.001	<0.002-0.005	<0.002		0.02±0.02	<0.002-0.05	0.002±0.0005	<0.002-0.004
Mo	**140±67**[A]	26-240	16±15	2-64	15±13	3-44	5±3	1-11
Ni	**230±110**[A]	93-460	13±12	<0.4-35	7±8	1-28	4±4	<0.4-12
Pb	1±1	0.5-3	**9±10**[A]	0.8-31	2±2	0.2-5	2±3	0.2-8
Sb[b]	**60±24**[A]	40-94	<5		5±1	<5-7	<5	
Se[b]	<7		**41±16**[A]	23-56	9±2	<7-12	8±1	<7-9
V[b]	3±1	2-4	**94±39**[A]	57-170	**43±3**[C]	40-47	20±13	11-39
Zn	**1300±940**[A]	190-3300	340±470	<0.4-1500	7±6	<0.4-22	5±5	<0.4-20

[a] 1998-2002
[b] 2006-2007
Values written in bold were statistically higher than the values for all (A), two (B) or one (C) of the other materials (p<0.05).
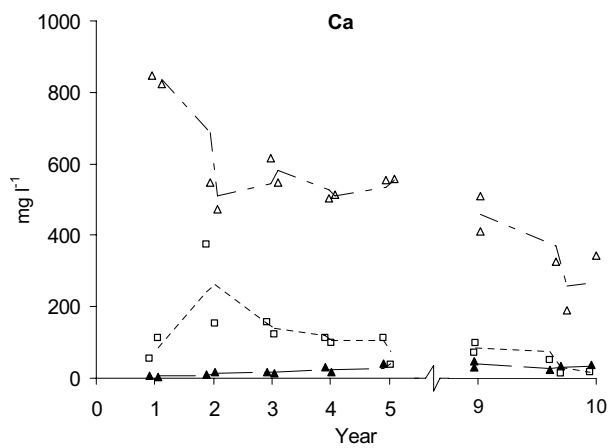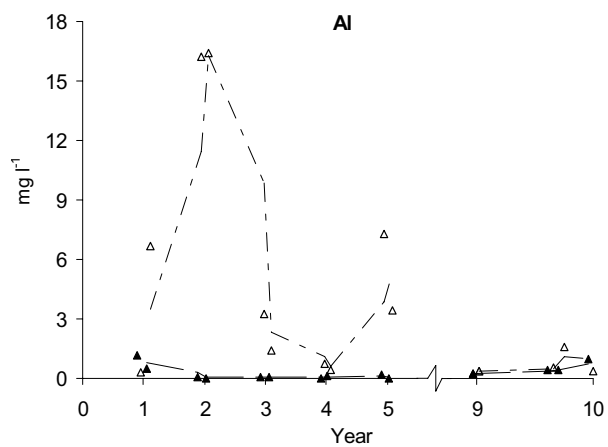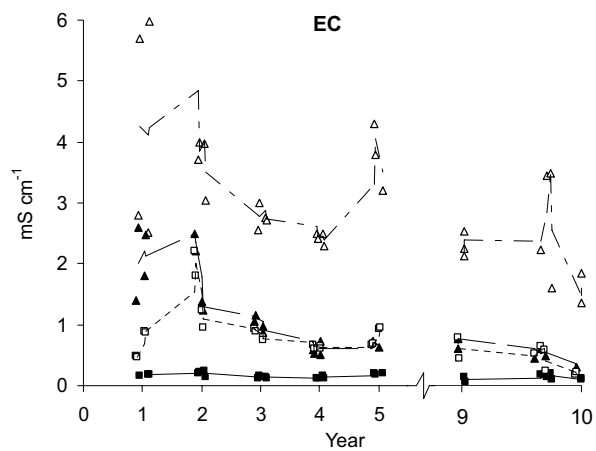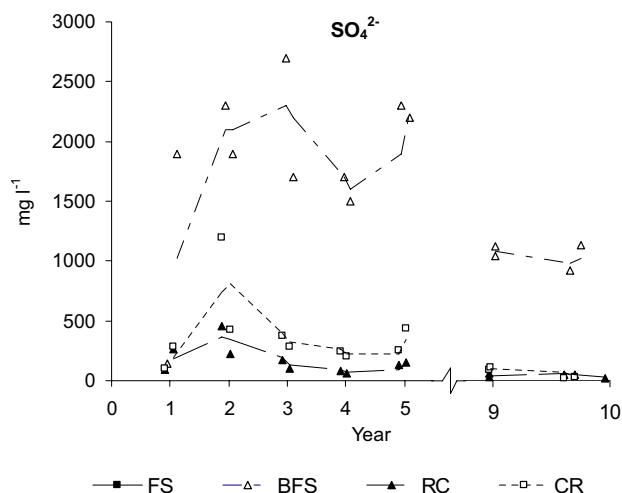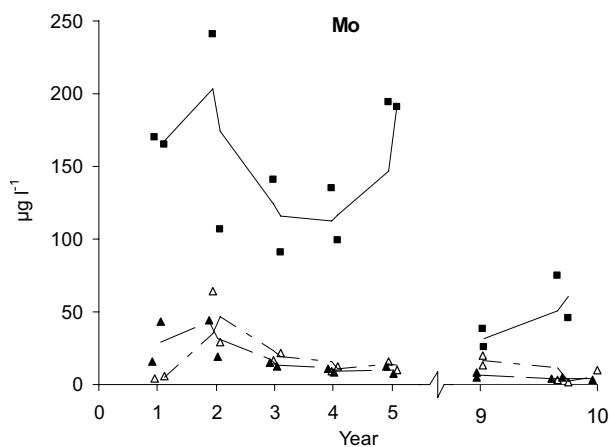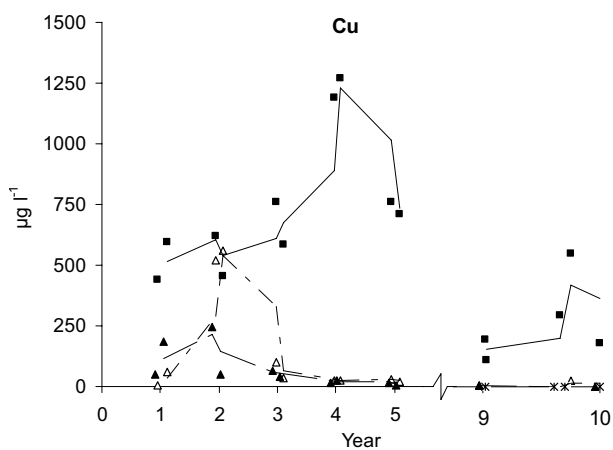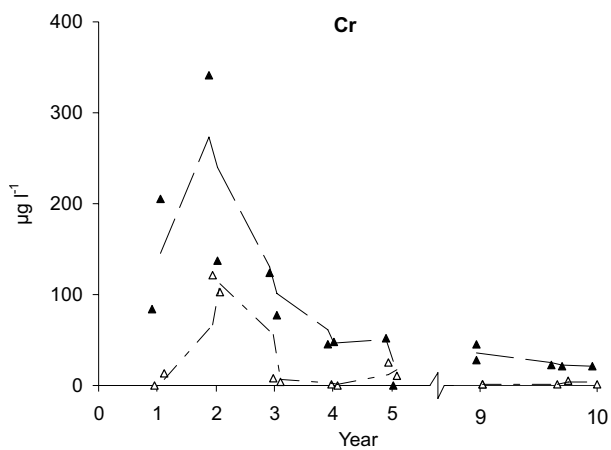
Figure 3   Changes in concentrations of EC, Al, Ca and SO_4^{2-} in leachates from the test
           sections over time. The lines represent moving averages.

The average release of Cu, Mo, Ni and Zn was significantly higher from the FS section than from the other sections (Table 2). Over time, the release of these elements from the FS section decreased by 50-90% (Fig. 4) but was still after ten years at least tenfold that from the other sections. Also the average release of Ba, Cd and Sb was significantly higher from the FS section than from the other sections (Table 2), although the concentrations of Ba and Cd from the BFS and the CR sections periodically reached similar levels. On average, the highest concentrations of Pb, Se and V were leached from the BFS section (Table 2). The leaching of several trace metals, *e.g.* Cr, Cu, Ni, Pb and Zn, from this section reached its maximum after about two years and was slightly elevated also after five and ten years (Fig. 4), thus indicating an inverse relation to the leachate pH (Fig. 2). The correlation coefficients showed significant negative correlations between the pH and the concentrations of Cr, Cu, Ni, Pb and Zn in leachate from the BFS section (r = -0.7 to -0.5). The highest leaching of Cr and As (on average) occurred from the RC section (Table 2), though it decreased by over 70% respective 90% from its maximum value reached during the second year (Fig. 4). During this year, also an increased release of *e.g.* Cu, Mo and Ni from the RC section was observed.
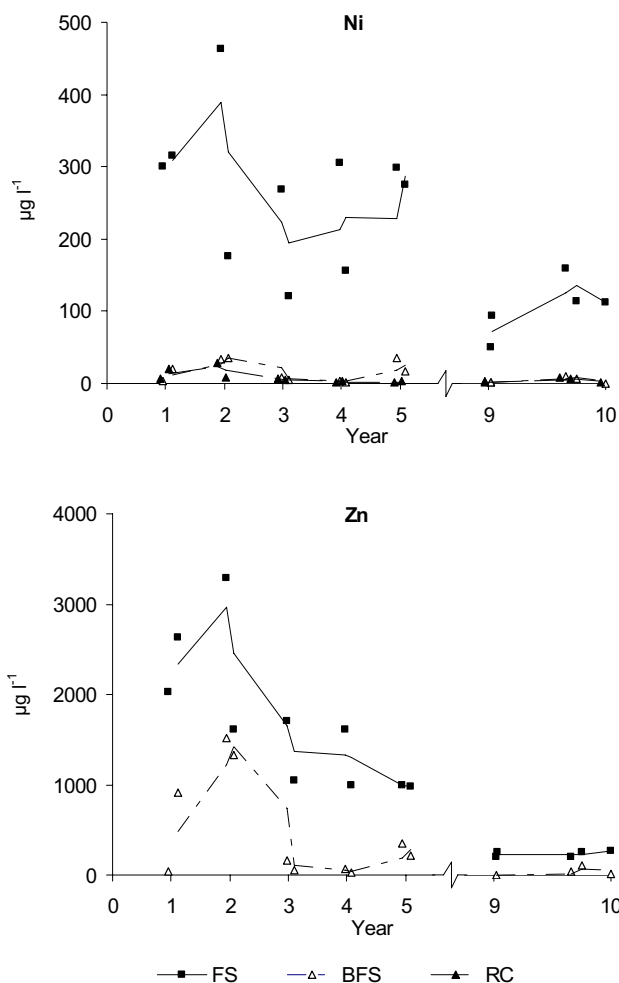
Figure 4   Changes in concentrations of Cr, Cu, Mo, Ni, and Zn in leachates from the test sections over time. The lines represent moving averages.

Geochemical modelling

Based on the geochemical modelling, several possible solubility controlling phases were identified (Table 3). However, the leachates were undersaturated with respect to all As and Sb minerals included in Minteq.

Table 3   Geochemical modelling results showing potential solubility controlling minerals for constituent release from FS, BFS, RC and CR sections. Symbols in parenthesis indicate the specific time period and pH range at which the given minerals could exhibit solubility control. Arrows indicate trends of saturation indices (SI) over time ($\leftarrow$ decreasing SI; $\rightarrow$ increasing SI).

	FS	BFS	RC	CR
Al	$Al(OH)_3$(am) ($\rightarrow$)	$Al(OH)_3$(am) (pH>6) $AlOHSO_4$ (pH<6)	Boehmite (98-02; $\rightarrow$) $Al(OH)_3$(am) (06-07; $\rightarrow$)	Al_2O_3 (98-02) $Al(OH)_3$(am) (06-07)
Ca		Calcite (98; pH>6) Gypsum (99-07)	$CaCO_3{:}H_2O$ (98-00; $\leftarrow$) Calcite (01-07; $\leftarrow$)	Dolomite (98-00; $\leftarrow$) Calcite (01-07; $\leftarrow$)
Cd	$CdMoO_4$ ($\leftarrow$)			
Cr			$Cr(OH)_3$ (am) ($\leftarrow$)	
Cu	Tenorite		Tenorite (99-01; $\leftarrow$)	
Mo		$PbMoO_4$		$PbMoO_4$ (06-07; $\rightarrow$)
Ni			$NiCO_3$ (98; $\leftarrow$)	
Pb		$PbMoO_4$		$PbMoO_4$ (06-07; $\rightarrow$)
Si	Chalcedony	Chalcedony (pH>6) SiO_2(am) (pH<6)	SiO_2(am)	Chalcedony
SO_4^{2-}	Brochantite (98-02; $\leftarrow$) Barite (06-07; $\leftarrow$)	Gypsum	Barite (99-07)	Barite
Zn	Smithsonite (98-01; $\leftarrow$)			
V		Chervetite (06-07; pH>6)	Chervetite (06-07)	Chervetite (06-07)

Boehmite, $AlOOH$; Barite, $BaSO_4$; Brochantite, $Cu_4(OH)_6(SO)_4$; Calcite, $CaCO_3$; Chalcedony, SiO_2; Chervetite, $Pb_2V_2O_7$; Dolomite, $CaMg(CO_3)_2$; Ferrihydrite, $Fe(OH)_3$; Gypsum, $CaSO_4{:}2H_2O$; Maghemite, Fe_2O_3; Smithsonite, $ZnCO_3$; Tenorite, CuO

Discussion

Environmental significance of the field leachates

The composition of the leachate samples might have been influenced by contamination from *e.g.* road runoff water and materials overlaying the sub-base. Compared to the normal quality of runoff from low trafficked roads (Table 4), Cd, Cu, Pb and Zn appear in similar or lower concentrations in the leachates, except for Cu in leachates from the FS, BFS and RC which exceeded this range by 1700%, 700% and 250%, respectively, and Zn in leachates from the FS and BFS which exceeded the range by at most 1100% and 450%, respectively. This indicates that the tested materials to a various extent contributed to elevated concentrations of different constituents in the leachate. Further, since the four test sections are identical, except for the sub-base, and are situated along the same road, thereby assumingly receiving similar contamination load through *e.g.* atmospheric deposition and road runoff, we may assume that any differences in their leachate compositions arise from the tested materials.

In this first step assessment, the environmental significance of the leachates is discussed with respect to the quality of leachate from the reference section with CR and quality criteria for natural freshwater (Table 4).

Table 4　Freshwater quality criteria and normal concentrations of priority substances in road runoff ($\mu g \ l^{-1}$).

	Freshwater quality criteria					Road runoff[e]
	Swedish EPA[a]			US EPA[b]		
	Class 1	Class 3	Class 5	Acute	Chronic	
As	≤0.4	5-15	>75	340 [d]	150[d]	n.a.
Cd	≤0.01	0.1-0.3	>1.5	2.0	0.25	0.3-0.9
Cr	≤0.3	5-15	>75	570/16[e]	74/11[e]	n.a.
Cu	≤0.5	3-9	>45	13	9	20-70
Hg	n.a.	n.a.	n.a.	1.4	0.77	n.a.
Ni	≤0.7	15-45	>225	470	52	n.a.
Pb	≤0.2	1-3	>15	65	2.5	10-50
Se	n.a.	n.a.	n.a.	n.a.	5	n.a.
Zn	≤5	20-60	>300	120	120	50-275

n.a. – data not available
[a] Classification of natural freshwater according to (SEPA, 2000). Class 1, 3 and 5 correspond to "low", "moderately high" and "very high" concentrations, respectively.
[b] An estimate of the highest concentration of a pollutant in surface water to which aquatic life can be exposed briefly (acute criterion) without resulting in an unacceptable effect (USEPA, 2006).
[c] Normal concentrations for runoff from roads with an ADT of <15 000 vehicles in Sweden (Olvik and Nimfeldt, 2001).
[d] Data derived for As(III) (USEPA, 2006).
[e] Cr(III)/Cr(VI)

Compared with natural water and leachate from the CR section, the concentrations of several trace elements in the leachates from the FS, BFS and RC were elevated. According to the classification of natural freshwater set by the Swedish Environmental Protection Agency (SEPA, 2000), leachate from the FS contained high or very high concentrations (class 4 or 5) of Cd, Cu, Ni and Zn throughout the ten years. In leachate from the BFS, the concentrations of Cr, Cu, Pb and Zn were after two years typical for natural water class 5 and the concentration of Zn reached this class also after five and ten years. Leachate from the RC corresponded to natural water class 4-5 for Cr, 4-5 for Cu during the first five years and 4 for As during the first three years. SEPA (2000) recommends that a biological examination is made of waters with metal concentrations which exceed class 3 due to the growing risk of biological effects such as impacts in the reproduction or survival of aquatic species.

The concentrations of priority toxic substances were below the acute criteria for aquatic life in freshwater issued by USEPA (2006), except for Cu in leachates from the FS, BFS and RC which exceeded these criteria during ten, five and four years, respectively, and Zn in leachates from the FS and BFS, which exceeded these criteria throughout the ten years and after two and five years, respectively. In leachate from the BFS, the concentration of Al (which is regarded a non-priority element by USEPA) exceeded the acute criterion of 750 $\mu g \ l^{-1}$ at several occasions during the observation period. Leaching of Cd and Ni from the FS exceeded the chronic criteria throughout the ten years, while the leaching of Pb from the BFS exceeded these criteria during the first five years. In leachate from the latter, Se (which was analysed only in samples from 2006-2007) also exceeded the chronic criterion. The toxicity of Cr strongly depends on its oxidation state (Table 4). The leaching of Cr from the RC exceeded the chronic criterion for Cr(III) during the first three years. As defined by the geochemical equilibrium calculations, Cr(III) was the predominant species in all leachates but those of the BFS section with pH<6 where Cr(VI) constituted 50-65% of the total Cr concentration. Hence, in samples

of the latter leachates collected after about two years, the concentration of Cr(VI) could reach 60-80 µg l^{-1}, which is 4-5 times over the acute criterion.

Hence, while the concentrations of all addressed constituents in leachate from the reference section were below the quality criteria, those of several elements in leachates from the test sections with FS, BFS and RC reached levels that could be toxic and, in the case of *e.g.* Cu and Zn, even acute toxic to an aquatic community. This stresses the need for a detailed characterisation of the leachate quality and quantity and the environmental status of the local recipients, *e.g.* ground water, roadside soil and vegetation, at the road site.

Mechanisms and conditions controlling the leaching of constituents in field

Smelter slags such as FS have been considered relatively inert in many environments because potentially toxic elements such as trace metals are incorporated in glass phases with high chemical durability. However, besides the solubility of the glass matrix, accessibility and solubility of metal minerals at the surfaces has an influence on the dissolved amounts. For example, the high concentrations (*e.g.* Zn, Cu; Table 1) and the small particle sizes of the FS imply an increased risk of trace metal leaching. The geochemical modelling indicated that solubility-control by $CdMoO_4$, tenorite and smithsonite was possible (Table 3). Although the total content of Cr and Pb was in the same range as that of Mo and Ni (Table 1), the release of these constituents was much lower (Fig. 4; Table 2). This contrasting behaviour is likely due to the mineralogy. Cr and Pb might occur *e.g.* as ion substitutes in low solubility silicates. Secondary minerals such as $Al(OH)_3$(am), ferrihydrite and chalcedony could limit the solubility of Al, Fe and S (Table 3). Future precipitation of these minerals could increase the potential for sorption control of trace elements. Despite the low dissolution rate of glass phases, such processes can not always be neglected, especially in low-flow systems providing relatively long reaction times (Yan and Neretnieks, 1995). Investigations of former mine areas (Kucha *et al.*, 1996; Parsons *et al.*, 2001; Piatak *et al.*, 2004) have shown that amorphous fayalitic smelter slags could cause significant long term releases of potentially toxic elements due to natural weathering. Upon weathering the glass phase is dissolved or transformed causing the inherent elements to be released and transported in solution or precipitated in secondary phases.

The generation of acidic leachates from the BFS was unexpected due to its high buffering capacity. According to (Bäverman, 1997), it will take several hundred thousand years before the pH-buffering capacity of the BFS is depleted if the only source of acidity is acid rain. However, Fällman and Hartlén (1994) observed leachates with a pH of about 4 and a subsequent increase in trace metal releases from coarse BFS readily exposed to the atmosphere in pilot-scale lysimeters. They attributed the low pH to the oxidation of reduced sulphides in the slag. Sulphur in BFS exists primarily in CaS crystallites (Kayashima *et al.*, 1982). At the time of slag tapping, S starts to oxidise due to contact with air and gradually changes into sulphate sulphur (SO_4^{2-}) (Watanabe *et al.*, 1981; Kayashima *et al.*, 1982). When the solubility limit for sulphate minerals is reached in the pore water, secondary weathering products can accumulate as mineral precipitates together with H$^+$. For example, jarosite ($KFe_3(SO_4)_2(OH)_6$) could precipitate (SI=1.9-4.7) from the BFS leachate at pH<6. Jarosite commonly precipitate upon weathering of sulphides and silicates in acidic, sulphate-rich environments such as acid mine drainage (Chapman *et al.*, 1983; Hudson-Edwards *et al.*, 1999) and oxidised portions of sulphide

ore deposits (Hammarstrom *et al.*, 2005). The weathering products accumulated in the void water represent stored acidity which either could be released to solution upon flushing or neutralised by buffering reactions. Flushing of the voids of the BFS likely occurs in the open road slopes during spring snow melt and rainstorms. The enhanced fluxes of elements during acidic leachate conditions probably resulted from the release of the weathering products. Initially, the pH of the BFS leachate was probably controlled by calcite (Table 3), which is formed when easily dissolved $Ca(OH)_2$ reacts with indiffusing CO_2 from the atmosphere. Calcite was detected by scanning electron microscopy on surfaces of leached BFS (Bäverman, 1997). Over time, $Ca(OH)_2$ dissolution probably became limited by diffusion from the core of the large particles. Studies of mining waste rock suggested that calcite within particles larger than 5-10 mm dissolves too slowly to neutralise the acid produced from sulphides (Strömberg and Banwart, 1999) and that, after available carbonates were depleted, the pH of the effluents was controlled by the relative rates of sulphide and silicate mineral dissolution (Strömberg and Banwart, 1994). However, because the rates of dissolution of primary silicates are much slower than for sulphides, acid conditions can prevail despite the presence of acid consuming minerals. Despite the acidic leachates generated after 5 and 10 years, the leaching of *e.g.* Cr and Cu was low (Fig. 4). This might be due to depletion of the fraction available for leaching since the total concentration of these elements in the BFS is low (Table 1). As indicated by the equilibrium modelling (Table 3), the release of Al and Si from the BFS could be controlled by $AlOHSO_4$ respective chalcedony below pH 6, while amorphous $Al(OH)_3$ and SiO_2 controlled it above this pH (Table 3). Sullivan *et al.* (1988) examined solubility relationships of minerals in acid mine drainage where pyrite was weathering and reported similar results for Al. Gypsum could control the release of Ca and SO_4^{2-} (Table 3), but are likely dissolved upon flushing of the BFS because of its high solubility.

The high initial pH of the RC leachate probably resulted from the leaching of free lime (CaO) which is liberated from the concrete during crushing (Wahlström *et al.*, 2000). After two years, the pH declined to 8.3 (Fig. 2), likely due to carbonation. Carbonation involves the reaction of portlandite and calcium silicate hydrates (C-S-H) in the concrete with CO_2 which can lower the pH to calcite equilibrium, *i.e.* pH 8.3 (Reardon and Dewaele, 1990; Bin-Shafique *et al.*, 1998). According to the equilibrium calculations, calcite was the most likely solubility controlling phase for Ca as from the forth year, whereas hydrated $CaCO_3$ could control Ca solubility before this (Table 3). The carbonation of C-S-H also results in the formation of silica gel (Valls and Vàzquez, 2001), which might exhibit solubility control on Si (Table 3). Upon carbonation, ettringite formed as a result of cement hydration decomposes to form $CaCO_3$, alumina gel and gypsum (Chen *et al.*, 1994). This might explain the indicated solubility control of amorphous Al-minerals (*e.g.* boehmite and $Al(OH)_3$) and barite formed by SO_4^{2-} released from gypsum dissolution. The decrease to pH 8.3 sharply increased the release of Cr (Fig. 4) which features its highest leachability at neutral to mild alkaline pH. Van der Sloot (2002) identified forms of $Cr(OH)_3$ to control the leaching of Cr from Portland cement at pH around 7-11. Our results indicate that amorphous $Cr(OH)_3$ may play a role as a controlling phase for Cr (Table 3). Also the release of As, Cu, Mo, Ni and SO_4^{2-} increased during the second year (Fig. 3-4). Similar to Cr, the leaching of As and Mo was probably enhanced by the decrease in pH. In addition, C-S-H and ettringite commonly have trace elements associated with their structure that could be released upon their decomposition. For V, chervetite provides possible solubility control (Table 3). Generally, the leaching of trace elements decreased over time (Fig. 4). This might be

due to either sorption control by secondary phases such as amorphous Si/Al-(hydr)oxides or to slow diffusion of elements from uncarbonated cores of cement minerals.

From the CR, elevated leaching of *e.g.* SO_4^{2-} was observed, especially after two years (Fig. 3). The concurrent slight decrease in leachate pH (Fig. 2) indicates that this might be an effect of oxidation of sulphides in the CR. However, leaching of SO_4^{2-} rapidly declined indicating a low existence of sulphides in the CR. The geochemical modelling also predicted solubility control by barite (Table 3). The pH of the CR leachate was probably buffered by the equilibrium with dolomite and calcite and remained alkaline.

In this study, we only assessed the potential solubility control for different constituents. Geochemical modelling based on kinetics of the dissolution of *e.g.* glass phases in the FS and sulphide and primary silicate minerals in the BFS could be useful to asses to what extent such processes could contribute to the leaching behaviour of these materials in the long-term. Mineralogical analyses of both fresh and leached materials from the test sections should also be performed to confirm potential secondary mineral formation and depletion.

Assessment and management of the recycled materials

Applying batch leaching tests on the FS, the concentrations of Cu, Ni and Zn were around 700, 60 and 600 µg l^{-1}, respectively, at a cumulative L/S ratio of 10 (Fällman and Carling, 1998). These concentrations differ by less than a factor of 4 from those of the FS leachate after ten years. The pH of 6-7, measured by Fällman and Carling, was also close to the pH of the leachate from the FS. These results suggest that the leaching was governed by the same mechanisms for both the laboratory and field tests. In short-term laboratory tests the kinetic factors of glass phase dissolution are ignored (Yan and Neretnieks, 1995), indicating that the release of trace metals from the FS mainly was solubility controlled. However, even though the leaching tests seem to provide a reasonable estimate of the results from the ten-year field study, supplementary investigations are necessary to account for potential glass dissolution in the long-term.

In batch and percolation leaching tests performed on the BFS leachates with pH 8-12 were obtained (Fällman and Hartlén, 1994; Bäverman, 1997; Lindgren, 1998), while the pH of the field leachate varied between 3-8 (Fig. 2). This discrepancy also led to differences in trace metal leaching. For example, the leaching of Cr, Cu and Pb was often below detection limit in the laboratory tests, while elevated concentrations were observed in the field test. For the laboratory tests, particles were crushed and sieved to obtain various particle sizes between 0-16 mm (Fällman and Hartlén, 1994; Bäverman, 1997; Lindgren, 1998). Unlike the lysimeter test, saturated conditions with limited access to air likely prevailed in these tests, thereby limiting the oxidation of sulphides and the subsequent pH decrease. pH dependence tests might be useful to predict the impact of changing pH on the leachate composition. However, supplementary tests allowing redox control are necessary for a proper leaching assessment since the change in pH in the field leachate in itself could be caused by redox reactions. Further, the fraction of BFS particles that significantly contribute to acidity and alkalinity generation should be investigated to assess the influence of differences in particle size between laboratory and field tests.

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Based on pH dependence leaching, Van der Sloot (2000) identified oxyanionic species (*e.g.* As, Cr, Mo and SO_4^{2-}) as the most environmentally relevant substances in cement-based products due to their increased leachability upon carbonation. In batch leaching tests on the RC, the leachate pH remained above 12 (Jacobsson and Mácsik, 1997), which led to an order of magnitude lower leaching of oxyanions such as Cr and SO_4^{2-} than in the field study. Our study indicates that it might take at least two years to reach calcite equilibrium between the RC and the percolating water in a road application. However, carbonation likely occurred mainly in the surface of larger particles and the increased release of oxyanions was of short duration. In order to characterise this evolution, integration of results from pH dependence and long term dynamic leaching test could be useful (Moszkowicz *et al.*, 1998).

In order to reduce the risk of pollution from the recycled materials, amendments to the materials (pre-treatment) or the utilisation scenario (application) could be attempted. For example, to prevent the hazard caused by oxidation of sulphides in the BFS, the slag could be burnt in an O_2-rich atmosphere (Kayashima *et al.*, 1982) or cooled by water granulation (Lee *et al.*, 2003). The use of alternative fuels and raw materials in the manufacture of cement could decrease the leachability of Cr from cement-based products (van der Sloot, 2000), while removal of wires and impregnated wood before demolition would reduce the risk of As, Cu and Mo leaching (Wahlström *et al.*, 2000). The particle size is an important property. The use of well-graded BFS with a relatively high portion of fines could reduce the access to air and percolation of water and, hence, the risk of acidity production and associated trace metal releases. Similarly, covering the slopes with soil or gravel would reduce the risk of constituent releases from the materials by decreasing the infiltration of water and the rate of weathering reactions. However, such practice increases the risk of accumulation of water in the road structure due to poor drainage, which could cause frost heave problems in cold climates.

Conclusions

The use of FS, BFS and RC as an aggregates substitute for CR in the sub-base of a road construction led to increased leaching of several constituents. Several trace metals were leached in concentrations corresponding to highly polluted natural freshwater that could be toxic to an aquatic community. The high concentrations of trace metals and the small particle size of the FS led to at least tenfold higher leaching of *e.g.* Cd, Cu, Ni and Zn from this material than from the other materials throughout the ten years. Oxidation of reduced sulphur compounds in the BFS caused the generation of acid leachates (pH<4) at several occasions, which accelerated the leaching of both major and minor elements such as Al, Cu and Zn. Most likely, this was due to the slower dissolution rates of the buffering reactions than the sulphide oxidation. Carbonation of the recycled concrete caused a substantial but short-term increase in the leaching of oxyanions such as Cr. In order to provide accurate estimations of the field releases, laboratory leaching tests have to be carefully designed to account for differences in redox potential, particle size distribution and degree of carbonation between laboratory and field conditions. Geochemical modelling based on reaction kinetics of mineral dissolution together with mineralogical analyses of weathered materials from the test sections should be given priority in further investigations. The environmental impact of the leachates on adjacent ground water, roadside soil and vegetation along the test section also need to be quantified.

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