Assessing potential forest and steel inter-industry residue utilisation by sequential chemical extraction

Mikko Mäkelä
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Abstract

Traditional process industries in Finland and abroad are facing an emerging waste disposal problem due recent regulatory development which has increased the costs of landfill disposal and difficulty in acquiring new sites. For large manufacturers, such as the forest and ferrous metals industries, symbiotic cooperation of formerly separate industrial sectors could enable the utilisation waste-labeled residues in manufacturing novel residue-derived materials suitable for replacing commercial virgin alternatives. Such efforts would allow transforming the current linear resource use and disposal models to more cyclical ones and thus attain savings in valuable materials and energy resources.

The work described in this thesis was aimed at utilising forest and carbon steel industry residues in the experimental manufacture of novel residue-derived materials technically and environmentally suitable for amending agricultural or forest soil properties. Single and sequential chemical extractions were used to compare the pseudo-total concentrations of trace elements in the manufactured amendment samples to relevant Finnish statutory limit values for the use of fertilizer products and to assess respective potential availability under natural conditions. In addition, the quality of analytical work and the suitability of sequential extraction in the analysis of an industrial solid sample were respectively evaluated through the analysis of a certified reference material and by X-ray diffraction of parallel sequential extraction residues.

According to the acquired data, the incorporation of both forest and steel industry residues, such as fly ashes, lime wastes, green liquor dregs, sludges and slags, led to amendment liming capacities (34.9-38.3%, Ca equiv., d.w.) comparable to relevant commercial alternatives. Only the first experimental samples showed increased concentrations of pseudo-total cadmium and chromium, of which the latter was specified as the trivalent Cr(III). Based on sequential extraction, dominant cadmium and chromium contents were respectively made available only through aggressive oxidation or dissolution by acid digestion. However, the pseudo-total concentrations of barium and vanadium, of which 17-31% and 12-46% were respectively recovered through desorption/dissolution by the use of acetic acid and moderate reduction by hydroxylamine hydrochloride, suggest the need for further research. The analytical performance during sequential extraction was validated through the analysis of a certified reference material as the analysis of parallel sequential extractions only suggested non-selectivity towards sample periclase coupled with potential redistribution of magnesium and the premature dissolution of sample silicates.

Keywords soil amendment, solid residue, solubility, trace element, waste management
Tiivistelmä


Työn tavoitteena oli hyödyntää metsä- ja terästeollisuuden kiinteitä prosessipoisteita uusien, maa- tai metsätalouteen soveltuvien, maanparannusaineiden kokeellisessa valmistuksessa. Valmistetuista näyteistä yksittäisillä uuttokokeilla määritettyjen haitta-aineiden pitoisuuksia verrattiin kansallisessa lainsäädännössä määriteltyihin raja-arvoihin sekä sekventiaalisten uuttosarjojen perusteella arvioimalla mahdollisesti luonnonolosuhteessa liukoisia haitta-aineitoisuuksia. Lisäksi, analyysin työn laatua sekä käytetyn sekventiaalisen uuttosarjan soveltuvuutta teollisuudesta peräisin olevan kiinteän prosessipoisteen analysointiin pyrittiin vastaavasti arvioimaan vertailumateriaalitulosten sekä rinnakkaisuuttojaanähkööksille suoritetutten röntgendiffraktioanalyysin avulla.

Tulosten perusteella metsä- ja terästeollisuudesta peräisin olevien poisteiden, kuten lentotuhkien, kalkkijätteiden, soodasakan, lietteiden ja kuonien, hyödyntämiseen johtui kaupallisii vaihtoehtoihin verrattaviin kalkitusarvoihin (34.9–38.3%, Ca ekv., ka.). Ainoastaan ensimmäisinä valmistetuista kokeillaneista todettiin sisältävän kadmiumia sekä kromin kokonaiskoitoisuksia, joista kromin todettiin esiintyvän tapahtumissa tapahtuneen kemialin haitta-aiheuttamisen. Sekventiaalisten uutosarjojen perusteella suurin osa vastaavista kemiallin ja kromin kokonaiscoitoisuksista saatiin muunnelmaa ulkiseen mitoontoon ainoastaan aggressivisten haittojen tai kemiallin haitojen hajoamisen tai pelkistymisen seurauksena, mikä on osoittamassa, että työn analyytinen laatu on hyvä sekä röntgendiffraktioanalyysin tukiessa selektiivisyyden puutteena havaittuja silikaattien sivutuotteiden liukenemisen seurauksena. Työn analyysin tuokse todettiin vertailumateriaalitulosten perusteella hyväksyi rinnakkaisuuttojaanähkööksille suoritetutten röntgendiffraktioanalyysin tukiessa selektiivisyyden puutetta poistettaessa tämän vastaavan liukenemisen seurauksena. Työn analyysiin tuokse todettiin vertailumateriaalitulosten perusteella hyväksyi rinnakkaisuuttojaanähkööksille suoritetutten röntgendiffraktioanalyysin tukiessa selektiivisyyden puutetta poistettaessa havaittujen silikaattien sivutuotteiden liukenemisen seurauksena.

Avainsanat: haitta-aine, liukoisuus, maanparannus, poiste, sivutuote, jätehuolto

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Preface

The research work reported in this thesis was carried out at the Departments of Forest Products Technology, Civil and Structural Engineering and Materials Science and Engineering at Aalto University in Espoo, Finland during 2009-2012. In addition to the Department of Forest Products Technology the work was financially supported by Rautaruukki Oyj, Maa- ja vesitekniikan tuki ry., the Walter Ahlström Foundation and the Finnish Foundation for Technology promotion (TES) which are all highly appreciated. Furthermore, the mills of Stora Enso Oyj in Oulu and Rautaruukki Oyj in Raahe are gratefully acknowledged for providing industrial samples and thus enabling the experimental work.

Personally I would like to thank Mervi Partanen and Jussi Kanste from the Stora Enso Oyj Oulu Mill for their interest in this research, and Sanna Nikola, Simo Isokääntä, Juha Laitinen and Tanja Muurinen from Rautaruukki Oyj Raahe Mill for stimulating discussions, sampling arrangements and analytical services within their site. Within the Department of Civil and Structural Engineering at Aalto University, School of Engineering I would like to acknowledge Veli-Antti Hakala and Pertti Alho for the kind possibility to work within their facilities under excellent guidance. From the Department of Materials Science and Engineering at Aalto University, School of Chemical Technology I would especially like to thank Erkki Heikinheimo, Janne Vuori and Prof. Kari Heiskanen for their help in SEM imaging and sample processing. Hopefully we will continue to work together in the future. From the Department of Forest Products Technology I am in great debt to Ms. Ono Mao, Saija Helasuo and Jenni Ala-Hongisto for their help in travelling arrangements and funding issues.

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independently. Finally, my utmost appreciation goes to my friends and family (Hannu, Helena, Riikka, Adrian, Kaarina and especially Seren) for being there, and providing meaning and happiness.

Espoo, September 18th 2012

Mikko Mäkelä
"The difficulty lies, not in the new ideas, but in escaping from the old ones, which ramify, for those brought up as most of us have been, into every corner of our minds."

John Maynard Keynes
List of publications

This thesis consists of an overview of the following five publications, which from here on are referred to as Roman numerals in the text:


Author's contribution

I Mikko Mäkelä carried out the literature review in collaboration with Gary Watkins and wrote half of the manuscript.

II Mikko Mäkelä was responsible of devising the conceptual approach with Gary Watkins, processing the industrial samples, manufacturing the investigated materials, devising the experimental plan in collaboration Risto Pöykiö and Hannu Nurmesniemi, interpreting the results and writing the manuscript.

III Mikko Mäkelä was responsible of manufacturing the investigated materials, devising the experimental plan, interpreting the results and writing the manuscript.

IV Mikko Mäkelä was responsible of manufacturing the investigated materials, devising the experimental plan and interpreting the results. The article manuscript was written in collaboration with Mari-Linda Harju-Oksanen, who was responsible of the legislative part of the investigation.

V Mikko Mäkelä processed the industrial samples, devised the experimental plan in collaboration with Ilkka Välimäki, interpreted the results and wrote the manuscript.
**Nomenclature**

**Abbreviations:**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCR</td>
<td>Community Bureau of Reference</td>
</tr>
<tr>
<td>BF</td>
<td>blast furnace</td>
</tr>
<tr>
<td>BOF</td>
<td>basic oxygen furnace</td>
</tr>
<tr>
<td>CRM</td>
<td>certified reference material</td>
</tr>
<tr>
<td>CVAAS</td>
<td>cold vapour atomic absorption spectrometry</td>
</tr>
<tr>
<td>EAF</td>
<td>electric arc furnace</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
</tr>
<tr>
<td>FAAS</td>
<td>flame atomic absorption spectrometry</td>
</tr>
<tr>
<td>GGBFS</td>
<td>ground granulated blast furnace slag</td>
</tr>
<tr>
<td>IC</td>
<td>ion chromatography</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>inductively coupled plasma–optical emission spectrometry</td>
</tr>
<tr>
<td>IRMM</td>
<td>Institute of Reference Materials and Measurements</td>
</tr>
<tr>
<td>NPEs</td>
<td>non-process elements</td>
</tr>
<tr>
<td>PCR</td>
<td>post-column reaction</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>UV/VIS</td>
<td>ultraviolet/visible spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
**Chemical compounds and minerals:**

\[
\begin{align*}
\text{Al}_2\text{Ca(SiO}_4)_2 & \quad \text{anorthite (mineral)} \\
\text{Al}_2\text{O}_3(\text{CaO})_3(\text{H}_2\text{O})_6 & \quad \text{hydrogarnet (mineral)} \\
\text{Al(OH)}_3 & \quad \text{gibbsite (mineral)} \\
\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 & \quad \text{kaolinite (mineral)} \\
\text{aqua regia} & \quad \text{a mixture of hydrochloric and nitric acid (3:1 v/v)} \\
\text{Ca}_{12}\text{Al}_{14}\text{O}_{33} & \quad \text{mayenite (mineral)} \\
\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3 & \quad \text{grossular (mineral)} \\
\text{Ca}_2\text{Al}_2\text{SiO}_7 & \quad \text{gehlenite (mineral)} \\
\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{1.25}(\text{OH})_7 & \quad \text{hibschite (mineral)} \\
\text{CaF}_2 & \quad \text{calcium fluoride} \\
\text{CaCO}_3 & \quad \text{calcium carbonate} \\
\text{Ca}_3\text{Mg( SiO}_4)_2 & \quad \text{merwinte (mineral)} \\
\text{CaO} & \quad \text{calcium oxide; ‘burned lime’} \\
\text{Ca(OH)}_2 & \quad \text{calcium hydroxide; portlandite (mineral)} \\
3\text{CaO}\cdot\text{SiO}_2 & \quad \text{tricalcium silicate; ‘alite’ (cement nomenclature)} \\
2\text{CaO}\cdot\text{SiO}_2, \text{Ca}_2\text{SiO}_4 & \quad \text{dicalcium silicate; larnite (mineral); ‘belite’ (cement nomenclature)} \\
\text{CO}_2 & \quad \text{carbon dioxide} \\
\text{H-citrate} & \quad \text{hydrogen citrate (C}_6\text{H}_8\text{O}_7\text{); citric acid} \\
\text{HCl} & \quad \text{hydrochloric acid} \\
\text{HClO}_4 & \quad \text{perchloric acid} \\
\text{HF} & \quad \text{hydrogen fluoride} \\
\text{H}_2\text{O} & \quad \text{water} \\
\text{H}_2\text{O}_2 & \quad \text{hydrogen peroxide} \\
\text{HOAc} & \quad \text{acetic acid (CH}_3\text{COOH)} \\
\text{MgAl}_2\text{O}_4 & \quad \text{spinel (mineral)} \\
\text{MgCl}_2 & \quad \text{magnesium chloride}
\end{align*}
\]
<table>
<thead>
<tr>
<th>Chemical</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td><em>periclase</em> (mineral)</td>
</tr>
<tr>
<td>Na-citrate</td>
<td>sodium citrate (C₆H₅Na₃O₇)</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>sodium carbonate</td>
</tr>
<tr>
<td>NaOAc</td>
<td>sodium acetate (CH₃COONa)</td>
</tr>
<tr>
<td>NaOH</td>
<td>sodium hydroxide</td>
</tr>
<tr>
<td>Na₂EDTA</td>
<td>ethylenediaminetetraacetic acid disodium salt (Na₂C₁₀H₁₄N₂O₈)</td>
</tr>
<tr>
<td>Na₂S</td>
<td>sodium sulphide</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>sodium sulphate</td>
</tr>
<tr>
<td>Na₂S₂O₄</td>
<td>sodium dithionate; sodium hydrosulphite</td>
</tr>
<tr>
<td>NH₄OAc</td>
<td>ammonium acetate (CH₃COONH₄)</td>
</tr>
<tr>
<td>NH₂OH</td>
<td>hydroxylamine</td>
</tr>
<tr>
<td>NH₂OH·HCl</td>
<td>hydroxylamine hydrochloride; hydroxylammonium chloride</td>
</tr>
<tr>
<td>SiO₂</td>
<td><em>quartz</em> (mineral)</td>
</tr>
</tbody>
</table>
Symbols:

$E^0$ standard electrode potential [V]

$EC$ electrical conductivity [mS cm$^{-1}$]

$E_{k}$ redox potential [V]

$F$ Faraday constant [C mol$^{-1}$]

$\Delta G^0_r$ Gibbs free energy change [kJ mol$^{-1}$]

LOI loss on ignition

$M$ molarity [mol dm$^{-3}$]

$n$ number of experimental repetitions

$n$ number of electrons transferred in a redox half reaction

$NV$ neutralizing value

$R$ universal gas constant [J mol$^{-1}$ K$^{-1}$]

$RV$ reactivity value

$T$ absolute temperature [K]

$TOC$ total organic carbon
## Contents

List of publications .............................................................................................................. i  
Author’s contribution........................................................................................................... ii  
Nomenclature.................................................................................................................... iii  

1 Introduction ................................................................................................................... 1  
  1.1 Thesis objective .................................................................................................... 3  

2 Background .................................................................................................................. 5  
  2.1 Integrated carbon steelmaking slag residues ..................................................... 5  
    2.1.1 Slag residue utilisation .............................................................................. 6  
  2.2 Pulp and papermaking residues .......................................................................... 11  
    2.2.1 Pulp and paper residue utilisation ........................................................... 13  
  2.3 Environmental considerations ........................................................................... 18  
    2.3.1 Single vs. sequential extraction procedures ............................................ 19  
  2.4 Summary ............................................................................................................. 23  

3 Materials and methods ............................................................................................... 24  
  3.1 Soil amendment manufacture ........................................................................... 24  
  3.2 Relevant physicochemical properties ............................................................... 26  
  3.3 Easily-available plant nutrients ......................................................................... 26  
  3.4 Pseudo-total element concentrations ............................................................... 26  
  3.5 Sequential extraction of trace elements ............................................................ 27  
  3.6 Method evaluation ............................................................................................ 27  

4 Results and discussion ............................................................................................... 29  
  4.1 Relevant physicochemical properties and easily-available nutrient concentrations ........................................................................................................ 29  
  4.2 Pseudo-total element concentrations and trace element availability .......... 31  
  4.3 Method performance ......................................................................................... 39  
  4.4 Legislative perspectives ..................................................................................... 43  

5 Conclusions ................................................................................................................ 46  
  5.1 Significance of this work .................................................................................. 47  
  5.2 Limitations and future research recommendations ......................................... 48  

References......................................................................................................................... 49  

Errata for appended publications
1 Introduction

Waste utilisation is an attractive alternative to disposal as it can reduce reliance on landfill practices, the extraction of virgin raw materials and possibly enable savings in valuable materials and energy resources otherwise consumed in the process of converting raw materials to products. As recent regulatory development has increased the costs of landfill disposal and the difficulty in acquiring new sites, an emerging waste disposal problem is arising for traditional process industries in Finland and abroad (Cabral et al. 2008; Dippenaar 2005; Monte et al. 2009). However, for large manufacturers such as the forest and ferrous metals industries, the quality of waste streams is often reflective of the quality of the main product and it is thus beneficial to strive towards the stability of process conditions and the homogeneity of waste streams promoting respective utilisation.

In manufacturing systems, elements which are detrimental to the quality of the main product or to the stability of production are willingly removed from the process by various alternatives thus generating environmental burden. As in any unit process, decisions for decreasing environmental burdens into a specific environmental media, such as atmospheric or waste-water emissions, can with the current technologies only be performed at the expense of solid waste generation (Fig. 1). This has relevance regarding forest and steel industry operations, which have increasingly been concentrating on the respective control of waste-water and atmospheric emissions during the past decades (EC 2001a, 2001b). Prior to the new Waste Act (646/2011), enforced in May 2012, Finnish environmental legislation did not recognise the concept of ‘residue’ or ‘by-product’ and thus all residues, which were not labeled as products, were treated as wastes (Sorvari 2008).

Fig. 1 A schematic illustration of the environmental burdens generated by a unit process (modified from Dahl 2008)
To respond to the increasing pressures related to the environmental burdens generated by different industrial sectors, society as a whole needs to consider industrial wastes as valuable resources and encourage further utilisation in subsequent processes, industries or even the surrounding ecosystems. Practical efforts are required to transform the current linear resource use and disposal models to more cyclical ones (Fig. 2) possibly enabling increased environmental efficiency on local, national and global levels. For individual industrial actors this could be realized as greater competitiveness through the optimisation of materials and energy consumption and thus represent a continuation of the inevitable drive towards efficiency (Curran and Williams 2011).

![Fig. 2 Linear and cyclical material flows (modified from Curran and Williams 2011)](image)

For long have separated industries improved respective production methodologies enabling increases in energy efficiency and decreased environmental burdens. As an example, modern chemical pulp mills can already be regarded as self-sufficient in terms of energy consumption as half of the wood raw material is dissolved and respectively used as fuel in the chemical recovery phase (Szabó et al. 2009). Excellent examples exist of integrated pulp and paper mills where the generation of wastes has decreased substantially due to the efficient internal utilisation of production residues (Gavrilescu 2008; Mladenov and Pelovski 2010). Since the first energy crisis during the mid-1970s the carbon steel industry has undertaken major improvements in energy utilisation efficiency, labour productivity and pollution control and succeeded in significant reductions in solid waste generation and CO₂ emissions (Szekely 1996).

A central argument of this thesis lies with the potential of an inter-industry approach applied within the forest and steel industries. Perhaps the way forward in attaining further
advances in the environmental efficiency of these manufacturing systems can be found through the cooperation of formerly separate industries engaging in a joint effort. One of the main challenges in residue utilisation is to find suitable applications for existing streams and, if not attainable, to find suitable material combinations for improving the inadequate properties of individual streams. Needless to say, decisions regarding the potentially beneficial use of waste-labelled residues or residue-derived alternative materials should always be based on sound judgements of the possible environmental consequences of such use (van der Sloot 2006).

1.1 Thesis objective

The objective of this thesis was to find applications for the inter-industry utilisation of forest and carbon steel industry residues. The volume of operations and increasing regulatory pressures further support the already existing need for utilisation. As a consequence of high calcium equivalents present in these residues, the pH values of certain soils could be raised significantly through the neutralization of soil acidity. Additional nutrient contents could enable utilisation for soil fertilization purposes in certain acidic soils, acting as amendments by increasing soil pH and nutrient content, thus enhancing seed germination and seedling growth. By a combination of pulp and paper, and steel industry residues processed into pellets, the risk of physiological shock effects from easily-soluble salts could be attenuated and potential alkaline contaminant release (Mahmoudkhani et al. 2004) controlled. The research tasks for achieving this were:

(i) To find candidate mills and experimentally manufacture potential soil amendment materials.
(ii) To evaluate the performance of a sequential extraction method in providing the necessary environmental assessment data.
(iii) To investigate whether the attained residue combinations would allow an end of waste legal definition.

As illustrated in Fig. 3, paper I provided background to the operations of these separate industrial sectors with a suggestion of relevant candidate facilities and discussed the characteristics of individual residue streams. Papers II and III respectively addressed the utilisation of primary and secondary slag residues from the suggested carbon steel mill in tandem with residues from the suggested pulp and paper mill complex in the experimental manufacture of potential soil amendment materials. Paper IV discussed the possibilities of inter-industry residue utilisation from a legislative perspective based on national and EU regulatory frameworks, the definition of waste and the end of waste criteria. Finally, paper V attempted to evaluate the suitability of the operationally defined sequential extraction method, used in papers II-IV, in the analysis of industrial solid samples, such as secondary steel ladle slag.
Fig. 3 Fields of research work described in this thesis

- Primary and secondary slags with pulp and paper residues for soil amendment (papers II & III)
- Material efficiency through symbiotic inter-industry residue utilisation (paper I)
- Sequential extraction for industrial residue analysis (paper V)
- Residue utilisation for soil amendment - legislative issues (paper IV)
2 Background

2.1 Integrated carbon steelmaking slag residues

The carbon steel and forest industries generate a variety of individual inorganic and organic residue streams. During integrated carbon steelmaking, a variety of non-metallic residues are generated due to the removal of raw material gangue by added fluxing agents and the molten impurities of iron or steel (Proctor et al. 2000). Conventional carbon steel manufacture from virgin ore is generally managed through the blast furnace (BF)/basic oxygen furnace (BOF) process route (Cottrell 1975). In the BF/BOF route, the top-charged iron ore raw material is first reduced with coke and possible additional reductants and the hot metal product of the BF (i.e., crude iron) subsequently refined in the BOF by the help of an oxygen blow (Dippenaar 2005). The main objective of these primary processes is to attain an efficient reduction degree of iron ore to crude iron, to remove material impurities, and to adjust the level of carbon, one of the most effective alloying elements of steel.

To remove material impurities from liquid metal, lime is generally used as a fluxing agent to generate a separate residual slag phase which can be effectively decoupled from the desired product. The separate slag phases generally have a comparatively lower density than the liquid metal thus allowing efficient separation. Alkalis, such as sodium and potassium, sulphur, phosphorus, or trace elements, such as arsenic, copper, chromium, lead, nickel, vanadium or zinc, can have undesired effects on the operation of the BF or the quality of carbon steel.

In addition to primary slags, secondary slag residues are generated during the intermediate desulphurisation of crude iron prior to converting in the BOF and during secondary metallurgy when the quality of liquid steel is finalised in a ladle prior to casting (Posch et al. 2002). As opposed to primary slags, generated in the range of 230 kg of BF and 70 kg of BOF steel slag per tonne of steel produced (Eloneva 2010a), the production volumes of secondary desulphurisation and steel ladle slags are significantly lower, i.e., in the range of 20-30 kg per tonne of steel produced (Eloneva 2010a; Manso et al. 2005). According to Teir (2008), the Finnish steel industry produced a total of 3.6 Mt of carbon steel in 2004, accompanied by approximately 1.1 Mt of primary steelmaking slag residues. Prior to further utilisation or disposal, the cooled or granulated solidified slags are generally processed for metal-removal and potentially crushed to a size-range of ≤2.5-25 mm (Proctor et al. 2000). The individual primary and secondary slag fractions generated during carbon steelmaking via the integrated BF/BOF process route are further illustrated in Fig. 4.
2.1.1 Slag residue utilisation

Based on the discussed literature below, research regarding the utilisation of carbon steelmaking slags has mainly focused on the development of cement composites, blended cements and road construction aggregates, use in solidification/stabilization or application to soils. For example, primary BF slags are commonly used in blended cements and other applications in Finland and abroad. As illustrated in Fig. 5, the utilisation rate of BOF steel slags is generally lower than that of BF slags as secondary desulphurisation and steel ladle slags lack commercial applications.

Motz and Geiseler (2001) reported the use of BOF and electric arc furnace (EAF) slags as road construction aggregates, stabilizers for hydraulic engineering constructions and as fertilizers for agricultural purposes. The authors concluded that the carbonatic solidification of steelmaking slags led to an increased bearing capacity of road layers without adverse environmental impacts of the unbound or bituminous bound aggregates due to trace element leaching. Shi (2002, 2004) and Shi and Hu (2003) reported extensively the cementitious properties of primary BOF slag and secondary ladle slags after EAF smelting. Although the EAF process is generally used for smelting recycled...
steel as opposed to steel from virgin ore, according to Manso et al. (2005), the subsequent ladle treatments can be regarded as comparable in both cases. Accordingly, the cementitious properties of slag residues were promoted by the presence of ‘alite’ (3CaO·SiO₂) and ‘β-belite’ (β-2CaO·SiO₂) phases and could be enhanced by the fineness of slag and the addition of suitable activators. It should be emphasized that for solidified slag materials, the respective properties and mineral compositions are largely dependent in the chemical composition of the molten phase and subsequent cooling conditions (Shi 2004).

The use of primary steel slag as an additive in Portland cement has been reported (Altun and Yılmaz 2002). Even though as much as one-third of ordinary Portland cement could be replaced by primary steel slag to satisfy the physical and mechanical properties stated in relevant national standards, the mechanical strength of manufactured mortars was inversely related to the quantity of additive slag. Manso et al. (2005) and Setién et al. (2009) investigated the use of ladle slag in construction. Both investigations provided supportive results regarding slag utilisation in construction and civil engineering applications, such as masonry mortars. However, respective incorporation in mortars or concrete could be hindered by the characteristic volume expansions due to calcium and magnesium oxide (CaO and MgO, respectively) hydration and larnite (2CaO·SiO₂) transformations (Setién et al. 2009).

Adolfsson et al. (2011) suggested the use of ladle slag as a binder supplement in BF briquettes, as it was not likely that the material could meet the requirements imposed for blended calcium aluminate cements. Shi and Fernández-Jiménez (2006) reviewed the use of alkali-activated cements incorporating, e.g., primary steel slag in stabilization/solidification applications to enable the disposal of low-level radioactive and hazardous wastes or the remediation of contaminated sites. Although the hydration of alkali-activated cements was less interfered with by the stabilization of wastes than commercial Portland cements, increased shrinkage upon hydration at room temperature could lead to the leaching of alkalis under environmental conditions.

Furthermore, Lampris et al. (2008) used ground granulated blast furnace slag (GGBFS) to solidify air pollution control residues, a mixture of lime, fly ash and carbon, to prevent excessive leaching of chlorides under landfill conditions. The authors concluded that more than half of GGBFS, compared to the final mass of the monolithic solid, would be required to attain leaching levels in accordance to relevant waste acceptance criteria which would, however, result in the reduction of free lime and therefore affect the activating capacity of the system. Kim et al. (2005) investigated the possibility of solidifying digested sewage sludge by primary steel slag and lime. The sequentially repeated batch leaching tests by distilled water at pH 5.8-6.3 and acetic acid (HOAc) indicated that the mixed and compacted material was more suitable for use as a landfill cover than the untreated sludge cake.
In addition, the use of primary BF or BOF steel slag residues in soil liming, as iron or magnesium fertilizers or as means to decrease trace element mobility in contaminated soils or sediments has been reported (Abou Seeda et al. 2002; Ali and Shahram 2007; Barth et al. 2007; Khan et al. 2007; Levonmäki and Hartikainen 2007; Munn et al. 2005; Nozoe et al. 1999; Peregrina et al. 2008; Wang and Cai 2006). Based on the reported investigations, BF slag was effective in increasing the pH, and calcium and magnesium content of acid sulphate soils (Khan et al. 2007), and was nearly as effective as reagent grade calcium carbonate (CaCO₃) in remediating extreme acidity of acid mine soil and improving plant growth (Munn et al. 2005). In addition, BF slag application was comparable to CaCO₃ treatment in immobilizing lead in shooting range soils (Levonmäki and Hartikainen 2007) and barium, nickel and zinc in contaminated sediments, but resulted in an increased copper availability in the latter (Barth et al. 2007).

On the basis of pot experiments (Abou Seeda et al. 2002; Ali and Shahram 2007; Peregrina et al. 2008; Wang and Cai 2006), incubation trials (Ali and Shahram 2007) and field experiments (Peregrina et al. 2008), the use of steel slag showed promise as an inexpensive source of iron and magnesium for deficient soils and in liming acidified soils. However, further decreases in soil redox potential should be avoided by the application of slags with high Fe(III) content (Nozoe et al. 1990), coupled with thorough investigation of the potential environmental impacts of, e.g., trace elements upon application. In summary, the available investigations concerning the utilisation of carbon steelmaking residues are further compiled in Table 1.
<table>
<thead>
<tr>
<th>Ref.</th>
<th>Residue(s)</th>
<th>Potential application(s)</th>
<th>Advantage(s)</th>
<th>Limitation(s)</th>
<th>Experimental conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adolfsson et al. (2011)</td>
<td>Secondary ladle slag</td>
<td>Blended cements</td>
<td>Cementitious properties</td>
<td>Insufficient properties for commercial use</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Abou Seeda et al. (2002)</td>
<td>Primary BOF slag</td>
<td>Soil amendment</td>
<td>Nutrient source and pH correction</td>
<td>Need for organic matter additions</td>
<td>Laboratory and greenhouse</td>
</tr>
<tr>
<td>Ali and Shahram (2007)</td>
<td>Primary BOF slag</td>
<td>Soil amendment</td>
<td>pH correction</td>
<td>Potential trace element contamination</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Altun and Yılmaz (2002)</td>
<td>Primary BOF slag</td>
<td>Blended cements</td>
<td>Satisfactory properties</td>
<td>Strength inversely related to slag quantity</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Barth et al. (2007)</td>
<td>Primary BF slag</td>
<td>Soil amendment</td>
<td>Trace element immobilization in dredged sediments</td>
<td>Trace element contamination</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Khan et al. (2007)</td>
<td>Basic slag</td>
<td>Soil amendment</td>
<td>Nutrient source and pH correction</td>
<td>-</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Kim et al. (2005)</td>
<td>Primary BOF slag</td>
<td>Solidification of digested sewage sludge</td>
<td>Structural properties and contaminant leaching</td>
<td>-</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Lampris et al. (2008)</td>
<td>Primary BF slag</td>
<td>Solidification of air pollution control residues</td>
<td>Structural properties</td>
<td>Chloride leaching</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Levommiäki and Hartikainen (2007)</td>
<td>Primary BF slag</td>
<td>Soil amendment</td>
<td>Pb immobilization in shooting range soils</td>
<td>Trace element contamination</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Manso et al. (2005)</td>
<td>Secondary ladle slag</td>
<td>Masonry mortars and road construction</td>
<td>Suitable properties</td>
<td>-</td>
<td>Laboratory</td>
</tr>
</tbody>
</table>

*Source process not specified*
<table>
<thead>
<tr>
<th><strong>Ref.</strong></th>
<th><strong>Residue(s)</strong></th>
<th><strong>Potential application(s)</strong></th>
<th><strong>Advantage(s)</strong></th>
<th><strong>Limitation(s)</strong></th>
<th><strong>Experimental conditions</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Motz and Geiseler (2001)</td>
<td>Primary BOF and EAF slags</td>
<td>Road aggregates, hydraulic engineering, fertilizers</td>
<td>Advantageous/comparable to virgin alternatives</td>
<td>-</td>
<td>Theoretical</td>
</tr>
<tr>
<td>Munn et al. (2005)</td>
<td>Primary BF and BOF slags</td>
<td>Soil amendment</td>
<td>Nutrient source and pH correction</td>
<td>-</td>
<td>Greenhouse</td>
</tr>
<tr>
<td>Nozoe et al. (1999)</td>
<td>Primary BOF slag</td>
<td>Soil amendment</td>
<td>Fe source and pH correction</td>
<td>Possible decrease in redox potential</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Peregrina et al. (2008)</td>
<td>Primary BOF slag</td>
<td>Soil amendment</td>
<td>Mg source for gypsum-amended acidic soils</td>
<td>Potential Al-F toxicity (phospho-gypsum)</td>
<td>Greenhouse and field</td>
</tr>
<tr>
<td>Setién et al. (2009)</td>
<td>Secondary ladle slag</td>
<td>Construction products</td>
<td>Potentially cementitious in the presence of activators</td>
<td>Volume instability</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Shi (2002)</td>
<td>Secondary ladle slag</td>
<td>Construction products</td>
<td>Highly cementitious in the presence of activators</td>
<td>Weakly cementitious under normal conditions</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Shi (2004)</td>
<td>Primary BOF and EAF slags</td>
<td>Blended cements</td>
<td>Advantageous properties in the presence of activators</td>
<td>Weakly cementitious, free CaO hydration</td>
<td>Review</td>
</tr>
<tr>
<td>Shi and Hu (2003)</td>
<td>Secondary ladle slag</td>
<td>Construction products</td>
<td>Highly cementitious under hydrothermal conditions</td>
<td>Cracking due to free CaO hydration</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Wang and Cai (2006)</td>
<td>Primary BOF slag</td>
<td>Soil amendment</td>
<td>Fe source for Fe chlorosis</td>
<td>Need for further trials</td>
<td>Laboratory</td>
</tr>
</tbody>
</table>
2.2 Pulp and papermaking residues

As opposed to the solid, inorganic slag residues generated in steelmaking, the pulp and paper industry generates a wider variety of solid to semi-solid, organic and inorganic residue streams. The characteristics of these residues are mainly dictated by the paper grade being produced, the raw materials used and the applied process techniques and desired paper properties (Monte et al. 2009). From a selection of chemical, semi-chemical or mechanical pulping methods the emphasis in this context is placed on the chemical separation of wood chip raw materials, more precisely on the alkaline sulphate (i.e., kraft) process using sodium hydroxide (NaOH) and sodium sulphide (Na₂S) as active cooking chemicals (Heinemann 2006; Sixta et al. 2006).

The nature of the pulping method has relevance regarding the characteristics of residue streams generated within the chemical recovery circuit (Fig. 6). In the sulphate process, the spent cooking chemical components are preserved in the black liquor stream subsequently concentrated and regenerated for further pulping. This requires the addition of make-up chemicals such as sodium sulphate (Na₂SO₄) for the regeneration of sodium sulphide, which together with sodium carbonate (Na₂CO₃) formed during combustion in the soda recovery boiler, act as feedstock for the causticizing reaction to attain ‘fresh’ white liquor (NaOH and Na₂S). Causticizing also necessitates the production of CaO to be hydrated to calcium hydroxide [Ca(OH)₂] for subsequent reactions with Na₂CO₃. This is generally managed through the calcination of CaCO₃, a by-product of the causticizing reaction (Järvensivu et al. 2001).

As illustrated in Fig. 6, the aforementioned combustion, causticizing and calcination stages generate respective green liquor dregs, slaker grits and lime waste residues, which are withdrawn from the chemical recovery circuit mainly for the removal of so-called non-process elements (NPEs) (Doldán et al. 2010; Martins et al. 2007). These NPEs, e.g., potassium, magnesium, manganese, barium, iron, aluminium, copper, nickel, chromium and zinc, are non-reactive or insoluble elements and possibly detrimental in the fibre line and chemical recovery (Grace and Tran 2009).
As pulp and papermaking is an energy-intensive industry with a characteristic high water consumption (Oral et al. 2005; Thompson et al. 2001), significant quantities of incineration ashes and waste-water treatment sludges are also produced. The incineration of wood residues, such as bark, wood chips and sawdust, and auxiliary fuels is generally managed in solid fuel boilers, which due to boiler operation and flue gas purification generate respective bottom and fly ash residues (Dahl et al. 2010). Waste-water treatment at pulp and paper mills can generally be managed by primary mechanical clarification followed by secondary aerobic or anaerobic methods. The choice of purification method depends entirely on the characteristics of the effluent. In pulp mill effluents the share of dissolved wood derived substances such as lignin, extracted during cooking and bleaching, is comparatively higher than in paper mill effluents (Thompson et al. 2001) which also contain paper additives, such as kaolinite \( \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \) and/or \( \text{CaCO}_3 \) (Kuokkanen et al. 2008). Hence, biological aerobic treatment is usually applied for pulp mill effluents, as anaerobic chemical methods may be more suitable in the case of paper and board mill effluents (Pokhrel and Viraraghavan 2004). Indicative values of the aforementioned chemical recovery circuit, ash and waste-water treatment sludge residues are presented in Table 2.
Table 2 Residue generation (t a⁻¹) at certain Finnish pulp and paper mill complexes (Dahl et al. 2010; Nurmesniemi et al. 2007, 2010a, 2010b)

<table>
<thead>
<tr>
<th>Residue</th>
<th>Green liquor dregs</th>
<th>Slaker grits</th>
<th>Lime waste</th>
<th>Fly ash</th>
<th>Bottom ash</th>
<th>Biosludge</th>
<th>Paper mill sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source process</td>
<td>Recovery boiler</td>
<td>Causticizing</td>
<td>Lime kiln</td>
<td>Solid fuel boiler</td>
<td>Solid fuel boiler</td>
<td>Biological waste-water treatment</td>
<td>Chemical waste-water treatment</td>
</tr>
<tr>
<td>Generationa (d.w.b)</td>
<td>3700c</td>
<td>670d</td>
<td>120c</td>
<td>14,000c</td>
<td>2600c</td>
<td>8700c</td>
<td>22,000c</td>
</tr>
</tbody>
</table>

*aProduction capacity in 2004: 400,000 t a⁻¹ bleached soft- and hardwood pulp; 550,000 t a⁻¹ uncoated fine paper; 500,000 t a⁻¹ coated magazine paper (Northern Finland Environmental Permit Authority 2007)

b d.w. = dry weight
c Data from 2004 (Nurmesniemi et al. 2007)
d Data from 2008 (Nurmesniemi et al. 2010a, 2010b)
e Data from 2009 (Dahl et al. 2010)

2.2.1 Pulp and paper residue utilisation

Available literature regarding the utilisation of pulp and papermaking residues has mainly concentrated on use in the construction industry or application to soil. As illustrated in Fig. 7, the landfill disposal of these residues within the European Union (EU) has declined in recent years due to utilisation in road construction and land reconstruction applications, energy recovery, inter-industry applications and respective application to soil (Monte et al. 2009). In 2004, the Finnish forest industry produced a total of 12 Mt of air-dried pulp and 14 Mt of paper and board products, accompanied by the generation of approx. 250 kt of ash, 500 kt of sludge, 80 kt of green liquor dregs and 20 kt of lime waste residues. Respectively, 59, 5, 95, and 41% of these residues remained without further utilisation and were sent to final disposal (Finnish Forest Industries Federation 2005).

Castro et al. (2009) reported the use of green liquor dregs and slaker grits as potential raw materials in cement clinker production. Utilisation was deemed as a potential alternative management option for these chemical recovery cycle residues, although respective incorporation should be kept low to avoid excessive sulphur emissions from the clinker kiln. Ahmadi and Al-Khaja (2001) investigated the utilisation of bio-chemical sludge from paper tissue waste-water treatment as an organic aggregate in concrete. The authors found that the sand aggregates of concrete could be replaced with the sludge residue in view of non-structural masonry applications. In addition, the utilisation of paper mill sludge in the production of lightweight bricks has been reported (Sutcu and Akkurt 2009). Although the authors were able to reduce brick density and thermal conductivity, sludge additions were inversely related to the respective compressive strength of brick samples.
Wang et al. (2008a, 2008b) studied extensively the use of biomass fly ash from, e.g., pure wood incineration in concrete. As a result, the properties of pure wood and mixed fly ashes were comparable to those from pure coal combustion and were thus recommended to be included in relevant standards concerning ash additions in concrete. In addition to use in structural applications, the utilisation of pulp and paper mill fly ash as a potential soil amendment has received significant attention in relevant research literature. As discussed by several authors (Augusto et al. 2008; Demeyer et al. 2001; Lundström et al. 2003; Meiwes 1995; Muse and Mitchell 1995; Pöykiö et al. 2005), fly ash or fly ash and lime application in the Northern hemisphere was most suitable for acidified soils suffering from acidic deposition or clear-cutting or for soils severely depleted in boron, calcium, magnesium or potassium. Acid neutralization capacity of the ash was also related to relieving soil aluminium and manganese toxicity (Demeyer et al. 2001; Lundström et al. 2003) as ash ineffectiveness in the case of, e.g., mineral soils was stated to derive from the lack of growth limiting nitrogen (Augusto et al. 2008; Demeyer et al. 2001). Ash application to catchment areas was stated to have minor short term effects on the water quality of humic lakes, however, increased application rates could stimulate the growth of phytoplankton and zooplankton (Tulonen et al. 2002). It should be emphasized that ash application to soils can also be seen as means to restore previously exported nutrients to forest ecosystems (Demeyer et al. 2001; Rothpfeffer 2007), thus indicating the need for increased industry-ecosystem interaction.

Fly ash has also been studied in tandem with waste-water treatment sludges in composting and subsequent application to soil (Hackett et al. 1999) and in the
manufacture of landfill covers (Ritter et al. 1992). The former alternative showed promise regarding nutrient provision and liming ability, but respective dioxin concentrations required careful monitoring. In the latter, fly ash and sludge were seen as suitable options for landfill and storage lagoon closures as trace element translocation was not seen as a restraint due to low concentrations and high pH of the admixture.

Pulp and paper mill sludge utilisation alone has also been under investigation by several authors. Cabral et al. (1998) and Camberato et al. (2006) reviewed the potential of pulp and paper mill sludge additions to agricultural and forest soils. Consequently, respective application to soil should be considered especially in areas with a characteristic shortage of soil organic matter content and a high risk of erosion. Trace element content, the presence of organochlorine compounds and leaching of nitrates leading to potential groundwater contamination and nutrient immobilization, especially in the case of low-nutrient sludges, were identified as main environmental limitations. Rato Nunes et al. (2008) reported the experimental effects of secondary paper mill sludge application on soil properties and wheat production. Although magnesium additions were deemed necessary for optimal grain yield, the performed greenhouse trials supported the use of sludge in increasing soil pH and organic matter content.

Furthermore, Jordan et al. (2002) and Jordan and Rodriguez (2004) studied the effects of various pulp and paper mill residue, i.e., ash, green liquor dregs, slaker grits and primary sludge, and soil substrates on the growth of several plants. In the case of, e.g., Monterey pine the use of ash and green liquor dregs substrates led to increased biomass production most likely due to the enhanced availability of nutrients caused by increased pH and water content. Negative effects were found especially in the case of slaker grits, which simultaneously provided increases in pH (>8.5), electrical conductivity (>5.5 mS cm\(^{-1}\)) and sodium content (266 mg dm\(^{-1}\)) of the respective soil substrates. Slaker grits were also investigated by Nurmesniemi et al. (2010a, 2010b). Although manganese, cobalt, nickel and sulphur showed significant extractability by HOAc during a sequential extraction procedure (Nurmesniemi et al. 2010a), trace element concentrations were below relevant national limit values and the authors supported utilisation as a soil amendment and pH buffer.

Cabral et al. (2008) reported an incubation study to investigate the liming potential of solid fuel boiler fly ash, green liquor dregs and slaker grits while using ground agricultural limestone as reference. The residues were characterised as potentially valid alternatives to commercial limestone, as no environmental concerns were related to soil exchangeable sodium in regards to additions needed to raise soil pH to 6.5. In addition, ash additions increased extractable potassium and phosphorus of the soils, indicating contributions to improve soil fertility. In summary, the utilisation of pulp and papermaking residues based on the aforementioned publications is further compiled in Table 3.
<table>
<thead>
<tr>
<th>Ref.</th>
<th>Residue(s)</th>
<th>Potential application(s)</th>
<th>Advantage(s)</th>
<th>Limitation(s)</th>
<th>Experimental conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ahmadi and Al-Khaja (2001)</td>
<td>Bio-chemical sludge</td>
<td>Concrete aggregate</td>
<td>Decreased density, suitable properties</td>
<td>Water absorption, reduced strength</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Augusto et al. (2008)</td>
<td>Wood (fly) ash</td>
<td>Soil amendment</td>
<td>Nutrient source and pH correction</td>
<td>Potential trace element contamination</td>
<td>Review</td>
</tr>
<tr>
<td>Cabral et al. (1998)</td>
<td>Pulp mill sludge</td>
<td>Soil amendment</td>
<td>Organic matter and nutrient source, pH correction</td>
<td>Potential trace element, organochlorine and nitrate contamination</td>
<td>Review</td>
</tr>
<tr>
<td>Cabral et al. (2008)</td>
<td>Fly ash, green liquor dregs, slaker grits</td>
<td>Soil amendment</td>
<td>Nutrient source and pH correction</td>
<td>-</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Camberato et al. (2006)</td>
<td>Pulp and paper mill sludge</td>
<td>Soil amendment</td>
<td>Organic matter and nutrient source, pH correction</td>
<td>Potential nutrient immobilization</td>
<td>Review</td>
</tr>
<tr>
<td>Castro et al. (2009)</td>
<td>Green liquor dregs and slaker grits</td>
<td>Cement production</td>
<td>Alternative waste management</td>
<td>Potentially increased sulphur emissions</td>
<td>Industrial</td>
</tr>
<tr>
<td>Demeyer et al. (2001)</td>
<td>Wood (fly) ash</td>
<td>Soil amendment</td>
<td>Nutrient source and pH correction</td>
<td>Limited application rates</td>
<td>Review</td>
</tr>
<tr>
<td>Hackett et al. (1999)</td>
<td>Pulp and paper mill biosludge and fly ash</td>
<td>Compost soil application</td>
<td>Nutrient source and pH correction</td>
<td>Potential dioxin contamination</td>
<td>Laboratory and soil application</td>
</tr>
<tr>
<td>Jordan et al. (2002)</td>
<td>Ashes, green liquor dregs, slaker grits</td>
<td>Soil amendment</td>
<td>Nutrient source and pH correction</td>
<td>Trace element contamination</td>
<td>Greenhouse</td>
</tr>
<tr>
<td>Jordan and Rodriguez (2004)</td>
<td>Ashes, green liquor dregs, slaker grits, primary sludge</td>
<td>Soil amendment</td>
<td>Organic matter and nutrient source, pH correction</td>
<td>Trace element contamination</td>
<td>Laboratory and greenhouse</td>
</tr>
<tr>
<td>Lundström et al. (2003)</td>
<td>Wood (fly) ash and lime</td>
<td>Soil amendment</td>
<td>Nutrient source and pH correction</td>
<td>Additional perturbations</td>
<td>Review</td>
</tr>
<tr>
<td>Ref.</td>
<td>Residue(s)</td>
<td>Potential application(s)</td>
<td>Advantage(s)</td>
<td>Limitation(s)</td>
<td>Experimental conditions</td>
</tr>
<tr>
<td>------</td>
<td>------------------------------------</td>
<td>--------------------------</td>
<td>-------------------------------------------</td>
<td>-------------------------------------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>Meiwes et al. (1995)</td>
<td>Wood (fly) ash and lime</td>
<td>Soil amendment</td>
<td>Nutrient source and pH correction</td>
<td>Nitrification and nitrate leaching</td>
<td>Theoretical</td>
</tr>
<tr>
<td>Muse and Mitchell (1995)</td>
<td>Paper mill fly ash and lime</td>
<td>Soil amendment</td>
<td>Nutrient source and pH correction</td>
<td>-</td>
<td>Laboratory and field</td>
</tr>
<tr>
<td>Nurmesniemi et al. (2010a)</td>
<td>Slaker grits</td>
<td>Soil amendment</td>
<td>Nutrient source and pH correction</td>
<td>Potential trace element contamination</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Nurmesniemi et al. (2010b)</td>
<td>Slaker grits</td>
<td>Soil amendment</td>
<td>Nutrient source and pH correction</td>
<td>-</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Pöykiö et al. (2005)</td>
<td>Pulp and paper mill fly ash</td>
<td>Soil amendment</td>
<td>Nutrient source and pH correction</td>
<td>Potential trace element contamination</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Ritter et al. (1992)</td>
<td>Paper mill sludge and fly ash</td>
<td>Soil amendment</td>
<td>Closure of landfill and sludge lagoons</td>
<td>-</td>
<td>Greenhouse and field</td>
</tr>
<tr>
<td>Sutcu and Akkurt (2001)</td>
<td>Paper mill sludge</td>
<td>Brick production</td>
<td>Decreased density and thermal conductivity</td>
<td>Compressive strength</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Tulonen et al. (2002)</td>
<td>Wood (fly) ash</td>
<td>Soil amendment</td>
<td>Nutrient source and pH correction</td>
<td>Potential increase in plankton growth of nearby lake systems</td>
<td>Laboratory and field</td>
</tr>
<tr>
<td>Wang et al. (2008a)</td>
<td>Pure wood and co-incineration fly ash</td>
<td>Concrete additive</td>
<td>Comparable properties</td>
<td>Increased water demand and decreased strength</td>
<td>Laboratory</td>
</tr>
<tr>
<td>Wang et al. (2008b)</td>
<td>Pure wood and co-incineration fly ash</td>
<td>Concrete additive</td>
<td>Increased reactivity with increased Fe content</td>
<td>Non-reactive particle cores</td>
<td>Laboratory</td>
</tr>
</tbody>
</table>
2.3 Environmental considerations

As industrial residue utilisation or disposal involves materials which have been willingly removed from a unit process to minimise the effect of NPEs to the properties of the main product or stability of production, the potential environmental impacts of such use should be investigated in detail. Consequently, special emphasis should be placed on applications where the materials are under direct influence of environmental conditions, such as application to soils or disposal to landfills. However, as potential contaminant mobility can primarily be regarded as a function of the mineralogy and solid fraction chemistry of a material, subsequently influenced by a complex range of possible environmental conditions, significant generalisations often have to be made in identifying some of the most important forms and transformations of contaminants likely to occur and to infer probable environmental consequences (Ryan et al. 2008; Ure and Davidson 2002).

At present it is widely recognised that the potential environmental impacts of contaminants, such as metal or metalloid trace elements, are not dependent on their total concentrations, but rather critically on the forms in which they occur (Adriano 2001; Bacon and Davidson 2008; Filgueiras et al. 2002). Potential trace element release occurs when these divergent forms are exposed to changes in the surrounding conditions creating a gradient to drive mobilisation (Cappuyns and Swennen 2008a; Linge 2008). Common driving gradients are changes in pH and redox potential, of which the latter under disposal conditions is either a result of microbiologically mediated processes due to the presence of organic material or abiotic transformations leading to the formation of reducing gases (Sabbas et al. 2003).

As a result of a driving gradient, potential trace element release from environmental solid samples can occur via two distinct mechanisms, i.e., desorption or dissolution. As these two processes (Fig. 8) are often hard to distinguish from one another, and in highly heterogeneous samples often take place concomitantly, the former generally involves the degradation of surface bonds (e.g., van der Waals forces, electrostatic or covalent bonds) as the latter inherently relates to the decomposition of a solid phase (Linge 2008).
2.3.1 Single vs. sequential extraction procedures

To attain quantitative information on potential trace element release over a wide range of possible residue management activities, such as recycling or reuse, the performance of treatment processes or final disposal, the use of extraction tests in which a solid sample is exposed to a reagent liquid under defined conditions is common procedure (Filgueiras et al. 2002). As an example, single extraction methods can be used for determining the total elemental composition of a sample matrix by dissolution with a combination of strong mineral acids (Yafa and Farmer 2008), for estimating available element fractions for, e.g., plant uptake or through desorption and possible dissolution of easily soluble solid phases (Cappuyns and Swennen 2008b; Rigo et al. 2009) or in support of risk assessment concerning residue utilisation or disposal (Fällman 2000; Krüger et al. 2012; Nordmark et al. 2011; Sorvari 2003; van der Sloot and Kosson 2012). The so-called ‘pseudo-total’ assessments adopted in many national guidelines entail the determination of the trace element content of strong acid or *aqua regia* (i.e., HCl + HNO₃ in 3:1 v/v, respectively) digests of environmental samples. These measures give an assessment of the maximum potentially soluble or mobile contents through dissolution of the entire, usually non-silicate, sample matrix in the long-term or under the most extreme environmental conditions (Rao et al. 2008).

Although very useful in certain contexts, single extraction measures can suffer from the inability to provide information for a more comprehensive evaluation of the effect of varying environmental conditions and the difficulty of finding a single reagent effective in dissolving, e.g., the non-residual trace element forms without attacking the residual...
matrix (Tessier et al. 1979). To facilitate the respective shortcomings of single extractions, Tessier et al. (1979) reported a sequential extraction procedure for investigating trace element speciation in sediments. In their investigation the authors extracted trace elements from the nominal exchangeable, carbonate, iron and manganese oxide, organic matter and residual target phases. Although operationally defined and laborious, the use of sequential extraction can provide more detailed information on the possible origin, mode of occurrence, physicochemical availability and mobility of trace elements (Tessier et al. 1979).

In principal, sequential extraction procedures are fractionation schemes which apply a series of isolated extractions, each subsequent extraction being comparatively more aggressive than the previous one (Zufiaurre et al. 1998). As illustrated in Fig. 9, the main objective of sequential extraction is to sub-divide the total or pseudo-total trace element content to distinct fractions, as the elements recovered in the first fractions are generally those more weakly bound to the solid phases and hence have a greater potential mobility and environmental impact (Bacon and Davidson 2008). According to Ryan et al. (2008), the Tessier et al. (1979) procedure was explicitly designed to extract elements from specific phases or sites, such as exchange sites, carbonates, hydroxides and organic matter or sulphides.

Fig. 9 An illustrative example of the characteristic recoveries of various extraction procedures (modified from Ure and Davidson 2002)

Although various sequential extraction procedures have been reported since the work of Tessier et al. (1979) (e.g., Arunachalam et al. 1996; Gómez et al. 2007; Polyák and Hlavay 2001; Van Herck and Vandecasteele 2001), most of which are variants of the original procedure, no single procedure to date has been unreservedly accepted by the scientific community (Fuentes et al. 2004). To tackle the diversity and poor comparability of available procedures, in 1987 the European Commission launched an inter-laboratory program aimed at harmonizing various sequential extraction procedures (Sutherland
As a result, the program proposed a standardized three-step BCR (Bureau Communautaire de Référence, i.e., the Community Bureau of Reference, now the Standards, Measurement and Testing Programme) sequential extraction program in 1993 (Ure et al. 1993), which was respectively revised in 1999 (Rauret et al. 1999) due to uncertainties related to the second extraction step (Sahuquillo et al. 1999) and the assessment of extraction recoveries. The proposed and revised procedures have since also been used for the development of certified reference materials (CRMs), primarily allowing enhanced inter-laboratory comparability and respective quality control of acquired data (López-Sánchez et al. 1998; Pueyo et al. 2001; Quevauviller et al. 1997; Rauret et al. 2000).

Similar to the Tessier et al. (1979) procedure, the original and revised BCR procedures were originally ‘designed’ for the analysis of sediment samples, but have since been used for analyzing trace element availability from, e.g., soil samples (Golia et al. 2007; Kaasalainen and Yli-Halla 2003; Pueyo et al. 2008) and industrial residues such as ashes (Bruder-Hubscher et al. 2002; Smeda and Zymicki 2002), sludges (Fernández Alborés et al. 2000; Kazi et al. 2005) and mining wastes (Anju and Banerjee 2010; Marguí et al. 2004). Although a large body of literature supports the use of the BCR procedure in the analysis of various environmental solid samples, the main drawbacks of sequential extraction, such as lack of additional data regarding selectivity, occurrence of redistribution and readsoption, methodological and interpretative issues, and tediousness of the procedures (Alonso Castillo et al. 2011; Bacon and Davidson 2008; Gleyzes et al. 2002; Jamali et al. 2009; Martínez-Fernández et al. 2011; Rao et al. 2008) remain valid also in the case of the BCR procedure. As opposed to the Tessier et al. (1979) procedure, the justification for the BCR extraction procedure lies in simulating possible natural and anthropogenic modifications of prevailing environmental conditions (Gleyzes et al. 2002; Ryan et al. 2008). In comparison, the reagents and extraction conditions of the original Tessier et al. (1979) and revised BCR (Rauret et al. 1999) procedures are further illustrated in Table 4.
<table>
<thead>
<tr>
<th>Step</th>
<th>Reagents (per 1 g dry sample)</th>
<th>Shaking time and temperature</th>
<th>Nominal target phases</th>
<th>Step</th>
<th>Reagents (per 1 g sample)</th>
<th>Shaking time and temperature</th>
<th>Nominal target phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8 mL MgCl₂ (1 M; pH 7.0) or NaOAc (1 M; pH 8.2)</td>
<td>1 h, room temp.</td>
<td>Exchangeable</td>
<td>1</td>
<td>40 mL HOAc (0.11 M; pH 2.9)</td>
<td>16 h, 22±5 °C</td>
<td>Acid-soluble; exchangeable; carbonate-bound</td>
</tr>
<tr>
<td>2</td>
<td>8 mL NaOAc (1 M; adjusted to pH 5.0 with HOAc)</td>
<td>5 h, room temp.</td>
<td>Carbonates</td>
<td>1</td>
<td>40 mL NH₂OH·HCl (0.5 M; adjusted to pH 1.5 with 25 mL 2 M HNO₃)</td>
<td>16 h, 22±5 °C</td>
<td>Reducible</td>
</tr>
<tr>
<td></td>
<td>20 mL Na₂S₂O₄ (0.3 M) + Na-citrate (0.175 M) + H-citrate (0.025 M) or NH₂OH·HCl (0.04 M in 25% v/v HOAc)</td>
<td>2 h, room temp. or 6 h, 96±3 °C</td>
<td>Fe and Mn oxides</td>
<td>2</td>
<td>40 mL NH₂OH·HCl (0.5 M; adjusted to pH 1.5 with 25 mL 2 M HNO₃)</td>
<td>16 h, 22±5 °C</td>
<td>Reducible</td>
</tr>
<tr>
<td>3</td>
<td>3 mL HNO₃ (0.02 M) + 5 mL H₂O₂ (8.8 M; adjusted to pH 2 with HNO₃), 5 mL NH₄OAc (3.2 M in 20% v/v HNO₃)</td>
<td>2 h, 85±2 °C</td>
<td>Organic matter</td>
<td>3</td>
<td>10 mL H₂O₂ (8.8 M; adjusted to pH 2-3), 50 mL NH₄OAc (1.0 M; adjusted to pH 2 with HNO₃)</td>
<td>1 h, room temp. 1 h, 85±2 °C</td>
<td>Oxidisable</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 h, 85±2 °C 30 min, room temp.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>10 mL HF + 2 mL HClO₄, 10 mL HF + 1 mL HClO₄</td>
<td>digestion</td>
<td>Residual</td>
<td>4</td>
<td>21 mL HCl (12.0 M) + 7 mL HNO₃ (15.8 M)</td>
<td>digestion</td>
<td>Residual</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*aAnderson and Jenne (1970)*

*bISO 11466 (1995) Soil quality – extraction of trace elements soluble in *aqua regia*
2.4 Summary

Based on the discussed literature, the utilisation of various slag residues in construction applications such as blended cements, masonry mortars or road construction was hindered by comparatively weaker or inadequate strength development (Adolfsson et al. 2011; Altun and Yılmaz 2002; Shi 2002; Shi 2004) and potential volume instability leading to possible crack propagation (Setién et al. 2009; Shi 2004; Shi and Hu 2003). In the case of sludge and ash residues from pulp and paper mills, construction use has been unsuccessful due to inherently increased water adsorption (Ahmadi and Al-Khaja 2001; Wang et al. 2008a) and decreased strength development (Ahmadi and Al-Khaja 2001; Sutcu and Akkurt 2001; Wang et al. 2008a, 2008b). However, some authors reported the beneficial properties of slag residues in immobilizing trace elements in dredged sediments (Barth et al. 2007) and shooting range soils (Levonmäki and Hartikainen 2007), or in providing nutrients and pH correction for soils (Abou Seeda et al. 2002; Ali and Shahram 2007; Khan et al. 2007; Munn et al. 2005; Wang and Cai 2006). A combination of slag and pulp and paper residues for soil amendment thus deserves further research attention, possibly able to provide the organic matter needed for slag additions to soils (Abou Seeda et al. 2002), sufficient pH control (Muse and Mitchell 1995; Nurmesniemi et al. 2010b) and means to control trace element contamination potentially induced by the use of individual streams (Augusto et al. 2008; Jordan et al. 2002; Jordan and Rodriguez 2004; Nurmesniemi et al. 2010a; Pöykiö et al. 2005). Recycling of useful elements to agricultural or forest environments by way of the application of soil amendments would also promote the closure of industrial systems, increase broader sustainability with respect to soil nutrient cycling and avoid the environmental impacts of primary inorganic fertilizer production.

Taking into consideration the shortcomings of single extraction procedures, the environmental assessment of potential soil amendment materials should include a wider range of conditions potentially evoked within the environment. Sequential extraction procedures, the application of which is not entirely straightforward (Bacon and Davidson 2008; Gleyzes et al. 2002; Rao et al. 2008), could offer such means. Especially the BCR procedure, with a wide range of scientific literature supporting its application, can through the calculation of internal step recoveries (Fuentes et al. 2004) and the analysis of CRMs (López-Sánchez et al. 1998; Quevauviller 1998; Rauret et al. 2000) allow enhanced quality control and inter-laboratory comparability of acquired data.
3 Materials and methods

3.1 Soil amendment manufacture

The experimental manufacture of potential residue-derived soil amendments was carried out by combining individual residue streams (e.g., Fig. 10) from two different industrial facilities (discussed in paper I). The work was carried out in the two subsequent phases (paper II and papers III & IV, respectively) by modeling the potential trace element contents of the soil amendments based on available literature reporting determined trace element concentrations of individual residue streams (Kuokkanen et al. 2008; Nurmesniemi et al. 2005; Nurmesniemi et al. 2008; Nurmesniemi and Pöykiö 2006; Pöykiö et al. 2005; Pöykiö et al. 2006a, 2006b).¹

![Fig. 10 Scanning electron microscope images of a) desulphurisation slag, b) fly ash, c) lime waste and d) dried paper mill sludge residues used for manufacturing potential soil amendments discussed in papers III & IV (unpublished data)](image)

The manufacturing method for the amendment samples was adopted from conventional cement testing and consisted of dry mixing the individual constituents (see Table 5) in a laboratory mixer prior to admixing water to enable slag/fly ash hydration. Water addition was followed by a second mixing period before respective quantities of the attained slurries were cast in cubic 1 dm³ (paper II, see Fig. 11), or cylindrical moulds of approx. 25 mm in width and 35 mm in height (papers III & IV), vibrated and cured in room temperature and humidity.

¹ For discussion on the technical properties of individual residue streams from these industrial sectors, see Mäkelä (2010).
<table>
<thead>
<tr>
<th>Residue</th>
<th>Paper II</th>
<th>Paper III</th>
<th>Paper IV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Matrix I</td>
<td>Matrix II</td>
<td>Matrix I</td>
</tr>
<tr>
<td><strong>Binder</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GGBFS</td>
<td>0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BOF steel slag</td>
<td>0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Desulphurization/mixer slag&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.15</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>Steel ladle slag</td>
<td>0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fly ash</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td><strong>Reactive alkali</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Green liquor dregs</td>
<td>0.10</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Lime waste</td>
<td>0.30</td>
<td>0.30</td>
<td>0.25</td>
</tr>
<tr>
<td>Paper mill sludge</td>
<td>0.30</td>
<td>0.30</td>
<td>0.45</td>
</tr>
</tbody>
</table>

<sup>a</sup>Detailed water/binder ratios presented in papers II-IV

<sup>b</sup>The terminology (in, e.g., the Finnish language) regarding the secondary desulphurization slag fraction is somewhat ambiguous, as the samples taken from the slag pit at the mill in question generally include fractions of slag excavated from the subsequent mixer process.

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**Fig. 11** Image of a cubic 1 dm³ specimen incorporating GGBFS, fly ash, lime waste, paper mill sludge and ground green liquor dregs discussed in paper II (unpublished data)
3.2 Relevant physicochemical properties

The alkalinites of the soil amendments discussed in papers II-IV, and the ladle slag residue investigated in paper V, were evaluated by pH determination subsequent to extraction with ultrapure water (solid to liquid; 1:2.5 v/v). The ionic strengths, describing respective dissolvable metal salts content, of the pH extracts were also evaluated by measuring characteristic electrical conductivity (EC). Dry and organic matter contents of the samples were respectively measured by oven-drying (105 °C, ISO 11465) and loss on ignition (LOI) during over-night dry-digestion at 550 °C (EN 12879). As the LOI parameter is likely to include the dehydration of metal hydroxides and possible loss of volatile salts or mineral inorganic carbon (Heiri et al. 2001), the total organic carbon (TOC) contents were also evaluated by calculation based on the total inorganic carbon, measured as the evolved carbon dioxide during combustion in an oxygen-containing gas flow by infrared spectroscopy, and total carbon contents (EN 13137).

Soil amendment and ladle slag performance in pH correction of, e.g., acidic soils was evaluated by determining respective neutralizing (NV) and reactivity (RV) values. The NVs were determined by back titration with NaOH from a solution made by mixing a specific quantity of standard hydrochloric acid (HCl) and a dried sample (EN 12945). The RVs were measured according to EN 13971 by determining the carbonate content by potentiometric titration with HCl. In addition, in paper III the mineralogies of the manufactured soil amendments were investigated by the X-ray diffraction (XRD) method and in paper V scanning electron microscopy (SEM) was used in characterizing the morphology of ladle slag particles. A more detailed description, including instrumentation, of the analytical methods is presented in papers II-V.

3.3 Easily-available plant nutrients

For the evaluation of easily-available nutrient (Ca, K, Mg, Na, P, S, Cu, Mn, Zn) contents, the method by Yli-Halla and Palko (1987) was adopted in papers II-V. Calcium, potassium, magnesium, sodium, phosphorus and sulphur were extracted with 0.5 M HOAc and 0.5 M ammonium acetate (NH₄OAc, pH 4.65), as the extraction of copper, manganese and zinc was performed with NH₄OAc coupled with 0.02 M ethylenediaminetetraacetic acid disodium salt (Na₂EDTA). Nutrient concentrations were subsequently quantified by inductively coupled plasma-optical emission spectrometry (ICP-OES; Ca, K, Mg, Na and S), flame atomic absorption spectrometry (FAAS; Cu, Mn and Zn) or by spectrophotometry through the molybdenum blue method (P).

3.4 Pseudo-total element concentrations

The pseudo-total element concentrations of the soil amendments discussed in papers II-IV were determined by HCl (3 mL) and nitric acid (HNO₃, 9 mL) microwave digestion
according to the guidelines of USEPA method 3051A (Yafa and Farmer 2006). In this work the term ‘pseudo-total’ will be reserved for element concentrations recovered through HCl and HNO₃ digestions according to the guidelines of USEPA 3051A (1:3 v/v, respectively, papers II-IV) or ISO 11466 (3:1 v/v, respectively, paper V). Although the USEPA 3051A method employs ‘reversed’ aqua regia for element extraction, respective extraction performance has been found comparable to extraction by aqua regia described in ISO 11466 for assessing soil quality (Yafa and Farmer 2006). Element concentrations in the attained extracts were quantified by ICP-OES, or in the case of mercury, by cold vapour atomic absorption spectrometry (CVAAS). Further details regarding the instrumentation are presented in papers II-IV.

### 3.5 Sequential extraction of trace elements

Trace element availability was investigated by the original three-step BCR sequential extraction procedure described in detail by Ure et al. (1993) with an additional residual fraction determination by calculation (Močko and Wachawek 2004; Pardo et al. 2004; Smeda and Zyrnicki 2002; paper II) or acid digestion by the equivalent USEPA 3051A method (papers III-IV). Trace element concentrations in the attained extracts were quantified as per section 3.4.

### 3.6 Method evaluation

As opposed to papers II-IV, the objective of paper V was to evaluate the suitability of the sequential extraction approach in the analysis of an industrial solid residue, mainly due to the original intent for sediment and soil analyses, and the reported lack of selectivity and occurrence of redistribution and readsorption (Dahlin et al. 2002; Gleyzes et al. 2002; Rao et al. 2008; Sutherland 2012; Ure et al. 1993). Due to these weaknesses, X-ray based analytical methods have been deemed necessary for acquiring supportive information on remaining sample components during sequential extraction (Bacon and Davidson 2008). To address these issues, a vigorous sampling and analytical program including the XRD analyses of parallel sequential extraction residues was performed for the analysis of ladle slag incorporated in the manufactured soil amendment discussed in paper III.

Trace element availability from a combined six-week ladle slag sample was investigated by the revised four-step BCR sequential extraction procedure reported by Rauret et al. (1999). The revised procedure was chosen as it also enabled quality control through the analysis of CRM BCR-701 provided by the Institute of Reference Materials and Measurements (IRMM, Geel, Belgium). BCR-701 is a lake sediment sample from Lake Orta, Piemonte, Italy certified for extractable trace element contents in the first three steps of the revised BCR extraction procedure and indicative values for aqua regia extraction.
Detailed information on the preparation and certification of BCR-701 is provided by Pueyo et al. (2001). Strict adherence to the procedure reported by Rauret et al. (1999) was maintained to guarantee compliance with the protocol. A full description of the analytical procedure, including relevant operating conditions of the ICP-OES and CVAAS instruments used for element quantification, is presented in paper V.
4 Results and discussion

4.1 Relevant physicochemical properties and easily-available nutrient concentrations

As supported by the data presented in Table 6, the manufactured soil amendments (papers II-IV) had strongly alkaline pH values (i.e., 12.1-13.0) indicating significant buffering capacity. The respective EC values (7.8-10.7 mS cm\(^{-1}\)), which were used as an index of the total dissolved electrolyte concentrations, suggest a comparable ionic strength of the soil amendment leachates with, e.g., sandy loam or loamy soil samples investigated by Wang and Cai (2006). Hence only a minor part of the dissolved metals could be expected to occur as dissolved basic metal salts (Hackett et al. 1999). The LOI determinations were used to provide information on the organics content of the soil amendments, which were found to be surprisingly low (<0.5-6.3%, d.w.) considering the paper mill sludge additions illustrated in Table 5 (pp. 25).

However, as opposed to pulp mills, paper mill effluents generally include significant quantities of inorganic paper additives resulting in a predominantly alkaline character of the effluent treatment sludge residues with significant inorganics content (Boni et al. 2004; Kuokkanen et al. 2008). The low organics content of the soil amendments, combined with characteristic high pH values, are encouraging as they respectively support the absence of possible organic contaminants and pathogens. In addition, as discussed by Thompson et al. (2001), the possible dissolved organic contaminants extracted from wood during chemical pulping are generally retained in the recovered liquors which are subsequently incinerated, and are thus not likely to be found in paper mill effluents. Even though the LOI parameter is frequently used in characterisation studies for quantifying the content of organic matter, its usefulness has been questioned due to the possible dehydration of metal hydroxides, loss of volatile salts, or loss of mineral inorganic carbon up to a temperature of 550 °C (Brown and Dykstra 1995; Heiri et al. 2001). Hence, the TOC parameter was also used to verify the low organic carbon contents of the samples (i.e., 5.0-20 g kg\(^{-1}\), d.w.).

The RV and NV values with easily available nutrient concentrations were determined to assess the potential of the manufactured samples in soil liming. As discussed by Manskinen et al. (2011), the NV value is generally one of the most important parameters for evaluating the capacity of a material in neutralizing soil acidity and depends on the level of soluble and hydrolysable bases, such as oxides, hydroxides, carbonates and silicates. According to the NVs provided in Table 6, the liming capacities of the soil amendments are nearly comparable to those of commercial alternatives, as a ground limestone product by SMA Mineral Ltd. has a characteristic NV of 38% (Ca equiv., d.w.). The easily-available nutrient concentrations suggest that the potential application of the
soil amendments would not only be restricted to relieving possible soil acidity, but would also contribute to soil fertility by providing especially calcium and magnesium commonly deficient in acidic soils (Bolan et al. 2003).

Table 6 Relevant physicochemical properties and easily-available nutrient concentrations of the manufactured soil amendments (papers II-IV) and respective average concentrations in local organic and coarse mineral soils located in the Ostrobothnia Region of Northern Finland (Nurmesniemi et al. 2010a, 2010b)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Paper II</th>
<th>Paper III</th>
<th>Paper IV</th>
<th>Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Matrix I</td>
<td>Matrix II</td>
<td>Matrix I</td>
<td>Matrix II</td>
</tr>
<tr>
<td>pH</td>
<td>-</td>
<td>12.9</td>
<td>13.0</td>
<td>12.1</td>
<td>12.2</td>
</tr>
<tr>
<td>EC</td>
<td>mS cm⁻¹</td>
<td>8.8</td>
<td>9.8</td>
<td>7.8</td>
<td>8.8</td>
</tr>
<tr>
<td>Dry matter content</td>
<td>%</td>
<td>97.1</td>
<td>97.0</td>
<td>97.3</td>
<td>97.2</td>
</tr>
<tr>
<td>LOI</td>
<td>% (d.w.)</td>
<td>6.3</td>
<td>5.1</td>
<td>5.2</td>
<td>3.4</td>
</tr>
<tr>
<td>TOC</td>
<td>g kg⁻¹ (d.w.)</td>
<td>18</td>
<td>20</td>
<td>10</td>
<td>8.0</td>
</tr>
<tr>
<td>NV</td>
<td>% (Ca equiv., d.w.)</td>
<td>36.6</td>
<td>35.8</td>
<td>35.6</td>
<td>34.9</td>
</tr>
<tr>
<td>RV</td>
<td>% (Ca equiv., d.w.)</td>
<td>34.1</td>
<td>33.3</td>
<td>35.5</td>
<td>32.8</td>
</tr>
<tr>
<td>Ca</td>
<td>mg kg⁻¹ (d.w.)</td>
<td>180,000</td>
<td>201,000</td>
<td>154,000</td>
<td>199,000</td>
</tr>
<tr>
<td>K</td>
<td>mg kg⁻¹ (d.w.)</td>
<td>950</td>
<td>750</td>
<td>720</td>
<td>730</td>
</tr>
<tr>
<td>Mg</td>
<td>mg kg⁻¹ (d.w.)</td>
<td>10,200</td>
<td>5000</td>
<td>4400</td>
<td>4400</td>
</tr>
<tr>
<td>Na</td>
<td>mg kg⁻¹ (d.w.)</td>
<td>4900</td>
<td>4100</td>
<td>3000</td>
<td>4900</td>
</tr>
<tr>
<td>P</td>
<td>mg kg⁻¹ (d.w.)</td>
<td>8</td>
<td>2</td>
<td>21</td>
<td>12</td>
</tr>
<tr>
<td>S</td>
<td>mg kg⁻¹ (d.w.)</td>
<td>3000</td>
<td>2700</td>
<td>1700</td>
<td>4300</td>
</tr>
<tr>
<td>Cu</td>
<td>mg kg⁻¹ (d.w.)</td>
<td>20</td>
<td>22</td>
<td>7</td>
<td>4.8</td>
</tr>
<tr>
<td>Mn</td>
<td>mg kg⁻¹ (d.w.)</td>
<td>1390</td>
<td>700</td>
<td>250</td>
<td>610</td>
</tr>
<tr>
<td>Zn</td>
<td>mg kg⁻¹ (d.w.)</td>
<td>110</td>
<td>96</td>
<td>13</td>
<td>16</td>
</tr>
</tbody>
</table>

*Individual matrix components discussed in papers II-IV are described in detail in Table 5, pp. 25 n=1

It is worth noting that the manufactured soil amendments discussed in papers II-IV also attested to elevated easily-available concentrations of sodium (3000-4900 mg kg⁻¹, d.w.) and sulphur (1700-4300 mg kg⁻¹, d.w.) as illustrated in Table 6. The presence of these elements is reasonable, while considering the processes from which the incorporated
residues were derived, and should be made aware of due to possible increases in soil salinity upon potential application. Within carbon steel industry operations, sulphur is willingly removed from hot metal during desulphurization (see Fig. 4, pp. 6) generally by calcium fluoride (CaF₂) injection and is thus transferred to the respective slag fraction. Hence, the sulphur content of EAF and BOF slags are generally lower than those of, e.g., BF slags (Proctor et al. 2000). In practical metallurgy sulphur dissolution to the liquid slag mainly occurs in the sulphidic (S²⁻) rather than the sulphatic (SO₄²⁻) form dictated by the partial pressure of oxygen, the composition of the slag and the prevailing temperature (Kytö 2011).

In addition to sulphur, alkalis, such as sodium and potassium, are detrimental to BF operation due to circulation and subsequent outgrowth formation in the furnace thus potentially disrupting the flow of reducing gases (Raipala 1994). In pulp and paper mill operations sodium is introduced to the system in the wood raw material and the use of NaOH, Na₂S and Na₂SO₄ as cooking or make-up chemicals in the kraft pulping process (Heinemann 2006; Sixta et al. 2006). The use of additional fuels, such as peat, in the solid fuel boilers of the facilities also contributes to the sulphur content of fly ashes. As discussed by Narodoslawsky and Obernberger (1996), element fractionation to the respective fly and bottom ash fractions during combustion is mainly dictated by the combustion temperature possible inducing volatilization. A combustion bed temperature of ca. 850 °C (Mäkelä et al. 2011) is sufficient to enable the volatilization and subsequent deposition of, e.g., sulphur (boiling point 445 °C) in the flue gas cleaning system.

4.2 Pseudo-total element concentrations and trace element availability

Based on the pseudo-total concentration data provided in Table 7, arsenic, copper, mercury, nickel, lead and zinc concentrations in the manufactured soil amendments discussed in papers II-IV were lower than the respective Finnish statutory limit values for fertilizer products (Decree on Fertilizer Products 24/11). Only the pseudo-total concentrations of cadmium in matrices I & II (2.8 and 3.3 mg kg⁻¹, d.w., respectively), discussed in paper II, exceeded the respective lower limit value (1.5 mg kg⁻¹, d.w.) set for fertilizers used in agriculture, however, were below the limit value imposed on ash fertilizers for use in forestry (25 mg kg⁻¹, d.w.). It must be noted that, at present, no applicable limit values exist for the soil amendments discussed in this thesis as the materials were manufactured by combining residues classified as different main fertilizer types in the type designation list of the relevant Decree (24/11). This complexity has been further discussed in section 4.4 and paper IV.
Table 7 Pseudo-total element concentrations of manufactured soil amendments (papers II-IV) and 
the Finnish statutory limit values set for the use of fertilizer products (24/11). All concentrations 
expressed as mg kg\(^{-1}\) (d.w.)

<table>
<thead>
<tr>
<th>Element</th>
<th>Paper II(^a)</th>
<th>Paper III(^a)</th>
<th>Paper IV(^{a,b})</th>
<th>Limit value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Matrix I(^b)</td>
<td>Matrix II(^b)</td>
<td>Matrix I(^b)</td>
<td>Matrix II(^b)</td>
</tr>
<tr>
<td>Al</td>
<td>15,200</td>
<td>9600</td>
<td>24,300</td>
<td>6080</td>
</tr>
<tr>
<td>As</td>
<td>6</td>
<td>6</td>
<td>3.7</td>
<td>3.8</td>
</tr>
<tr>
<td>B</td>
<td>20</td>
<td>21</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>Ba</td>
<td>400</td>
<td>340</td>
<td>280</td>
<td>280</td>
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<tr>
<td>Ca</td>
<td>307,000</td>
<td>317,000</td>
<td>373,000</td>
<td>371,000</td>
</tr>
<tr>
<td>Cd</td>
<td>2.8</td>
<td>3.3</td>
<td>0.80</td>
<td>0.83</td>
</tr>
<tr>
<td>Co</td>
<td>3</td>
<td>3</td>
<td>1.0</td>
<td>2.8</td>
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<tr>
<td>Cr</td>
<td>75</td>
<td>370</td>
<td>94</td>
<td>82</td>
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<td>11,800</td>
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<tr>
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<td>1940</td>
<td>1420</td>
</tr>
<tr>
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<td>&lt;1</td>
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<td>1.4</td>
</tr>
<tr>
<td>Na</td>
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<td>5660</td>
<td>5490</td>
<td>6850</td>
</tr>
<tr>
<td>Ni</td>
<td>16</td>
<td>16</td>
<td>15</td>
<td>17</td>
</tr>
<tr>
<td>P</td>
<td>4350</td>
<td>5150</td>
<td>5250</td>
<td>5520</td>
</tr>
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<td>Pb</td>
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<td>&lt;4</td>
<td>&lt;4</td>
<td>&lt;4</td>
</tr>
<tr>
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<td>&lt;4</td>
<td>&lt;4</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Sn</td>
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<td>Ti</td>
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<td>820</td>
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<td>V</td>
<td>140</td>
<td>2740</td>
<td>240</td>
<td>220</td>
</tr>
<tr>
<td>Zn</td>
<td>300</td>
<td>320</td>
<td>53.5</td>
<td>41.0</td>
</tr>
</tbody>
</table>

\(^{a}\)Microwave digestion according to USEPA method 3051A
\(^{b}\)Individual matrix components discussed in papers II-IV are described in detail in Table 5, pp. 25
\(^{c}\)Maximum concentration in inorganic fertilizers and liming materials by HNO\(_3\) extraction and in other fertilizer products by aqua regia microwave digestion (24/11)
\(^{d}\)Maximum concentration in ash fertilizers used in forestry (24/11)
n=1

In addition, as discussed in paper II, the pseudo-total concentration of chromium in 
matrix II (370 mg kg\(^{-1}\), d.w.) also exceeded both limit values (300 mg kg\(^{-1}\), d.w.) most 
likely due to the inclusion of BOF steel slag. The presence and speciation of chromium is 
especially relevant as it is the only trace element which in the relevant Decree (24/11) is 
regulated differently based on the respective presence of trivalent Cr(III) and hexavalent
Cr(VI). The former is generally considered an essential micronutrient, as the latter is a known carcinogen which occurs mainly due to anthropogenic activities (Chrysochoou et al. 2012; Fandeur et al. 2009; Rock et al. 2001; Vitale et al. 1997). As discussed by Rai et al. (1989), the environmental chemistry of chromium is mainly controlled by redox transformations, precipitation/dissolution, and adsorption/desorption reactions. Under changing redox conditions, chromium valence is dictated by the presence of oxidants capable of accepting electrons, and reductants capable of donating electrons. The measure of the oxidising/reducing conditions in, e.g., soils is the redox potential, $E_h$ (Sposito 2008; Ure and Davidson 2002), which relates the standard electrode potential, $E_0$, of a redox half reaction (Equation 1) by the Gibbs free energy change of that redox reaction, $\Delta G^0_{\text{red}}$ (Equation 2), and the relative activities of the oxidant and reductant through the Nernst equation (Equation 3):

$$
E^0 = \frac{\Delta G^0_{\text{red}}}{nF} = \frac{\Sigma \Delta G^0_{\text{(reductants)}} - \Sigma \Delta G^0_{\text{(oxidants)}}}{nF}
$$

$$
E_h = E^0 - \frac{RT}{nF} \ln \left( \frac{[\text{reductants}]}{[\text{oxidants}]} \right)
$$

where $n$ denotes the number of electrons transferred in the redox half reaction, $\Delta G^0$ the specific free energy of formation, $F$ the Faraday constant, $R$ the universal gas constant and $T$ the absolute temperature. Hence, high $E_h$ values depict the ability of a system to accept or transfer electrons, and thus favour oxidation, as low $E_h$ values favour respective reduction.

However, in addition to $E_h$ describing electron activity, the mobility and availability of chromium as the trivalent Cr(III) cation or the hexavalent chromate anions ($\text{CrO}_4^{2-}$ and $\text{Cr}_2\text{O}_7^{2-}$) in aqueous solutions is significantly affected by the proton activity, pH. In general, pH controls directly the precipitation and dissolution phenomena of trace element-bearing phases and indirectly affects, e.g., the amount of positively or negatively charged sites available for adsorption of charged species (Van Herreweghe et al. 2002). As discussed by several authors (Baes and Mesmer 1976; Kimbrough et al. 1999; Kumpiene et al. 2008; Ražić and Đogo 2010; Richard and Bourg 1991; Shtiza et al. 2009), the trivalent cation is more easily hydrolysed and will tend to precipitate as the trihydroxide $\text{Cr(OH)}_3$ under circumneutral to alkaline conditions, but can be expected to remain soluble under acidic conditions. However, the chromate and dichromate anions are extremely soluble under the entire pH range affected only by the potential hydrolysis of the mononuclear species $\text{CrO}_4^{2-}$ to $\text{HCrO}_4^-$ under acidic conditions.
To attain information on the valence state(s) of chromium in Matrix II, discussed in paper II, the following methods were applied to determine (i) soluble Cr(VI) and (ii) pseudo-total Cr(VI) as follows:

(i) Soluble Cr(VI) concentration was determined from a cumulative L/S 10 extract of a two-stage batch test according to EN 12457-3. Soluble Cr(VI) was quantified by ion chromatography (IC) using post-column reaction (PCR) followed by ultraviolet/visible spectroscopy (UV/VIS) and the respective total soluble chromium by ICP-OES as per section 3.4.

(ii) Pseudo-total Cr(VI) concentration was determined according to USEPA method 3060A, where Cr(VI) is extracted with Na₂CO₃ and NaOH solution (pH 12) under heating (90-95 °C) for 1 h. Quantification was performed by IC UV/VIS-PCR as described above.

As a result, soluble chromium occurred only in the hexavalent Cr(VI) form, as the concentrations of soluble Cr(VI) and total soluble chromium were 0.41 mg kg⁻¹ (d.w.) and 0.40 mg kg⁻¹ (d.w.), respectively. However, the pseudo-total concentration of Cr(VI) determined according to USEPA method 3060A remained below the limit of detection (i.e., <3 mg kg⁻¹, d.w.) suggesting that the pseudo-total concentration of chromium consisted entirely of Cr(III). The use of Na₂CO₃ and NaOH has been found effective in extracting both soluble Cr(VI) and insoluble Cr(VI), as the former compounds remain soluble under these conditions (extractant pH 12) and the latter are transposed to soluble sodium chromate (Na₂CrO₄), but concerns remained regarding the potential oxidation of Cr(III) (Katz 1991). As discussed by Kimborough et al. (1999), the interconversion of the valence states of chromium is relevant also during the sampling, extraction and quantification steps required for solid sample analysis. In addition, the analysis of Cr(VI) is generally more complex than that of pseudo-total or total chromium (Kimborough et al. 1999) and, coupled with the uncertainties of quantification at trace concentrations, serves to explain the slightly divergent concentrations of soluble Cr(VI) and total soluble chromium (0.41 and 0.40 mg kg⁻¹, d.w., respectively) quantified from the EN 12457-3 extracts as described above. In the Decree on Fertilizer Products (24/11), the statutory limit value for soluble Cr(VI) in BOF steel slag used as such for soil liming is 2 mg kg⁻¹ (d.w.), and if applicable, would thus not limit the use of the soil amendment in liming based on chromium speciation.

Furthermore, as the pseudo-total concentration of chromium in matrix II (paper II) exceeded the respective limit value of 300 mg kg⁻¹ (d.w.) stipulated for fertilizer products other than BOF steel slag, respective potential mobility and the mobility of cadmium in both matrices I and II (paper II) can be evaluated based on the results of performed sequential extractions. As illustrated in Figs. 12-13, a majority of the pseudo-total concentrations of cadmium in matrices I and II (i.e., 68 and 70%, respectively) were recovered in the oxidisable fraction during step 3 of the extraction procedure as 81% of
the respective pseudo-total concentration of chromium in matrix II was attained in the residual fraction during step 4. As discussed by Filgueiras et al. (2002), the objective of using hydrogen peroxide (H₂O₂) in a heated medium is a compromise between the complete dissolution of organic matter and minimum alteration of sample silicates during step 3 of the sequential extraction procedure. In addition, the subsequently added NH₄OAc has the ability to complex a wide range of cations (Rauret et al. 1998) and thus maintain solubility for element quantification. As discussed in section 3.5, the residual fraction was determined by calculation following the work of Močko and Waclawek (2004), Pardo et al. (2004) and Smeda and Zynicki (2002).

The respective oxidisable and residual fractions are not considered very labile as the oxidation of, e.g., stable high molecular weight humic substances, inorganic sulphides, or the dissolution of primary or secondary minerals is generally slow under natural conditions (Močko and Waclawek 2004; Nemati et al. 2011). However, as discussed in papers II-IV, the trace elements vanadium and barium occurred in notable pseudo-total concentrations in the manufactured soil amendments and were relatively more labile than cadmium and chromium. The recovered pseudo-total concentrations of barium in the potential soil amendments discussed in papers III-IV were in the range of 200-280 mg kg⁻¹ (d.w., Table 7) of which 17-31% were attained during step 1 of the sequential extraction procedure using 0.11 M HOAc (see, e.g., Fig. 14). Furthermore, the recovered pseudo-total concentrations of vanadium discussed in papers II-IV were in the range of 140-2740 mg kg⁻¹ (d.w., Table 7) of which 12-46% were attained during step 2 by 0.1 M hydroxylamine hydrochloride (NH₂OH·HCl) adjusted to pH 2 with HNO₃.
Fig. 12 Arsenic, cadmium, chromium and copper mobility (mg kg\(^{-1}\), d.w.) according to the three-stage sequential BCR extraction procedure (modified from paper II)

Fig. 13 Nickel, lead, vanadium and zinc mobility (mg kg\(^{-1}\), d.w.) according to the three-stage sequential BCR extraction procedure (modified from paper II)
Fig. 14 Individual fraction recoveries (% of the respective pseudo-total concentration) of trace elements As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, V and Zn in fractions 1-4 during the modified BCR approach with respective pseudo-total concentrations (in parentheses, d.w.) (modified from paper IV).
A Finnish background value of 400-900 mg kg\(^{-1}\) was reported for soil barium (Sorvari 2003) with common plant range and moderate toxicity values of 2-13 and 500 mg kg\(^{-1}\), respectively (Noqueira et al. 2010). In pulp and paper mill fly ashes barium was found in the range of 1100-1108 mg kg\(^{-1}\) whereas a value of 509 mg kg\(^{-1}\) was reported for lime waste (Nurmesniemi 2008; Pöykiö et al. 2005; Pöykiö et al. 2006). For steel mill BF and BOF slags respective mean values of 273 and 57 mg kg\(^{-1}\) were reported by Proctor et al. (2000). In general, recovery during the first step of the sequential extraction procedure has been considered approximately equivalent to the sum of water-soluble, exchangeable and carbonate-bound fractions and thus represents the potentially most mobile and available phase of an element (Janoš et al. 2010; Li et al. 2010).

In the case of vanadium, respective Finnish background and average soil values of 30-180 and 10-220 mg kg\(^{-1}\) have been reported with a dominant occurrence in the organic fraction of the soil analysed (Sorvari 2003; Poledniok and Buhl 2003). In addition, plant concentrations lower than 2 mg kg\(^{-1}\) were stated to positively influence chlorophyll synthesis, as higher concentrations could cause chlorosis and limit growth (Poledniok and Buhl 2003). Reported concentrations for pulp and paper mill residues, such as fly ashes, lime waste and paper mill sludge, were in the range of <1-155 mg kg\(^{-1}\) (Nurmesniemi 2008; Kuokkanen et al. 2008; Pöykiö et al. 2005; Pöykiö et al. 2006a; Sorvari 2003) suggesting that comparably higher concentrations in the soil amendments discussed in papers II-IV were most likely due to steel mill slag inclusions. Mean values of 54 and 992 mg kg\(^{-1}\) were reported by Proctor et al. (2000) for BF and BOF slags, respectively.

The use of NH\(_2\)OH·HCl, a salt of the reducing base hydroxylamine (NH\(_2\)OH) and HCl, in an acidic medium during step 2 of the sequential extraction procedure is aimed at recovering easily or moderately reducible phases made available through changes in prevailing redox conditions and thus simulates anoxic conditions likely to occur in a natural medium (Álvarez-Valero et al. 2009; Filgueiras et al. 2002; Rao et al. 2008). As discussed by Gleyzes et al. (2002), efficient extraction of reducible sample components requires the use of both a reducing agent and a ligand able to retain released ions (see, e.g., Equations 4-5 according to Linge 2008) in a soluble form. It must be noted that the concentration of NH\(_2\)OH·HCl was revised from 0.1 to 0.5 M for the revised BCR procedure (Rauret et al. 1999) with a fixed volume of dilute HNO\(_3\) due to uncertainties related to the selectivity of extraction and respective rise in pH (Davidson et al. 2004; Sahuquillo et al. 1999). However, the original reagent concentration and acid addition (0.1 M NH\(_2\)OH·HCl adjusted to pH 2 with HNO\(_3\)) were used in the experiments discussed in papers II-IV.

\[
\text{MnO}_2(s) + 4H^+(aq) + 2e^- \leftrightarrow \text{Mn}^{2+}(aq) + 2H_2O, \ E_h = 0.450\ V \quad (4)
\]

\[
\text{FeOOH}(s) + 3H^+(aq) + 2e^- \leftrightarrow \text{Fe}^{2+}(aq) + 2H_2O, \ E_h = 0.100\ V \quad (5)
\]
Neither of the discussed potentially soluble trace elements barium or vanadium are currently regulated in Finland regarding the use of fertilizer products in agriculture or forestry (Decree 24/11). The complex chemistry of vanadium is especially relevant as, similar to chromium, the element can exist in a large number of valence states, which in the case of the tetravalent V(IV) and pentavalent V(V) affect respective toxicity and charge (e.g., cationic VO$^{2+}$ and anionic VO$_4^{3-}$, respectively) in aqueous solutions (Baes and Mesmer 1979; Cornelis et al. 2008; Shafer et al. 2012). Interestingly, the use of 0.1 M Na$_2$CO$_3$, included in USEPA method 3060A for pseudo-total Cr(VI) determination, in extracting V(V) from soil and plant samples collected from a potentially contaminated site in the vicinity of a vanadium mine has been reported (Panichev et al. 2006).

4.3 Method performance

As illustrated in Fig. 15 and discussed in paper V, the X-ray diffractograms attained from the analysis of parallel sequential extraction residues of an industrial ladle slag sample suggested non-selectivity of the adopted approach towards sample periclase (MgO) and potential redistribution of magnesium to the merwinite [Ca$_3$Mg(SiO$_4$)$_2$] and spinel group structures (MgAl$_2$O$_4$) found from the residues of extraction steps 3 and 4, respectively. As discussed by Young et al. (2005), redistribution during sequential extraction from soil samples could arise from increases in element ion activity in solution, changes in pH or the exposure of new adsorption surfaces causing readsorption on remaining sample adsorbents. In addition, the disappearance of larnite (Ca$_2$SiO$_4$) peaks during step 3 (see step 1-3 res., Fig. 15) indicates potential dissolution, which argues against the general insolubility of silicates prior to the residual fraction determination during sequential extraction of, e.g., sediment and soil samples (Filgueiras et al. 2002; Gleyzes et al. 2002).

Although the detection limit of an X-ray diffractometer is generally in the range of 1-2% (w/w) making the use of XRD in the evaluation of sample dissolution during sequential extraction merely supportive, the attained data confirm the purely operational nature of sequential extraction procedures also highlighted by previous authors (Cappuyns et al. 2007; Larner et al. 2008; Ryan et al. 2008; Sulkowski and Hirner 2006). In addition, the fact that sequential extraction procedures were originally designed for sediment and soil analysis (Tessier et al. 1979; Ure et al. 1993), but are increasingly used in characterising potential trace element solubility from industrial solid residues (Álvarez-Valero et al. 2009; Anju and Banerjee 2010; Filgueiras et al. 2002; Marguí et al. 2004), further emphasizes the need for method evaluation on a case-by-case basis due to inherent differences in the chemical and mineralogical compositions of analysable samples. Alternative approaches for the use of XRD in support of sequential extraction are limited as maintaining comparability between different laboratories requires strict adherence to the procedures (Bacon and Davidson 2008; Pueyo et al. 2001). Thus, more research is
**Fig. 15** X-ray diffractograms of the combined ladle slag sample (base sample) and the respective step residues (step 1-4 res.) from the revised four-stage BCR extraction procedure (*paper V*)
needed regarding the use of intermediate, non-destructive analytical techniques in tandem with sequential extraction procedures which would, however, increase the frequently criticized tediousness of the procedures (Jamali et al. 2009; Nemati et al. 2011).

In addition to the uncertainties related to potential readsorption, redistribution and lack of selectivity, the analysis of a certified reference material is frequently omitted from BCR extraction studies as an essential part of quality control (Quevauviller 1998; Sutherland 2010). Hence the analysed step values (n=9) of the certified reference material BCR-701 were compared with certified and indicative values for cadmium, chromium, copper, nickel, lead and zinc reported by Pueyo et al. (2001) as illustrated in Table 8. As a result, the analysed values of CRM BCR-701 were generally within the reported uncertainty limits, with only four exceptions, i.e., zinc recovery during step 1, copper recovery during step 2, chromium recovery during step 4 and the four step sum of chromium.

Similar difficulties regarding zinc recovery during step 1 and copper recovery during step 2 with the certified precision have been reported by other authors (Cappuyns et al. 2007; Marguí et al. 2004; Nemati et al. 2011). According to Sutherland (2010), who examined the data quality of published BCR-701 results, reported values have been most problematic for zinc during step 1 being significantly lower than the certified value and exhibiting the greatest bias. In the case of copper, the greatest amount of extreme outliers were found while 25% of values reported for step 2 were at or above the certified value (Sutherland 2010). Furthermore, a plausible explanation for the high deviation of step 4 and the four step sum values of chromium can perhaps be found from the microwave-assisted digestion used during step 4 of the BCR procedure (paper V). However, the use of microwaves during sample digestion is a major advantage in terms of the duration and sample size required for analysis compared with, e.g., the ISO 11466 procedure (Yafa and Farmer 2006) and did not lead to notable deviations in case of the other certified elements. Finally, as illustrated in Table 8, the standard deviations of attained results were generally lower than the certified or indicative inter-laboratory values hence indicating overall good quality of the analytical work.

\[ \text{Bias} = \left( \frac{\text{Measured value} - \text{Certified value}}{\text{Certified value}} \right) \times 100\% \]

\[ \text{2 The term 'outlier' is used to describe observations which are significantly different from the majority of other observations. For details, see Sutherland (2010), pp. 12.} \]
Table 8 Reported (Pueyo et al. 2001) and analysed trace element concentrations (mg kg\(^{-1}\), d.w.) in the CRM BCR-701 according to the revised four-stage BCR extraction procedure and direct aqua regia extraction from the base sample (Rauret et al. 1999, paper V)

<table>
<thead>
<tr>
<th>Element</th>
<th>Step 1</th>
<th>Step 2</th>
<th>Step 3</th>
<th>AR extraction step 3 residue</th>
<th>4 step sum</th>
<th>Direct AR extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reported(^a)</td>
<td>Analysed</td>
<td>Reported(^a)</td>
<td>Analysed</td>
<td>Reported(^a)</td>
<td>Analysed</td>
</tr>
<tr>
<td>Cd</td>
<td>7.34 ± 0.35</td>
<td>7.13 ± 0.04</td>
<td>3.77 ± 0.28</td>
<td>3.74 ± 0.06</td>
<td>0.27 ± 0.06</td>
<td>0.26 ± 0.02</td>
</tr>
<tr>
<td>Cr</td>
<td>2.26 ± 0.16</td>
<td>2.32 ± 0.02</td>
<td>45.7 ± 2.0</td>
<td>47.1 ± 1.0</td>
<td>143 ± 7</td>
<td>143 ± 9</td>
</tr>
<tr>
<td>Cu</td>
<td>49.3 ± 1.7</td>
<td>50.6 ± 0.67</td>
<td>124 ± 3</td>
<td>131 ± 2</td>
<td>55.2 ± 3.7</td>
<td>53.6 ± 3.1</td>
</tr>
<tr>
<td>Ni</td>
<td>15.4 ± 0.9</td>
<td>15.1 ± 0.7</td>
<td>26.6 ± 1.3</td>
<td>27.1 ± 0.7</td>
<td>15.3 ± 0.9</td>
<td>15.8 ± 0.8</td>
</tr>
<tr>
<td>Pb</td>
<td>3.18 ± 0.21</td>
<td>3.04 ± 0.14</td>
<td>126 ± 3</td>
<td>125 ± 5</td>
<td>9.28 ± 1.92</td>
<td>7.70 ± 0.40</td>
</tr>
<tr>
<td>Zn</td>
<td>205 ± 6</td>
<td>196 ± 6</td>
<td>114 ± 5</td>
<td>118 ± 6</td>
<td>45.7 ± 3.4</td>
<td>44.6 ± 2.1</td>
</tr>
</tbody>
</table>

AR = aqua regia
\(^{a}\)Certified values (Pueyo et al. 2001)
\(^{b}\)Indicative values (Pueyo et al. 2001)

n=9
4.4 Legislative perspectives

The general starting point of waste legislation and policy in EU member states is the waste hierarchy, which describes a general priority order of what constitutes the best overall environmental option in waste management. As discussed in paper IV, waste disposal is considered as the last alternative waste management option after energy recovery, reutilisation and recycling of materials, and waste prevention. The EU Waste Framework Directive (WFD, 2008/98/EC) forms the basis for the management of waste and aims at moving the EU closer to a ‘recycling society’ seeking to avoid waste generation and to use waste as a resource (Introduction to the WFD, scenes 1 and 28).

The interpretation of the concept of waste in the WFD (art. 3) defines the scope of waste legislation and waste management obligations. The utilisation of waste-based materials is strongly regulated compared to materials reaching a non-waste status. In general, materials which are defined as waste can be recycled and reused under the waste regime, but the waste status often leads to higher administrative burdens followed by economic impacts when compared to products (EC 2009). The waste stigma of materials may also influence the users’ decisions to use a secondary material instead of primary materials due to prejudice against respective quality (EC 2009).

In the WFD, the general definition of waste is supplemented by the concept of by-product (art. 5) and end of waste (EoW) criteria (art. 6). Prior to the renewal of the directive in 2008 these concepts were merely based on case law of the European Court of Justice interpreting the definition of waste in numerous decisions, which still remain relevant (Eloneva et al. 2010b). The EoW criteria have been formulated in order to clarify when waste ceases to be waste and can be dealt with as recovered material freely traded as such in the open market. According to EC (2009), this is expected to facilitate and promote recycling, ensure a high level of environmental protection, reduce the consumption of natural resources and the quantity of waste sent to disposal.

According to the general EoW criteria defined in article 6(1) of the WFD, the requirement for certain specified waste to cease to be waste is that it has undergone a recovery operation, including recycling, provided that:

(a) the substance or object is commonly used for specific purposes;
(b) a market of demand exists for a substance or object;
(c) the substance or object fulfills the technical requirements for the specific purpose and meets the existing legislation and standards applicable to products, and;
(d) the use of the substance or object will not lead to overall adverse environmental or human health impacts.

The starting point in reaching EoW status is that waste has undergone a recovery operation. Assuming that none of the industrial residues from which the soil amendments
could be produced would be defined as recycled raw materials according to existing legislation, that is “reprocessed into products, materials or substances whether for the original or other purposes” [WFD art. 3(17)], before entering the possible production process of soil amendment materials, the requirement “undergone a recovery operation” could, in this case, be fulfilled if the manufacturing process of the soil amendments as a whole would be regarded as a recovery operation.\(^4\)

The soil amendments described in papers II-IV could possibly fulfill also the first two conditions set in the EoW criteria, that is (a) “the substance or object is commonly used for specific purposes” and (b) “a market or demand exists for such a substance or object” [WFD art. 6(1)]. These conditions are meant to ensure that the material or substance is more likely to be put in a useful purpose and less likely to be discarded, and prevent the definition of EoW criteria for material for which demand and markets are not yet developed (EC 2009). On a general level it can be assumed that the global demand for fertilizers and liming materials that fulfill ecological and health standards continues to be strong in the future and, in order to avoid harmful impacts of fertilization, there is a continuous need for product development in the field.

The product-based legislative standards as referred to in point (c) of the EoW criteria have a central role in considering whether a substance or object may be considered as a product instead of waste. A substance or object can only cease to be waste if it is fit for lawful use (EC 2009). When waste ceases to be waste, the requirements set in, e.g., REACH [Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals] may become applicable, unless covered by an exemption. In the case of soil amendments, the substance must fulfil the requirements of both the applicable EU legislation, such as Regulation [(EC) 2003/2003] relating to fertilizers, and national fertilizer/soil amendment legislation in force in countries where the substance would be used. Since none of EU level fertilizer/soil amendment legislation would apply as such to a combination of residues constituting the soil amendments discussed in this thesis, the analysis must focus on national legislation and standards applicable to soil amendment products in force in Finland where the amendments would most likely be used.

The EoW criteria of the WFD are implemented in Finland by the new Waste Act (646/2011), which was approved in March 2011 and took effect in May 2012. The main intention is to demonstrate that the potential use of soil amendments discussed in, e.g., papers III-IV “will not lead to overall adverse environmental or human health impacts” as referred to in point (d) of the EoW criteria. This condition means that the use of the

\(^4\) Analysis concerning the legal prerequisites under which the mixing of wastes may be possible was considered beyond the scope of paper IV [for further details see, e.g., WFD art. 10.2 and Section 15 of the new Finnish Waste Act (646/2011)].
substance or object does not merit the application of the waste legislation (EC 2009). Hence the quality of the soil amendments has been assessed primarily from the point of view of the limit values for fertilizers in use in Finland (see section 4.2, and especially Table 7, pp. 32) described in Annex IV of the Decree on Fertilizer Products (24/11) by the Finnish Ministry of Agriculture and Forestry.

In Finland soil amendments are regulated mainly by the Fertilizer Product Act (539/2006). The general requirements for fertilizers are described in Section 5 of the Act according to which a fertilizer, e.g., may not contain such an amount of harmful substances, products, or organisms that the fertilizer used in accordance with its instructions may cause harm to human or animal health or safety, or plant health or the environment. In addition, the aforementioned Decree (24/11) establishes a type designation list for fertilizers that forms the basis for the quality requirements set in the Decree. In general, the Decree recognizes six different fertilizer types: inorganic fertilizers, organic fertilizers, liming materials, soil enrichment materials, micro-organism products and breeding grounds. Comparing the type designation list to the potential soil amendment discussed in, e.g., paper IV demonstrates the complexity of applying existing legislation to innovative material solutions. The amendment discussed in paper IV is a mixture of desulphurization slag and:

(i) an inorganic ash fertilizer (fly ash);
(ii) a liming substance (lime waste), and;
(iii) a soil enrichment substance (paper mill sludge).

As discussed in section 4.2 (and illustrated in Table 7, pp. 32), Annex IV of the Decree (24/11) stipulates pseudo-total concentration limit values (mg kg$^{-1}$, d.w.) for trace elements (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) depending on whether the fertilizer product is used for agricultural or forest applications. In addition, for, e.g., inorganic by-product fertilizers the Decree stipulates a minimum concentration of 2.0% for the sum of nitrogen, phosphorus and potassium, and 8.0% for the sum of calcium, magnesium, sodium and sulphur. In the case of inorganic ash residues used in forest fertilization the respective minimum values are 2.0% (K + P) and 6.0% (Ca). However, these minimum values are implemented for by-products and ash residues utilised as such for fertilization and, therefore, could not be applied for the soil amendments discussed in this thesis.

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5 It has been stated that a comparison between the environmental impact of using the substance or object under the waste legislation and its use under non-waste product legislation should be performed to assess the overall impact of the EoW criteria (EC 2009).
5 Conclusions

Innovative approaches are needed to tackle the emerging waste disposal problem confronted by the forest and carbon steel industries in Finland and abroad. The increasing difficulties related to current linear resource use and disposal models should be perceived as incentives to develop the operations of large manufacturing systems to more cyclical ones possibly enabling savings in valuable materials and energy resources. Symbiotic cooperation of two formerly separate industrial sectors could enable the utilisation of waste-labelled residues in manufacturing novel residue-derived materials technically and environmentally suitable for replacing virgin commercial alternatives.

The experimental manufacture of residue-derived materials described in this thesis showed promise as potential amendments for agricultural or forest soils. By the incorporation of both forest and steel industry residues, such as fly ashes, lime wastes, green liquor dregs, sludges and slags, the soil amendments showed liming capacities (34.9-38.3%, Ca equiv., d.w.) comparable to relevant commercial alternatives with additional easily-soluble calcium and magnesium contents. Additional nutrient contents suggest that the potential use of the amendments would not only be restricted to relieving, e.g., potential soil acidity but could also contribute to soil fertility.

The environmental suitability of the attained materials was investigated by comparing the results of single extractions (HCl + HNO₃ in 1:3 v/v, respectively) according to the guidelines of USEPA method 3051A to relevant statutory Finnish limit values for fertilizer products. Based on the acquired data, only the first experimental samples showed increased concentrations of pseudo-total cadmium (2.8-3.3 mg kg⁻¹, d.w.) and chromium (370 mg kg⁻¹, d.w.), of which the latter was specified as the trivalent Cr(III). Subsequently, in the following amendment samples the respective pseudo-total concentrations of these trace elements were decreased substantially (i.e., Cd: 0.71-0.83 mg kg⁻¹, d.w.; Cr: 67-94 mg kg⁻¹, d.w.).

In addition to single extractions, the use of the BCR sequential extraction procedure indicated that the dominant cadmium and chromium contents were respectively made available only through aggressive oxidation by the use of H₂O₂ + NH₄OAc or dissolution by HCl + HNO₃ digestion, and that the development of such conditions is generally slow under natural environments. However, the pseudo-total concentrations of barium (200-280 mg kg⁻¹, d.w.) and vanadium (140-2740 mg kg⁻¹, d.w.), of which 17-31% and 12-46% were respectively recovered through desorption/dissolution by the use of HOAc and moderate reduction by NH₂OH·HCl, suggest the need for further research supported by the current situation in which these trace elements are not included in relevant Finnish regulation regarding agricultural of forest fertilization.
The overall analytical performance during sequential extraction was found to be good through the analysis of the certified reference material BCR-701 with certified or indicative values for trace elements cadmium, chromium, copper, nickel, lead and zinc. In addition, a vigorous sampling and analytical programme was performed to investigate the suitability of sequential extraction in the analysis of an industrial residue by identifying the mineralogical compositions of parallel extraction residues, which only suggested non-selectivity towards sample MgO coupled with potential redistribution of magnesium and the premature dissolution of sample silicates. Based on the observations the suitability of sequential extraction for industrial residue analysis should be assessed on a case-by-case basis due to the inherent differences in the characteristics of industrial solid samples.

Finally, the incorporated legislative perspective illustrated the complexity of applying existing legislation to innovative inter-industry material solutions. However, the discussed soil amendments would likely fulfill some of the essential elements highlighted in the EoW criteria of the WFD regarding the circumstances under which losing the waste status of individual residue streams might come at issue. In general, reusing and recycling industrial residues decreases the utilisation of virgin raw materials and most likely the amount of generated waste in need of final disposal thus also supporting the implementation of the general priority order of waste management set in the EU waste hierarchy (WFD art. 4).

### 5.1 Significance of this work

The presented work describes novel and unreported practical efforts to develop novel solutions for industrial solid residue utilisation through potential industrial symbiosis in Finland. The technical and environmental characteristics of the manufactured samples support the potential of a simple manufacturing process in attaining suitable materials for possibly amending soil properties coupled with increased materials and energy efficiency through the potential replacement of commercial virgin alternatives.

Furthermore, the described analytical accomplishments promote the prevalent perception that the need for investigating the environmental impacts of trace elements goes beyond mere pseudo-total concentration determinations, and should thus take into consideration respective potential solubility under natural conditions. Through such efforts, attention and future work can be realistically aligned to investigate and respectively decrease the impacts of trace elements with potentially the most detrimental effects under natural conditions even though not currently covered by relevant national or international legislation.
5.2 Limitations and future research recommendations

Even though the presented work reports significant findings regarding the possibility to manufacture residue-derived soil amendments and the respective potential impacts of such materials under natural conditions, further research is needed to simplify and optimise the raw materials of such process. In addition, in regards to trace element solubility a real advantage of sequential extraction procedures would lie in investigating solubility before and after processing thus enabling an assessment of the effectiveness of the process in stabilizing potential contaminants. Furthermore, the effects of acid neutralizing capacity of industrial residues on trace element recoveries during sequential extraction should be elucidated as it is likely to influence respective hydrolysis and subsequent precipitation leading to underestimations in the recoveries of cationic species.

Future research in the realm of industrial symbiosis should include more practical efforts for investigating potential future applications for, e.g., solid residue utilisation. In this context the reluctance to take risks is likely to manifest itself in the prevailing state, where the inherently more sustainable cyclical resource use models can remain an unrealistic objective.
References


Errata for appended publications

**Paper II:** In section 3.2.2, the quantification of the total soluble chromium concentration was performed with *ICP-OES* described in section 2.4, and not with *IC UV/VIS-PCR* used for soluble Cr(VI) quantification.

**Paper III:** The sentence “However, it must be noted that an X-ray *spectrometer* is…”, in the first paragraph of section 3.1, should be “However, it must be noted that an X-ray *diffractometer* is…”.

**Paper V:** In section 3.3, the quantification of soluble Cr(VI) in the SFS-EN 12457-3 extracts was performed by *(1,5-)*diphenylcarbazide addition followed by absorbance quantification on the 540 nm wavelength with a PerkinElmer (PerkinElmer, Norwalk, USA) Lambda 25 spectrophotometer, and not by ICP-MS *(X-series, Thermo Electron Corp., Winsford, U.K.)*.
This doctoral dissertation describes novel and unreported practical efforts to develop new solutions for industrial solid residue utilisation through potential industrial symbiosis within the Bothnian Arc Region in Northern Finland. Potential symbiotic cooperation of formerly separate industrial sectors could alleviate recent regulatory and economic pressures by enabling the manufacture of residue-derived materials suitable for replacing commercial virgin alternatives. Through such efforts, the current linear resource use and disposal models could possibly be shaped to more cyclical ones thus enabling savings in valuable primary materials and energy resources.