



Total and extractable non-process elements in green liquor dregs from the chemical recovery circuit of a semi-chemical pulp mill

Kati Manskinen^a, Hannu Nurmesniemi^b, Risto Pöykio^{c,*}

^a *Stora Enso Oyj, Heinola Fluting Mill, FI-18101 Heinola, Finland*

^b *Stora Enso Oyj, Veitsiluoto Mill, FI-94800 Kemi, Finland*

^c *City of Kemi, Valtakatu 26, FI-94100 Kemi, Finland*

ARTICLE INFO

Article history:

Received 12 September 2010

Received in revised form

20 November 2010

Accepted 22 November 2010

Keywords:

BCR

Chemical recovery

Extraction

NPE

Semi-chemical pulping

Waste

ABSTRACT

The total heavy metal concentrations in green liquor dregs investigated in this study were clearly lower than the current Finnish statutory limit values for fertilizer used in forestry. This is an advantage if applying for an environmental permit to utilize the green liquor dregs. They contained only carbonate minerals, were strongly alkaline (pH 11.7), and had a neutralizing value of 34.2% (Ca equivalents; d.w.), according to which 1.1 tonnes of green liquor dregs would be required to replace 1 tonne of a commercial ground limestone product produced by SMA Mineral Ltd. These properties support the utilization and re-use of this residue, for instance as a soil conditioning agent. Before such use, it would be necessary to assess the mobility of non-process elements in the dregs. Three-stage sequential extraction procedure development by the European Community Bureau of Reference (BCR) was therefore carried out, in which elements in the residue were fractionated between acid soluble (CH_3COOH ; BCR 1), reducible ($\text{NH}_2\text{OH-HCl}$; BCR 2) and oxidizable ($\text{H}_2\text{O}_2 + \text{CH}_3\text{COONH}_4$; BCR 3) fractions. Except for Co and Ni, the highest extractable concentrations of non-process elements (Al, As, Ba, Be, Cd, Cr, Cu, Fe, Mn, Mo, Pb, Sb, Se, V and Zn) were in the oxidizable fraction, although certain non-process elements were also extractable and quantitatively detectable in fractions BCR 1 and BCR 2. The results are discussed from various perspectives and in relation to observations in the literature concerning the release of heavy metals and sulphur from the sample matrix under different extraction conditions.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Wood is converted into pulp by mechanical, chemical or semi-chemical pulping processes [1]. The aim of these processes is to dissolve lignin and to liberate the wood fibres from the wood matrix. Semi-chemical pulping is generally defined as a two-stage pulping process, involving chemical treatment to remove part of the lignin or fibre-bonding substances followed by mechanical refining to complete the separation of the fibres. Semi-chemical pulp can be produced by modifying nearly any presently used chemical pulping procedure: sulphate, sulphite, soda or cold caustic [1–3]. As pulp mills move towards minimum impact manufacturing, one of the most difficult challenges in the recycling and reuse of both water and the various aqueous streams is the development of strategies for effectively dealing with the build-up and recovery of cationic and anionic non-process elements (NPEs). NPEs or more correctly inorganic process contaminants are elements such as potassium, manganese, barium, iron, aluminium, copper,

nickel, chromium and zinc that have no active part in the process and are detrimental to pulping, bleaching or recovery. The term “non-process elements” usually refers to all of the chemicals in the system other than sodium, sulphur, carbon, hydrogen, and oxygen [1–3].

Non-process elements are introduced into the process in fibre raw materials (wood chips, sawdust), the make-up chemicals and process waters, and from the corrosion of process equipment. It is important to control the input of NPEs, since they tend to accumulate in the different cycles, leading to operating problems as well as dead load [4]. However, since different elements are active in different parts of the pulp process, an element may be considered an NPE in one location but not in another. Cooking chemicals used in pulping are recovered in the chemical recovery unit, which is used to recover valuable inorganic chemicals used in the cooking liquor. The accumulation of NPEs in pulping processes may result in scaling problems and filtration failures. Therefore, non-process elements have to be taken out of the process, for instance by precipitation in the form of green liquor dregs [5].

Green liquor dregs are usually dumped in landfills. In Finland, and elsewhere in the European Union (EU), the properties of solid wastes and industrial residues, especially when they are utilized

* Corresponding author. Tel.: +358 16 259 673; fax: +358 16 259 481.
E-mail address: risto.poykio@kemi.fi (R. Pöykio).

or taken to a landfill, have to be investigated. The general principles applied in landfill approval are that the composition and extractability of the waste have to be known. The total element concentrations represent a source term only for the unrealistic environmental scenario in which the entire mineral structure of the solid material is dissolved. Measurement of the total concentration of metals provides relatively misleading information for assessing the possible bioavailability and mobility of metals. In order to estimate the bioavailability of metals and their potential toxicity, it is necessary not only to determine the total concentrations but also the different forms or processes binding the heavy metals to the solid phase of the sample [6].

Extraction is a procedure that puts solids and liquid in contact with each other under defined conditions. Extraction tests are widely used as tools to estimate the release potential of constituents from waste materials over a range of possible waste management activities, including recycling or reuse, for assessing the efficacy of waste treatment processes, and after disposal. Sequential extraction tests are designed to treat the material with different solutions, resulting in the allocation of constituents into separate fractions. Such an approach provides information on which chemical conditions are needed to obtain different extraction efficiencies. In the sequential extraction procedure, chemical extractants of various types are applied to the sample, with each successive treatment being more aggressive than the previous one [7]. The goal of this method is to divide the total extractable concentration of metals into separate fractions in order to assess the form in which the metals occur in the waste material. Extraction studies are carried out in the assessment of worst-case environmental scenarios, in which the components of the sample become soluble and mobile.

2. Experimental

2.1. Description of the cooking process, chemical recovery circuit and sampling of green liquor dregs

The integrated pulp and board mill investigated in this study produces high-quality semi-chemical fluting, which is the corrugated medium between the liners of corrugated board. In the semi-chemical process, the wood chips are treated partly by cooking chemicals under pressure and partly mechanically to process them into fibres, hence the name semi-chemical. This process is required to maintain high hemicellulose and lignin contents in order to retain the stiffness of the fibres in the semi-chemical fluting pulp [1–3]. A simplified schematic diagram of the semi-chemical pulping process, the chemical recovery circuit and the green liquor dregs outlet at the pulp mill investigated in this study is presented in Fig. 1.

In this study, the wood chips were cooked with a mixture of sodium sulphite (Na_2SO_3), sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3). Due to the chemical losses of S and Na compounds in the pulping process, they are added to the process in the form of elemental sulphur and sodium hydroxide. After cooking, the cooked chips are mechanically defibred to form raw pulp. Dissolved organic materials and spent inorganic chemicals are washed out from the raw pulp which yields dirty washing water, i.e. weak black liquor. The pulp is used in the board mill and the weak black liquor is concentrated by evaporation to yield strong black liquor. The terms “weak black liquor” and “strong black liquor” relate to the very dark colour imparted by the dissolved lignin-derived material and the concentrations of dissolved organic compounds in the liquors. The strong black liquor is then fed into a soda recovery boiler for energy generation and to yield an inorganic molten form, known as smelt. Due to the controlled oxygen-deficient conditions in the bottom of the soda recovery boiler ($T \sim 1000\text{--}1200^\circ\text{C}$), the sodium

sulphite (Na_2SO_3) and other oxidised sulphur compounds of the strong black liquor are converted to sodium sulphide (Na_2S) [1–3]. In addition, sodium carbonate (Na_2CO_3) is formed by the reaction of sodium compounds (primarily sodium oxide and sodium sulphide) with CO_2 , a product of the combustion of wood-derived material in the black liquor (i.e. biomass).

The molten material is discharged from the bottom of the soda recovery boiler and dissolved in water to form green liquor. According to Morris et al. [8], the sodium hydrosulphide gives the solution its green colour; hence the name “green liquor”. The insoluble impurities and non-reactive metals (i.e. non-process elements) left from the black liquor, termed green liquor dregs, are precipitated from the green liquor by polymers. The separated green liquor dregs are further dried under pressure in a separate pressing unit. The green liquor is recovered and regenerated into new cooking chemicals in a separate regeneration unit and used for pulping more wood.

The sampling of green liquor dregs was carried out over a period of one week, with individual daily samples being combined to give one composite sample with a weight of 10 kg (wet weight). The sampling period represented the normal process operating conditions for the pulp mill. During the sampling period, 83% of the wood material used for pulping was roundwood and 17% consisted of wood chips. Approximately 73% of the wood material was birch (*Betula verrucosa* and *Betula pubescens*), 23% was aspen (*Populus tremula*) and 4% was spruce (*Picea abies*). Except for the roundwood aspen which originated from Russia, the wood material used for cooking mainly originated from Finland. The aspen roundwood was not debarked like the other roundwood tree species. After sampling, the samples were stored in polyethylene bottles in a refrigerator ($+4^\circ\text{C}$). A coning and quartering method [9] was repeatedly applied to reduce the sample of grits to a size suitable for conducting laboratory analyses.

2.2. Determination of the mineral composition, physical and chemical properties of the dregs

For the determination of the mineralogical composition of the green liquor dregs, X-ray diffractograms of powdered samples were obtained with a Siemens D 5000 diffractometer (Siemens AG, Karlsruhe, Germany) using $\text{CuK}\alpha$ radiation. The scan was run from 12° to 55° (2θ -scale), with increments of 0.02° and a counting time of 1.0 second per step. Operating conditions were 40 kV and 40 mA. Peak identification was carried out with the DIFFRACplus BASIC Evaluation Package PDFMaint 12 (Bruker axs, Germany) and ICDD PDF-2 Release 2006 software package (PA, USA).

Determination of pH and the electrical conductivity (EC) in the dregs was carried out according to European standard SFS-EN 13037 at a solid-to-liquid (i.e. ultrapure water) ratio of 1:5. Determination of the dry matter content of the dregs was carried out according to European standard SFS-EN 12880, in which a sample is dried overnight to a constant mass in an oven at 105°C . The loss-on-ignition (LOI) value was determined according to European standard SFS-EN 12879 at the temperature of 550°C , and the total organic carbon (TOC) content was determined according to European standard SFS-EN 13137. The neutralizing (liming effect) value (NV) was determined according to European standard SFS-EN 12945. In this procedure, the dried sample is dissolved in a specific quantity of a standard hydrochloric acid solution and the neutralizing value of a sample is determined by back titration with sodium hydroxide. The reactivity value (RV) was determined according to European standard SFS-EN 1397. In this procedure, the carbonates of a sample are determined by potentiometric titration with hydrochloric acid. A comprehensive review of the determination of pH, EC, dry matter content, LOI, TOC, neutralizing and reactivity values is given in our previous paper [10].

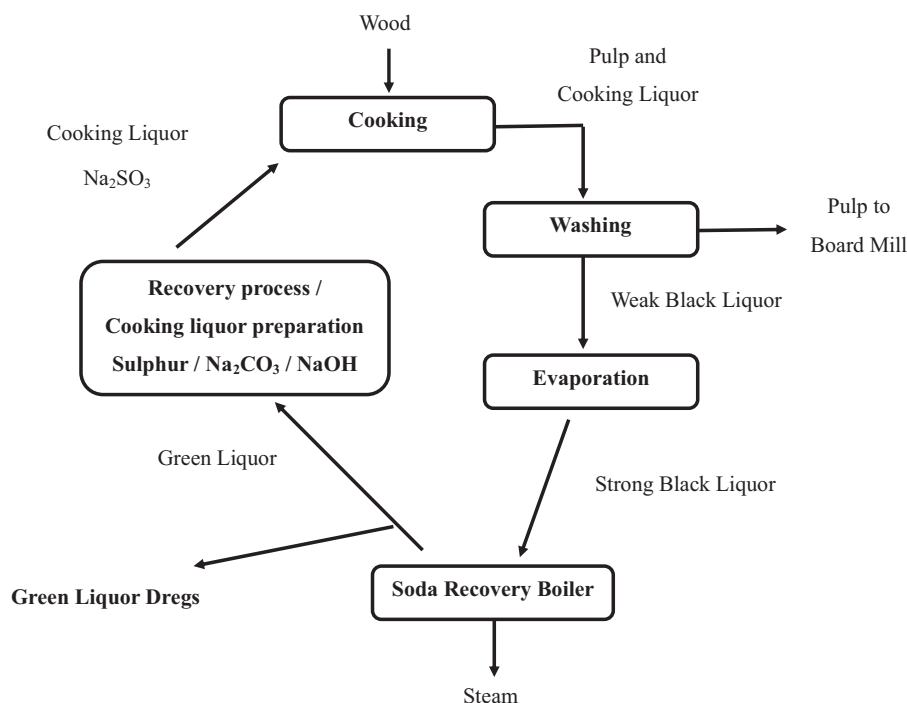


Fig. 1. Schematic diagram of the semi-chemical pulping process, the chemical recovery circuit and the green liquor dregs outlet at the pulp mill investigated in this study.

2.3. Determination of the easily soluble plant nutrient concentrations

The determination of the easily soluble plant nutrient concentrations (P, Ca, Na, K, Mg, S, Mn, Cu and Zn) in the green liquor dregs was carried out according to the procedure of Yli-Halla and Palko [11]. In this procedure, the easily soluble forms of P, Ca, Na, K, Mg and S are extracted with 0.5 M acidic ammonium acetate (pH 4.65), and in the extraction of Mn, Cu and Zn, the acidic (pH 4.65) ammonium acetate extract contains 0.02 M ethylenediaminetetra-acetic acid disodium salt (Na_2EDTA). In both extraction procedures, one volume part of a dry sample was shaken with ten parts of the extraction solution for 1 h. Before analysis, the extract was separated from the solid residue by filtration through 12.5 mm diameter Schleicher & Schull 589 blue ribbon filter paper (Schleicher & Schull, Dassel, Germany).

The concentrations of Ca, Na, K, Mg and S were determined with a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES), and the concentrations of Mn, Cu and Zn by flame atomic absorption spectrometer (FAAS, Perkin Elmer Analyst 700, Norwalk, USA). The concentration of P in the extract was determined spectrophotometrically by the molybdenum blue method using an automatic Foss-Tecator FIAStar 500 Flow Injection Analyser (Högnes, Sweden). Before the nutrient determination of the dregs, the sample was dried overnight to constant mass at 105 °C in a drying oven (Termaks) according to European standard SFS-EN 12880. A comprehensive review of the standards, analytical methods and instrumentation is given in our previous paper [10].

2.4. Determination of total non-process element concentrations in the dregs

For the determination of total non-process element concentrations in the green liquor dregs, the dried sample was digested with a mixture of HCl (3 mL) and HNO_3 (9 mL) in a CEM Mars 5 micro-processor controlled microwave oven with CEM HP 500 Teflon

vessels (CEM Corp., Matthews, USA) using USEPA method 3051A [12]. The cooled solution was transferred to a 100 mL volumetric flask and the solution was diluted to volume with ultrapure water. All reagents and acids were suprapure or pro analysis quality. Except for Hg and fluorine (F), the total non-process element concentrations in the green liquor dregs were determined with a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES). The concentration of Hg in the dregs was determined with a Perkin Elmer Analyst 700 cold-vapour atomic absorption spectrometer (Norwalk, USA) equipped with a Perkin Elmer FIAS 400 and AS 90 plus autosampler. The concentration of fluorine (F) in the cooled solution was carried out according to European standard SFS-EN ISO 10304-1 [13] using a Dionex DX500 ion chromatography system (Dionex Corp., USA).

2.5. Sequential extraction partitioning of non-process elements in the dregs

For the partitioning of non-process elements in the green liquor dregs between the exchangeable (CH_3COOH), easily reduced ($\text{NH}_2\text{OH-HCl}$ in nitric acid medium) and oxidizable ($\text{H}_2\text{O}_2 + \text{CH}_3\text{COONH}_4$) fractions, we used the three-stage sequential extraction procedure illustrated in Fig. 2. This extraction procedure was developed by the European Community Bureau of Reference (BCR) in an attempt to harmonize the different extraction schemes. This extraction procedure is a widely applied for heavy metal fractionation in various environmental matrices, e.g. ash, soil, sediment and sludge [6].

Extraction was carried out by shaking 5 g of the green liquor dregs in a polypropylene bottle. In order to minimize possible chemical and/or microbiological changes in the material, the extraction was carried out using an undried sample instead of a dried sample since, according to Kosson et al. [7], it is preferable to avoid sample drying before extraction. After each extraction step the extracts were separated from the solid residue by filtration through a 0.45 μm membrane filter (47 mm diameter; Schleicher

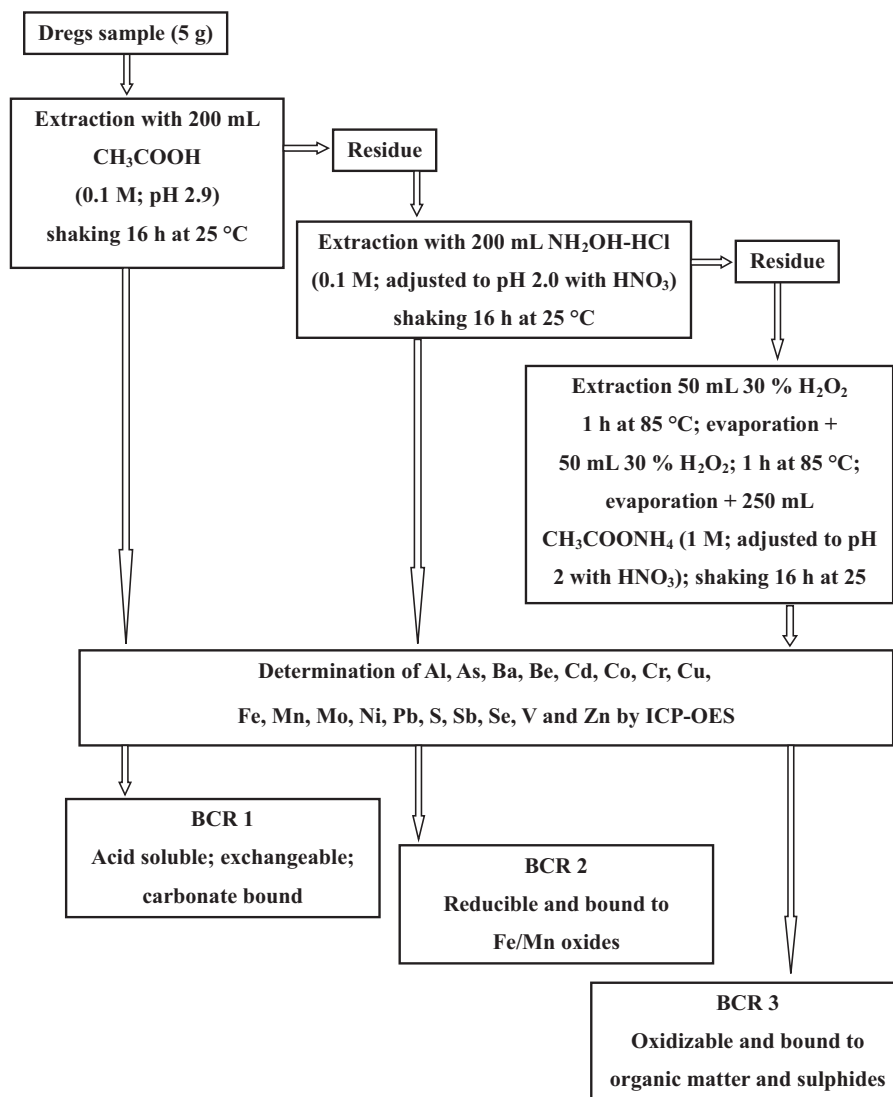


Fig. 2. Schematic diagram of the sequential extraction procedure for non-process elements partitioning between acid soluble (BCR 1), reducible (BCR 2) and oxidizable (BCR 3) fractions [43; modified].

& Schuell, Dassel, Germany). In order to avoid losses between the extraction stages, the filters and adhering dregs particles from the previous extraction stage were also included in the next stage. After the addition of 200 μ L of 65% HNO_3 to the supernatant phase, it was stored in a refrigerator (+4 $^\circ\text{C}$) until the element determinations. The element concentrations in the extracts (i.e. extraction stages 1–3) were determined with a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES).

3. Results and discussion

3.1. Mineral composition, physical and chemical properties of the green liquor dregs

The XRD spectra in Fig. 3 shows that the green liquor dregs contained only pirssonite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$), which is a carbonate mineral. Therefore, our XRD data is consistent with the findings of Taylor and McGuffie [14], who reported the existence of pirssonite in the dregs, although they also detected silicate and sulphate minerals. However, our XRD data is not in agreement with the study of Martins et al. [15], who reported the existence of calcite in the dregs. One reason for the different mineral compositions of our

dregs compared to those of Taylor and McGuffie [14] and Martins et al. [15] may be differences in the processes carried out at the mills, since according to Toikka [16], the physical and chemical properties of green liquor dregs vary significantly depending on the process conditions in which the dregs are formed. Furthermore, an XRD spectrometer is unable to identify the amorphous (glass) phase (i.e. non-crystallised matter), and its detection limit is normally 1–2% (w/w). This is probably why crystalline compounds containing the non-process elements in Table 2 were not identified by XRD, despite the fact that the concentrations of these elements could be quantitatively measured by ICP-OES.

The most important physical and chemical properties of the dregs are summarised in Table 1, which presents the means of triplicate samples, expressed on a dry weight (d.w.) basis. However, the standard deviations are not given for pH, because the triplicate samples had exactly the same values. The pH of the dregs was strongly alkaline (pH 11.7), which is consistent with the findings of other researchers [16–20], who have reported pH values between 10.0 and 12.8 for green liquor dregs. The alkaline pH value and the existence of calcium carbonate, which is an active ingredient in agricultural lime, mean that the green liquor dregs have a liming effect and are therefore a potential soil conditioning or amendment agent. According to the electrical conductivity value

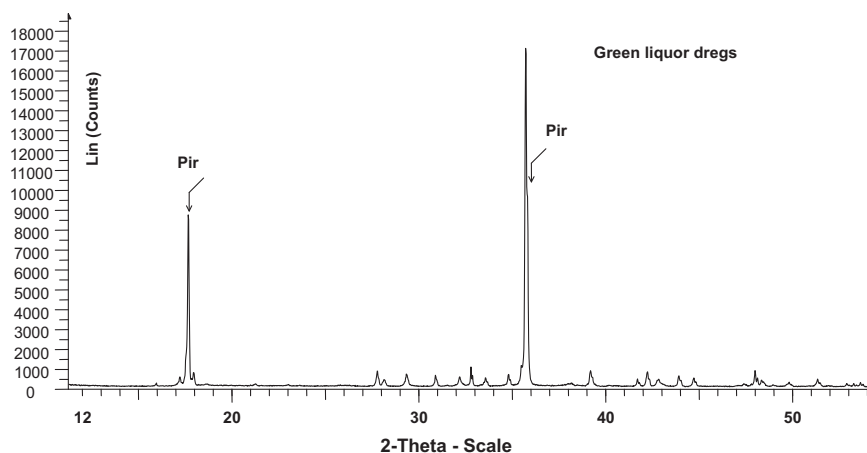


Fig. 3. XRD pattern for the green liquor dregs.

(23.7 mS/cm), which is an index of the total dissolved electrolyte concentrations, the leaching solution of the dregs has a relatively high ionic strength, indicating that part of the dissolved metals occur in the green liquor dregs as dissolved basic metal salts.

The neutralizing value (NV) is one of the most important indices in evaluating the liming effect value of a material. The capacity of a liming agent to neutralize soil acidity depends on the levels of soluble and hydrolysable bases such as oxides, hydroxides, carbonates and silicates. Cations such as calcium, magnesium, and potassium are the inactive counter-ions. According to the results in Table 1, the NV of 34.2% for green liquor dregs expressed as Ca equivalents (d.w.) indicates that 1.1 tonnes of green liquor dregs would be required to replace 1 tonne of a commercial ground limestone product produced by SMA Mineral Ltd., the neutralizing value of which is 38% (Ca equivalents; d.w.). The reactivity value (RV) was determined in order to assess the speed and effectiveness of the neutralizing potential of green liquor dregs as a liming material. The RV/NV ratio indicates that the so-called “fast acting” capacity is ca. 95.6% for green liquor dregs. Thus, they are a potential soil conditioning agent and pH buffer for acidic soils [21]. Due to the strong alkaline nature and high liming effect value, the green liquor dregs are also a potential neutralizing agent at the sulphite pulp mill investigated in this study. In this context, it is worth noting that according to our mill-scale studies, the green liquor dregs can be utilized as a neutralizing agent for acidic wastewaters at sulphate pulp mills [10]. However, to the best of our knowledge,

green liquor dregs have not previously been utilized as a neutralizing agent for acidic wastewaters at sulphite mills, such as the mill investigated in this study. Therefore, on the basis of the pH and NV values of the green liquor dregs, this is worth clarifying in a mill-scale study.

The total organic carbon (TOC) value of 14.5 g/kg (d.w.) observed by us is in good agreement with the values reported in the literature [16,21], and indicates that the green liquor dregs contain organic material. The loss-on-ignition (LOI) value of 14.5% (d.w.) indicates that the green liquor dregs contain volatile fractions. Although LOI is a common and widely used method to estimate the organic matter content of waste materials, according to Heiri et al. [22], reactions other than the burning of organic matter, e.g. dehydration of clay minerals or metal oxides, the loss of volatile compounds, or loss of inorganic carbon (i.e. CO₂) in minerals, can take place during the determination of LOI at 550 °C.

The concentrations of easily soluble plant nutrients (P, Ca, Na, K, Mn, Mg, S, Cu and Zn) in the grits, as well as in the local coarse mineral soils located in the Ostrobothnia region in the province of Oulu are also provided in Table 1. Except for the easily soluble Ca concentration in the green liquor dregs, the other easily soluble plant nutrient concentrations in the dregs were ca. 1.8 (P) and 13 430 (Na) times higher than their average concentration in the local coarse mineral soil. According to Österås et al. [23], these results indicate that the green liquor dregs are therefore a potential agent for use in counteracting nutrient depletion in forest soils. The find-

Table 1

The physical and chemical properties of green liquor dregs, the easily soluble plant nutrient concentrations (i.e. NH₄Ac or NH₄Ac + Na₂EDTA extractable forms) in the dregs and their average concentrations in local coarse mineral soil located in the Ostrobothnia region in the province of Oulu, as well as the literature values for parameters and nutrients in dregs and the enrichment values (*R*) of nutrients in the dregs of this study.

Parameter/nutrient	Unit	Green liquor dregs	Literature value	Coarse mineral soil	<i>R</i> ^a
pH (1:5)		11.7	10.0–12.8		
Loss on ignition (LOI; 550 °C)	% (d.w.)	14.5 ± 0.1	8.3–27.4		
Total organic carbon (TOC)	g/kg (d.w.)	14.5 ± 0.5	3.5–32		
Dry matter content (105 °C)	%	80.8 ± 0.4	50.8–96.8		
Electrical conductivity (EC; 1:2.5)	mS/cm	23.7 ± 0.3	26.2		
Neutralizing value (NV)	% (Ca; d.w.)	34.2 ± 0.1			
Reactivity value (RV)	% (Ca; d.w.)	32.7 ± 0.1			
P (NH ₄ Ac)	mg/kg (d.w.)	20.7 ± 0.6	100	11.7	1.8
Ca (NH ₄ Ac)	mg/kg (d.w.)	900 ± 70		960	0.9
Na (NH ₄ Ac)	g/kg (d.w.)	134.3 ± 0.6		0.01	13,430
K (NH ₄ Ac)	mg/kg (d.w.)	1200 ± 10	800	77	15.6
Mg (NH ₄ Ac)	mg/kg (d.w.)	5900 ± 200		135	43.7
S (NH ₄ Ac)	mg/kg (d.w.)	5790 ± 40		23	251.7
Mn (NH ₄ Ac + Na ₂ EDTA)	mg/kg (d.w.)	1358 ± 35		28	48.5
Cu (NH ₄ Ac + Na ₂ EDTA)	mg/kg (d.w.)	26.2 ± 0.8		3.3	7.9
Zn (NH ₄ Ac + Na ₂ EDTA)	mg/kg (d.w.)	740 ± 14		3.8	194.7

^a *R* is the nutrient concentration in dregs/nutrient concentration in soil.

ing of elevated sodium and sulphur concentrations in the dregs is reasonable as Na_2CO_3 , NaOH and Na_2SO_3 are employed as cooking chemicals in the sulphite pulping process investigated in this study and elemental sulphur and NaOH are added to the process in order to compensate for the losses of S and Na in the cycle (see Fig. 1). Sodium and other non-process elements also enter the system in a moderate amount from the wood raw materials, but they can additionally originate from corrosion in the recovery process [4,24].

3.2. Total non-process element concentrations in the green liquor dregs

Table 2 presents the total non-process element and fluorine (F) concentrations in the dregs as well as their literature values [8,16,19,20,25,26]. Except for Ba, with a clearly higher concentration, and for Cr and Ni, with clearly lower concentrations in the dregs than those in the literature, the non-process element concentrations in the green liquor dregs agree well with the literature values. The concentration of fluorine (F) in the green liquor dregs was lower than the detection limit (20 mg/kg; d.w.). In a pulp mill system, the levels of non-process elements in process streams depend on factors such as the intake of elements, process configuration and equipment operating conditions, as well as on the types of raw materials and the degree of closure of the system. Thus, the concentrations of non-process elements vary from one mill to another [5,16,27]. In this context it is worth noting that all “non-process” elements are not necessarily heavy metals. Although the term “heavy metal” has never been defined by the International Union of Pure and Applied Chemistry (IUPAC), density is in most cases taken to be the defining factor [28]. According to Järup [29] and to many other researchers [28], heavy metals are commonly defined as those with a density of greater than 5 g/cm^3 , and therefore aluminium, barium, beryllium, selenium, silicon and fluorine in Table 2 may not be termed “heavy metals”, because their density is lower.

The low values for total non-process element concentrations in the green liquor dregs become apparent if we compare them to Finnish statutory limit values for maximum allowable heavy metal concentrations in fertilizers used in forestry. These limit values, which came into force in March 2007, are currently only set for As, Cd, Cr, Cu, Ni, Pb, Zn and Hg, and are applied if wood-, peat- and coal-derived ashes are used as a forest fertilizer. However, if green liquor dregs are to be used in landscaping or in the hydraulic barrier layers of landfills, or in the earthwork of industrial areas, an environmental permit is needed. Although the limit values for forest fertilizers are at present only applied for wood-, peat- and coal-derived ashes, we wanted to compare the non-process element concentrations in the green liquor dregs to these limit values. According to the results in Table 2, the total heavy metal concentrations in green liquor dregs are clearly lower than the current Finnish statutory limit values for fertilizer used in forestry, which is an advantage if applying for an environmental permit for the utilization and re-use of the green liquor dregs investigated in this study.

Due to restrictions in the current Finnish environmental legislation on the utilization of industrial residues, which currently only enable certain wastes to be utilized without an environmental permit, new strategies for the management of wastes from the cellulose industry should be developed, and this prompted us to make this comparison. As environmental and legislative authorities assimilate more information about the beneficial properties of industrial residues, this may promote the possibilities to reuse and recycle industrial residues and by-products. Finnish environmental legislation does not currently recognize the concept of a “by-product” and thus, if industrial residues other than coal, peat

Table 2
Total and extractable concentrations of non-process elements in green liquor dregs, the literature values for the total concentrations of non-process elements in dregs, the current Finnish limit values for the maximum allowable heavy metal concentrations in fertilizers, e.g. ash, used in forestry, as well as extractable non-process element concentrations in extraction stages BCR 1–BCR 3, and the sum of extraction stages BCR 1–BCR 3 (i.e. Σ 1–3).

Non-process element	Total concentration of non-process element in green liquor dregs (mg/kg; d.w.)	Literature value for the total concentration of non-process element in green liquor dregs (mg/kg; d.w.)	Limit value for forest fertilizers (mg/kg; d.w.)	Extractable concentration of non-process elements in green liquor dregs (mg/kg; d.w.)			
				BCR 1	BCR 2	BCR 3	Σ (1–3)
Al	820	1500–15 000		6.7	<1.0	349	<356.7
As	<3	2.8–12.2	30	<0.6	<0.6	<0.8	<2.0
Ba	910	120–676		5.3	300	490	795.3
Be	<1.0	n.d.		<0.2	<0.2	<0.3	<0.7
Cd	3.8	4.0–24	17.5	<0.1	0.1	3.4	<3.6
Co	8.0	9.6–22.3		<0.1	3.0	2.8	<5.9
Cr	14.0	34–280	300	<0.4	<0.4	8.2	<9.0
Cu	61.0	51–290	700	<0.4	<0.4	53.5	<54.3
Fe	600	400–14,000		<1.0	5.4	9.3	<15.7
Mn	4150	4000–43,000		18.7	1880	2130	4028.7
Mo	<1.0	1.1–2.4		<0.2	<0.2	<0.3	<0.7
Ni	14.0	16–110	150	<0.2	6.0	4.7	<10.9
Pb	13.0	8–45	150	<0.6	<0.6	6.0	7.2
Sb	<4.0	n.d.		<0.6	<0.6	<0.8	<2.0
Se	<4.0	0.2–7.8		<0.8	<0.8	<1.0	<2.6
V	<50.0	1.6–2.3		<0.4	<0.4	<0.5	<1.3
Zn	1320	190–5400	4500	1.1	90.1	877	968.2
Hg	<0.04	0.07–0.2	1.0	n.d.	n.d.	n.d.	n.d.
Si	270			n.d.	n.d.	n.d.	n.d.
F	<20.0			n.d.	n.d.	n.d.	n.d.

n.d., not determined.

and biomass-derived ash or crushed concrete materials are re-used, an environmental permit is required [30,31]. According to Finnish environmental legislation, all industrial by-products and residues are actually classified as waste, and anyone who intends to reprocess, reuse or recycle on a large scale normally has to apply for an environmental permit.

3.3. Partitioning of non-process elements in the green liquor dregs

If inorganic materials and by-products such as green liquor dregs are disposed of in landfills or utilized as an earth construction agent, low heavy metal concentrations and tight binding of the elements to the matrix are favourable [32]. When sequential extraction is applied in the fractionation of heavy metals in environmental samples, the ability of different extraction agents to release metal ions depends on their association with specific fractions in the sample. Extractants such as electrolytes, weak acids and chelating agents release metals from the coordination sites, while strong acids and redox agents are capable of releasing additional quantities of metals as a result of the decomposition of the solid matrix [33]. Thus, consecutive extraction techniques allow us to obtain information about the mobility and thus the bioassessability of major and trace elements under different environmental conditions, such as acidic or alkaline, oxidizing or reducing conditions or the action of chelating agents [6].

The distribution of non-process elements in the green liquor dregs after a three-stage BCR extraction (leaching) procedure between acid soluble (CH_3COOH), reducible ($\text{NH}_2\text{OH-HCl}$ in nitric acid medium) and oxidizable ($\text{H}_2\text{O}_2 + \text{CH}_3\text{COONH}_4$) fractions is presented in Table 2.

The acid soluble fraction (i.e. BCR 1 fraction), extractable with acetic acid (CH_3COOH), gives an indication of the amount of metals bound on the surface of the particles, as well as those that are released as acid-soluble salts such as carbonates [34]. This fraction is potentially bioavailable and corresponds to the form of metals that is most available for plant uptake, and can be released by merely changing the ionic strength of the medium [6]. The use of acetic acid as leachant emulates the organic acids produced from decomposing waste in anaerobic environments such as landfill sites, since in the acetogenesis phase during the anaerobic degradation of organic matter, carboxylic acids (e.g. acetic acid), volatile fatty acids and ethanol are produced and transformed into acetate, carbon dioxide and hydrogen by acidogenic bacteria. Thus, the elevated concentrations of elements in this fraction may be due to the complexing ability of the mono-dentated organic ligand of acetate [35]. The use of acetic acid as leachant has been questioned because it does not occur in nature. However, according to Svensson et al. [36], acetic acid is a realistic choice to simulate a plausible worst-case scenario for waste material co-disposed with municipal solid waste. Landfills may cause contaminant release into the environment as the pH decreases. Therefore, this fraction also indicates the proportion of elements that are capable of being released from the matrix into the environment if conditions become acidic [37]. If we disregard the non-process elements whose concentrations were lower than the detection limits, according to the results in Table 2, acetic acid (CH_3COOH) was only capable of releasing aluminium (6.7 mg/kg; d.w.), barium (5.3 mg/kg; d.w.) magnesium (18.7 mg/kg; d.w.) and zinc (1.1 mg/kg; d.w.) from the green liquor dregs. Compared to the total concentrations, the partitioning of these elements in this fraction was low and was as follows: Al (0.8%), Ba (0.6%), Mg (0.5%) and Zn (<0.1%).

The reducible fraction (i.e. BCR 2 fraction), extractable with a reducing agent of hydroxylamine hydrochloride ($\text{NH}_2\text{OH-HCl}$) in nitric acid medium, simulates anoxic conditions that are likely to occur in a natural medium [6]. According to Sabbas et al. [38], under disposal conditions, redox reactions can occur as a result

of microbiologically mediated processes due to the presence of organic material or abiotic transformations, leading to the formation of reducing gases (H_2). However, in a well-constructed landfill with a top layer, no oxygen or surface water will be available below the topmost layer. Thus, the heavy metal leaching might be slightly affected by an influx of surface water and of oxygen. Leachates consisting of various types of dissolved organic matter and inorganic salts are the only carriers of heavy metal migration in a landfill [37]. The use of $\text{NH}_2\text{OH-HCl}$ in a nitric acid medium as an extractant for this fraction influences the complexation of metals with chloride [6]. This fraction represents the content of metals bound to iron and manganese oxides that would be released if the substrate was subjected to reductive conditions [39]. The metals in this fraction can be mobilised by increasing the reducing or oxidising conditions in the environment, which means that they are potentially bioavailable [6]. If we disregard the non-process elements whose concentrations were lower than the detection limits, according to the results in Table 2, hydroxylamine hydrochloride ($\text{NH}_2\text{OH-HCl}$) was capable of releasing a negligible amount of Cd (0.1 mg/kg; d.w.), whereas the extractability of Co (3.0 mg/kg; d.w.), Fe (5.4 mg/kg; d.w.) and Ni (6.0 mg/kg; d.w.) was moderate and the extractability of Zn (90.3 mg/kg; d.w.), Ba (300 mg/kg; d.w.) and Mn (1880 mg/kg; d.w.) was relatively high. Compared to the total concentrations, the partitioning of these elements in this fraction was as follows: Cd (2.6%), Co (37.5%), Fe (0.9%), Ni (42.8%), Zn (6.8%), Ba (32.9%) and Mn (45.3%).

The oxidizable fraction (i.e. BCR 3 fraction), in which the combination of $\text{H}_2\text{O}_2/\text{CH}_3\text{COONH}_4$ is used, corresponds to metals that are organically bound or occur as oxidizable minerals, e.g. sulphides [6]. As metals bound to this fraction can be released under oxidising conditions, an oxidation process is usually applied to extract metals associated with the above-mentioned phase. Hydrogen peroxide (H_2O_2), which is used as an oxidising reagent in this fraction, is a strong oxidant. In general, hydrogen peroxide applied to a heated medium (i.e. 85 °C) is the reagent preferred for dissolving organic matter as a compromise between the complete degradation of organic matter and the minimum alteration of silicates. Heating promotes the oxidation process [6]. Furthermore, hydrogen peroxide also oxidises sulphides to sulphates [40]. Besides the extraction of cations by ammonium ions, partial removal of some elements may occur due to complexation with acetate anions [41]. According to the TOC value (14.5 g/kg; d.w.), this residue contains organic material (Table 1). Therefore, the release of metals and sulphur bound to the organic matter of this residue is possible, if conditions become oxidative and the organic matter in the green liquor dregs degrades. However, according to Smichowski et al. [42], the organic fraction released in the oxidizable step is not considered to be very mobile or available. If we disregard the non-process elements whose concentrations were lower than the detection limits, except for Co (2.8 mg/kg; d.w.) and Ni (4.7 mg/kg; d.w.), the extractable concentrations of other non-process elements in this fraction were higher than in the previous fractions. The proportions of Co (2.8 mg/kg; d.w.), Cd (3.4 mg/kg; d.w.), Ni (4.7 mg/kg; d.w.), Pb (6.0 mg/kg; d.w.), Cr (8.2 mg/kg; d.w.) and Fe (9.3 mg/kg; d.w.) were moderate in this fraction, whereas the proportion of Cu (53.5 mg/kg; d.w.) was relatively high, and the proportions of Al (349 mg/kg; d.w.), Ba (490 mg/kg; d.w.), Zn (877 mg/kg; d.w.) and Mn (2130 mg/kg; d.w.) were high.

4. Conclusions

The results of this study showed that green liquor dregs originating from the chemical recovery circuit of a semi-chemical pulp mill were enriched in Na (134.3 g/kg; d.w.), K (1200 mg/kg; d.w.), Mn (1358 mg/kg; d.w.), Mg (5900 mg/kg; d.w.) and Zn (740 mg/kg;

d.w.). The green liquor dregs were strongly alkaline (pH 11.7), and contained only pirssonite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2\cdot 2\text{H}_2\text{O}$), which is a carbonate mineral. These results, together with the fact that the dregs have a neutralizing value of 34.2% (Ca equivalents; d.w.), according to which 1.1 tonnes of green liquor dregs would be required to replace 1 tonne of a commercial ground limestone product produced by SMA Mineral Ltd., the neutralizing value of which is 38% (Ca equivalents; d.w.), support the utilization and re-use of this residue e.g. as a soil ameliorant agent and pH buffer.

If green liquor dregs are to be utilized, an environmental permit is needed. However, the low concentrations of total non-process elements (i.e. heavy metals), which were clearly lower than the current Finnish statutory limit values for fertilizers used in forestry, are an advantage if an environmental permit is applied for. Furthermore, the results from the sequential extraction procedure showed that except for Co and Ni, the highest extractable concentrations of other non-process elements (Al, As, Ba, Be, Cd, Cr, Cu, Fe, Mn, Mo, Pb, Sb, Se, V and Zn) were in the oxidizable fraction (BCR 3 fraction), although certain non-process elements were also extractable and quantitatively detectable in fractions BCR 1 (CH_3COOH), and BCR 2 ($\text{NH}_2\text{OH}-\text{HCl}$). These results also support the utilization of green liquor dregs instead of final disposal at landfills.

Acknowledgements

The authors wish to thank the technical staff of Suomen Ympäristöpalvelu Oy who kindly conducted all the chemical analyses. Thanks also to Mr. Olli-Taikina Aho at the Institute of Electronic Optics, University of Oulu, for the XRD data, and Dr. Roy Siddall for correcting the English language.

References

- [1] C.J. Biermann, Handbook of Pulping and Papermaking, second ed., Academic Press, New York, 1996.
- [2] H. Sixta, A. Potthast, A.W. Krottschek, Chemical pulping processes, in: H. Sixta (Ed.), Handbook of Pulp, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006, pp. 109–510.
- [3] S. Heinemann, Chemical pulp, in: H. Holik (Ed.), Handbook of Paper and Board, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006, pp. 21–22.
- [4] M.J. Ellis, J. Empie, Towards kraft mill closure: influence of non-process elements on green liquor dregs settling and filterability, *Appita J.* 56 (2003) 466–470.
- [5] N. Jemaa, R. Thompson, R. Paleologou, R.M. Berry, Non-process elements in the kraft cycle, part I: source, levels and process effects, *Pulp Pap. Canada* 100 (1999) 47–51.
- [6] A.V. Filgueiras, I. Lavilla, C. Bendicho, Chemical sequential extraction for metal partitioning in environmental solid samples, *J. Environ. Monit.* 4 (2002) 823–857.
- [7] D.S. Kosson, H.A. van der Sloot, F. Sanchez, A.C. Garrabrants, An integrated framework for evaluating leaching in waste management and utilization of secondary materials, *Environ. Eng. Sci.* 19 (2002) 159–204.
- [8] L.A. Morris, W.L. Nutter, E.A. Ogden, J.F. Sanders, M.H. Golabi, W.P. Miller, M.E. Sumner, F.M. Saunders, Mill Residue and Byproduct Utilization Project. First Annual Report, December 1995. <http://www.p2pays.org> (15.06.2010).
- [9] R.W. Gerlach, D.E. Dobb, G.A. Raab, J.M. Nocerino, Gy sampling theory in environmental studies. 1. Assessing soil splitting protocols, *J. Chemom.* 16 (2002) 321–328.
- [10] R. Pöykiö, H. Nurmesniemi, T. Kuokkanen, P. Perämäki, Green liquor dregs as an alternative neutralizing agent at a pulp mill, *Environ. Chem. Lett.* 4 (2006) 37–40.
- [11] M. Yli-Halla, J. Palko, Mineral elemental content of oats (*Avena sativa L.*) in an acid sulphate soil area of Tuopus village, northern Finland, *J. Agr. Sci. Finland* 59 (1987) 73–78.
- [12] C. Yafa, J.G. Farmer, A comparative study of acid-extractable and total digestion methods for the determination of inorganic elements in peat material by inductively coupled plasma-optical emission spectrometry, *Anal. Chim. Acta* 557 (2006) 296–303.
- [13] SFS-EN ISO 10304-1:2007 Standard, Water Quality, Determination of Dissolved Anions by Liquid Chromatography of Ions. Part 1: Determination of Bromide, Chloride, Fluoride, Nitrate, Nitrite, Phosphate and Sulfate, Finnish Standards Association, SFS, Helsinki, Finland, 2009.
- [14] K. Taylor, B.M. McGuffie, Investigation of non-process element chemistry at Elk Falls mill—green liquor clarifier and lime cycle, *Pulp Pap. Canada* 108 (2007) 27–32.
- [15] F.M. Martins, J.M. Martins, L.C. Ferracin, C.J. da Cunha, Mineral phases of green liquor dregs, slaker grits, lime mud and wood ash of a kraft pulp and paper mill, *J. Hazard. Mater.* 147 (2007) 610–617.
- [16] M. Toikka, Minimization and utilization of green liquor dregs and ashes in pulp and paper, in: Regional Environmental Publication No. 82, Southeast Finland Regional Environment Centre, Oy Edita Ab, Helsinki, Finland, 1998.
- [17] M. Jordan, M.A. Sánchez, L. Padilla, R. Céspedes, M. Osses, B. González, Kraft mill residues effects on Monterey pine growth and soil microbial activity, *J. Environ. Qual.* 31 (2002) 1004–1009.
- [18] M. Zambrano, C. Pichün, M. Alvear, M. Villarroel, I. Velásquez, J. Beaza, G. Vidal, Green liquor dregs effect on kraft mill secondary sludge composting, *Bioresour. Technol.* 101 (2010) 1028–1035.
- [19] M. Mahmoudkhani, T. Richards, H. Theliander, Recycling of solid residues to the forest. Experimental and theoretical study of the release of sodium from lime mud and green liquor dregs aggregates, *Process Saf. Environ. Prot.* 82 (2004) 230–237.
- [20] R. Modolo, A. Benta, V.M. Ferreira, L.M. Machado, Pulp and paper plant wastes volatilisation in bituminous mixes, *Waste Manage.* 30 (2010) 685–696.
- [21] M. Zambrano, V. Parodi, J. Baeza, G. Vidal, Acids soils pH and nutrient improvement when amended with inorganic solid wastes from kraft mill, *J. Chil. Chem. Soc.* 52 (2007) 1169–1172.
- [22] O. Heiri, A.F. Lotter, G. Lemcke, Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results, *J. Paleolim.* 25 (2001) 101–110.
- [23] A.H. Österås, I. Sunnerdahl, M. Greger, The impact of wood ash and green liquor dregs application on Ca, Cu, Zn and Cd contents in bark and wood of Norway spruce, *Water Air Soil Pollut.* 166 (2005) 17–29.
- [24] A. Jaretun, G. Aly, Removal of chloride and potassium from kraft chemical recovery cycles, *Sep. Sci. Technol.* 35 (2000) 421–438.
- [25] A. Liard, R. Lessard, J. Leclerd, L. Désilets, Product from residue: standard setting for alkaline mill residues in Quebec, *Pulp Pap. Canada* 100 (1999) 27–29.
- [26] C. Rothpfeffer, From wood to waste and waste to wood. Aspects on recycling waste products from the pulp mill to the forest soil, Doctoral Thesis, Swedish University of Agricultural Sciences, Uppsala, Sweden, 2007, pp. 1–46.
- [27] Y. Gu, L. Edwards, Prediction of metals distribution in mill process, part 2: fiber line metal profiles, *Tappi J.* 3 (2004) 13–20.
- [28] J.H. Duffus, “Heavy metals”—a meaningless term? *Pure Appl. Chem.* 74 (2002) 793–807.
- [29] L. Järup, Hazards of heavy metal contamination, *Br. Med. Bull.* 68 (2003) 167–182.
- [30] J. Sorvari, By-products in earth construction: environmental assessments, *J. Environ. Eng.* 129 (2003) 899–909.
- [31] U.M. Mroueh, M. Wahlström, By-products and recycled materials in earth construction in Finland—an assessment of applicability, *Resour. Conserv. Recy.* 35 (2002) 117–129.
- [32] M. Wahlström, J. Laine-Ylijoki, Standardized leaching test methods recommended for environmental studies on materials to be used in earth works, Technical Research Centre of Finland (VTT), Research Notes 1801, 1996, pp. 1–44.
- [33] A. Das, R. Chakroborty, M. Ververa, M. de la Guardia, Metal speciation in solid matrices, *Talanta* 42 (1995) 1007–1030.
- [34] P.K. Ndiaba, L. Axe, Sequential extraction of phosphate- and thermal-treated New York/New Jersey Harbor dredged sediments, *Environ. Eng. Sci.* 26 (2009) 1755–1764.
- [35] T. Townsend, T. Tolaymat, H. Solo-Gabriele, B. Dubey, K. Stook, L. Wadanambi, Leaching of CCA-treated wood: implications for waste disposal, *J. Hazard. Mater.* 114 (2004) 75–91.
- [36] B.M. Svensson, L. Mårtensson, L. Mathiasson, L. Eskilsson, Leachability testing of metallic wastes, *Waste Manage. Res.* 23 (2005) 457–467.
- [37] Y.-Y. Long, L.-F. Hu, C.-R. Fang, Y.-Y. Wu, D.-S. Shen, An evaluation of the modified BCR sequential extraction procedure to assess the mobility of copper and zinc in MSW, *Microchem. J.* 91 (2009) 1–5.
- [38] T. Sabbas, A. Poletini, R. Pomi, T. Astrup, O. Hjelm, P. Mostbauer, G. Cappai, G. Magel, S. Salhofer, C. Speiser, S. Heuss-Assbichler, R. Klein, P. Lechner, Management of municipal solid waste incineration residues, *Waste Manage.* 23 (2003) 61–68.
- [39] I. Yousfi, A. Bermond, Chemical reactivity of trace metals in two polluted soils as affected by a reducing compound, *Environ. Technol.* 18 (1997) 139–149.
- [40] G. Rauret, Extraction procedures for the determination of heavy metals in contaminated soil and sediment, *Talanta* 46 (1998) 449–455.
- [41] J. Arunachalam, H. Emons, B. Krasnodebska, C. Mohl, Sequential extraction studies on homogenized forest soil samples, *Sci. Total Environ.* 181 (1996) 147–159.
- [42] P. Smichowski, G. Polla, D. Gómez, Metal fractionation of atmospheric aerosols via sequential chemical extraction: a review, *Anal. Bioanal. Chem.* 381 (2005) 302–316.
- [43] E. Alonso, P. Villar, A. Santos, I. Aparicio, Fractionation of heavy metals in sludge from anaerobic wastewater stabilization ponds in southern Spain, *Waste Manage.* 26 (2006) 1270–1276.