

Earth Construction and Landfill Disposal Options for Slaker Grits

¹G. Watkins, ²R. Pöykiö, ³H. Nurmesniemi and ¹O. Dahl

¹Aalto University, School of Science and Technology, Department of Forest Products
Technology, Laboratory of Chemical Pulping and Environmental Technology,
P.O. Box 16300, FI-00076 Aalto, Finland

²City of Kemi, Valtakatu 26, FI-94100 Kemi, Finland

³Stora Enso Oyj, Veitsiluoto Mill, FI-94800 Kemi, Finland

Abstract: Slaker grits, an industrial residue originating from the chemical recovery process at sulfate (kraft) pulp mills, are typically disposed of to landfill in Finland. However, due to the relatively low total heavy metal and low leachable heavy metal, chloride, fluoride, sulfate, Dissolved Organic Carbon (DOC) and Total Dissolved Solids (TDS) concentrations, the residue is a potential earth construction material. This paper gives an overview of the relevant Finnish legislation on the use of industrial waste as an earth construction agent, the classification of waste into one of three classes: hazardous waste, non-hazardous waste and inert waste, as well as the broad waste policy goals under EU law that affects their management.

Key words: Causticizing, environmental permit, leaching, non-process elements, pulp mill, waste

INTRODUCTION

The management of solid wastes such as slaker grits, derived from the chemical recovery cycle of the kraft (sulfate) pulping process, has traditionally been via landfilling. However, the rise in the costs of landfill, as a waste management options, driven by regulation designed to protect human health and the environment, has led to problems in acquiring new sites for disposal purposes and has increased costs for their development and operation, such that solid waste generation represents a continuing disposal problem for the forest industry. The utilization of solid wastes allows industry to reduce its reliance on the landfill options, reuse and recycle residues or even utilize materials as beneficial products in line with the objectives of European Union laws (EC, 1991, 2006, 2008). There is therefore a growing trend towards seeking options for the utilization of solid wastes in the Finnish pulp and paper industry.

According to the European Council Waste Framework Directive (WFD) (2006/12/EC) as amended by the new WFD (Directive 2008/98/EC), coming into force in December 2010, waste policy should aim at reducing resource usage (EC, 2006, 2008). The use of waste prevention approaches and the re-use and recycling of materials are therefore at the forefront of this policy, where waste recovery needs to be encouraged to reduce the use of natural resources and promote sustainability. Article 3 of the new WFD restates the order of preferred approach to the issue of waste called the waste hierarchy where the principle of primarily focusing on the reduction of the amount of waste produced and its harmfulness is

augmented by a secondary target of the recovery of waste by means of recycling, re-use and reclamation. Processes aimed at extracting secondary raw materials are included in this latter group. If any of these methods are not feasible, waste should be used as a source of energy. The safe disposal of waste via landfill is specified only as a last resort in the priority ranking of waste management method. A definition of recycling has also been added to the new WFD, where "recycling" means "the recovery of waste into products, materials or substances whether for the original or other purposes".

The new WFD offers the possibility for more straight forward approach to the development of residue based products through the introduction of new concepts such as i.e., new legal terms for substances falling between the waste and non-waste (product) classifications - namely the term side-product. Further changes under the new WFD will see the introduction of criteria to define the so called "end-of-waste" status (promulgation of which is to be via a process of EC comitology or binding norms in environmental permits). The possible categories of waste that the new WFD recognizes as candidates for end-of-waste criteria include construction and demolition waste, some ashes and slags, scrap metals, aggregates, tyres, textiles, compost, waste paper and glass. The possibility of extending the list of end-of-waste candidates to other residue streams (including residues such as slaker grits) would depend upon the stream conforming to a set of criteria:

- The substance or object is commonly used for special purposes
- A market or demand exists for such a substance or object

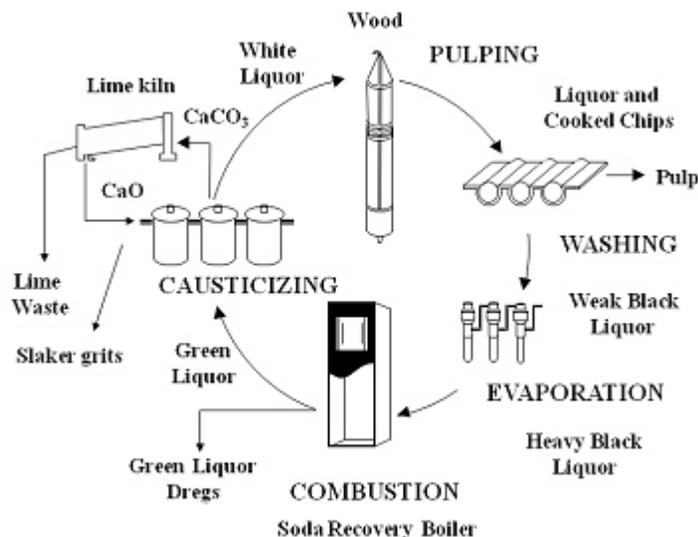


Fig. 1: The causticizing process as a part of pulp mill chemical recovery circuit (Järvensivu *et al.*, 2001; modified)

- The substance or object fulfills the technical requirements for the special purposes and meets the existing legislation and standards applicable to products, and
- The use of the substance or object will not lead to overall adverse environmental or human health impacts.

This study looks at the characteristics of slaker grits, their potential utilization as an earth construction material and the legal implication of such usage. The study is part of a major project focusing on reducing, reusing and recycling different waste materials originating from Finnish pulp and paper mills (Pöykiö *et al.*, 2006; Nurmesniemi *et al.*, 2007, 2010a, b).

EXPERIMENTAL

The Kraft pulping and chemical recovery process - slaker grits sampling: Pulping is a process for separating individual fibres in wood chips or recycled paper by chemical, semi-chemical, or mechanical methods. Chemical pulping is dominated by two processes - the sulfate (kraft) and the sulfite processes. In the alkaline sulfate process, the active chemicals are sodium hydroxide (NaOH) and sodium sulfide (Na₂S), whereas in acid sulfite process, the active chemical in the cooking liquor is hydrogen sulfite (HSO₃⁻). Nowadays, the alkaline sulfate (kraft) pulping process is the main method used for the production of chemical pulp (Monte *et al.*, 2009).

The causticizing process is a part of the pulp mill's chemical recovery system, in which the chemicals used in the pulping process are recovered. The main purpose of

this process is to convert inactive sodium carbonate (Na₂CO₃) back into sodium hydroxide (NaOH), which is an active cooking chemical, and to insure that this conversion rate is as high as possible. The recycling and reuse of various aqueous streams present in the sulfate pulping process leads to the build-up of non-process elements (NPEs), e.g., potassium, magnesium, manganese, barium, iron, aluminum, copper, nickel, chromium and zinc, the majority of which are detrimental to the pulping, bleaching or recovery processes. The introduced or NPEs into the process occurs via the fibre raw materials themselves (i.e., wood chips and sawdust), the make-up chemicals, process waters and from the corrosion of process equipments. The accumulation of NPEs in the pulp mill's bleach plant may result in scaling problems and filtration failures, and they can also catalyse the decomposition of bleaching chemicals, thereby reducing bleaching efficiency (Jemaa *et al.*, 1999). In addition, NPEs cause operational problems such as scale formation on washers and the plugging of process equipment. The removal of NPEs from the recovery cycle is therefore necessary in order to reduce operational problems caused by their build-up and precipitation. The NPEs and other insoluble materials are purged from chemical recovery cycle in the form of green liquor dregs (from the main recovery cycle) and as slaker grits (from make-up chemical addition) (Parthasarathy and Krishnagopalan, 1999).

The slaker grits investigated in this study were sampled from the outlet of the causticizing process at a pulp mill located in Finland (Fig. 1). In 2008, the pulp mill produced approximately 665 tonnes of slaker grits expressed on a dry weight (d.w.) basis, which was all disposed off to landfill. The sampling was carried out

over a period of five days, where individual daily samples of one kg were combined to give one composite sample with a weight of 5 kg (wet weight). The sampling period represented normal process operating conditions for the pulp mill. After sampling, the samples were stored in polyethylene bottles in a refrigerator (+4°C). A coning and quartering method was applied repeatedly to reduce the grit sample to a size suitable for conducting laboratory analyses (Gerlach *et al.*, 2002).

Determination of the mineral composition, physical and chemical properties: For the determination of the mineralogical composition of the grits, an X-ray diffractogram was obtained with a Siemens D 5000 diffractometer (Siemens AG, Karlsruhe, Germany) using CuK α radiation. The scan was run from 2 to 70° (2-theta-scale), with increments of 0.02° and a counting time of 1.5 sec per step. Operating conditions were 40 kV and 40 mA. Peak identification was carried out with a DIFFRACplus BASIC Evaluation Package PDFMaint 12 (Bruker axs, Germany) and ICDD PDF-2 Release 2006 software package (Pennsylvania, USA).

Determination of pH and the Electrical Conductivity (EC) in the grits 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 grits 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 organic matter content, as measured by the loss-on-ignition (LOI), was determined according to European standard SFS-EN 12879, in which an oven-dried (105°C) sample is heated overnight in a muffle furnace (Box Furnace, Lindberg, Blue M, Asheville, USA) at the temperature of 550°C.

The Total Organic Carbon (TOC) content was determined according to European standard SFS-EN 13137 using a Leco CHN-600 analyser (Leco Inc., USA), in which a sample is combusted and the evolved carbon dioxide is measured by infrared spectrometry. A comprehensive review of the standards, analytical methods and instrumentation is given in our previous study (Nurmesniemi *et al.*, 2008).

Determination of total element concentrations: For the determination of total element concentrations in the grits, dried samples were digested with a mixture of HCl (3 mL) and HNO₃ (9 mL) in a CEM Mars 5 microprocessor controlled microwave oven with CEM HP 500 Teflon vessels (CEM Corp., Matthews, USA) using USEPA method 3051A (Yafa and Farmer, 2006). The cooled solutions were transferred to 100 mL volumetric flasks and the solutions were diluted to volume with ultrapure water. All reagents and acids were suprapure or pro analysis quality.

Except for Hg, the total element concentrations in the grits were determined with a Thermo Elemental IRIS Intrepid II XDL Duo (Franklin, USA) inductively coupled plasma optical emission spectrometer (ICP-OES). The concentration of Hg in the grits was determined with a Perkin Elmer AAnalyst 700 cold-vapour atomic absorption spectrometer (Norwalk, USA) equipped with a Perkin Elmer FIAS 400 and AS 90 plus autosampler. The comprehensive review of the analytical methods and instrumentation is given in our previous study (Nurmesniemi *et al.*, 2008).

Leaching procedures and determination of leachable concentrations in extracts: For the determination of the leachable concentrations of Sb, As, Ba, Cd, Cr, Cu, Hg, Pb, Mo, Ni, V, Zn, Se, DOC, fluoride, sulfate and chloride in the slaker grits, the European standard SFS-EN 12457-3 was used. This procedure is a two-stage batch test at a liquid-to-solid ratio (L/S) of 2 and 8 L/kg, with an extractant containing ultrapure water (H₂O), and the sum of leachable concentrations (i.e., L/S 10 L/kg) is compared to the maximum allowable concentrations which, in turn, together with the total element concentrations determine whether the residue may be used as an earth construction agent or whether it may be disposed of to an inert-waste, non-hazardous waste or hazardous waste landfill.

The metal (i.e., Sb, As, Ba, Cd, Cr, Cu, Hg, Pb, Mo, Ni, V, Zn and Se) concentrations in the extracts were determined with a Thermo Elemental IRIS Intrepid II XDL inductively coupled plasma optical emission spectrometer (Franklin, USA). Determination of the Dissolved Organic Carbon (DOC) concentration in the extract was carried out according to the European standard SFS-EN 1484 using a Leco CHN-600 analyser (Leco Inc., USA). Determination of the fluoride and chloride concentrations in the extract were carried out according to the European standard SFS-EN ISO 10304-1 using a Dionex ICS 2000 ion chromatography with conductivity detection (Dionex Corp., USA). Comprehensive reviews of the standards, analytical methods and instrumentation are given in our previous studies (Nurmesniemi *et al.*, 2008; Pöykiö *et al.*, 2008).

RESULTS AND DISCUSSION

Mineral composition, physical and chemical properties of the slaker grits: The most important physical and chemical properties of the slaker grits are given in Table 1, which are means of triplicate samples, expressed on a dry weight (d.w.) basis. However, the standard deviations are not given for the pH and TOC values, because the triplicate samples had exactly the same values. The pH of the grits was strongly alkaline (pH 13.1), and agrees with the findings of Cabral *et al.* (2008), who reported pH values between of 12.4 and 13.1 for

Table 1: Physical and chemical properties of the slaker grits

Parameter	Unit	Slaker grits
pH (1:5)		13.1
Electrical Conductivity (EC)	mS/cm	94.3±0.3
Loss-on-ignition (LOI; 550°C)	% (d.w.)	1.4±0.2
Total Organic Carbon (TOC)	g/kg (d.w.)	<1.0
Dry matter content (105°C)	%	71.6±0.1

Table 2: Total element concentrations (mg/kg; d.w.) in the slaker grits and the variation in element concentrations (mg/kg; d.w.) in a Finnish non-contaminated fine till soil (Sorvari, 2003), as well as the current limit values (mg/kg; d.w.) in Finnish legislation for maximum allowable metal concentrations for materials (i.e., coal, peat and biomass-derived ash) used as an earth construction agent (Vna, 2006)

Element	Slaker grits	Finnish soil	
		(till; <0.06 mm)	Limit value
Al	1540.0±43.6		
As	<3	-20	50
Ba	228.7±4.2	400-900	3000
Ca	331333±3786		
Cd	0.3	1.1	15
Co	1.1±0.1	-30	
Cr	12.6±0.4	-300	400
Cu	<10	10-70	400
K	3073±32		
Mg	4910±114		
Mn	273.3±5.8		
Na	35033±586		
P	4217±71		
Mo	<1	-2	50
Ni	23.9±1.2	10-100	
Pb	<3	0.1-20	300
S	9630±102		
V	39.0±0.6	30-180	400
Zn	9.9±0.3	30-400	2000
Hg	<0.03		
Ti	113.3±5.8		

slaker grits. The alkaline pH value means that the slaker grits have a liming effect and are therefore a potential soil conditioning or amendment agent. According to the electrical conductivity value (94.3 mS/cm), which is an index of the total dissolved electrolyte concentrations, the leaching solution of the grits has a relatively high ionic strength, indicating that part of the dissolved metals occur as dissolved basic metal salts.

The Total Organic Carbon (TOC) value being lower than 1.0 g/kg (d.w.) and the loss-on-ignition (LOI) value of 1.4 % (d.w.) indicate that the organic matter content in the grits is very low. However, although loss-on-ignition (LOI) is a common and widely used method to estimate the organic matter content of waste materials, according to Heiri *et al.* (2001), 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. Thus, LOI is an indirect measure of the organic matter content of the grits. The relatively low dry matter content (71.6%) of slaker grits is an advantage, since dust problems during handling are not very likely.

Although XRD analysis can be useful in identifying the chemical species of crystalline particles, in our case

only calcite (CaCO₃) could be identified (Fig. 2). Thus, our XRD data agrees with the findings of Castro *et al.* (2009) and of Martins *et al.* (2007), who both reported that calcite is the dominant phase in slaker grits. However, we did not detect sodium carbonate (Na₂CO₃ × H₂O) as reported by Castro *et al.* (2009), nor the existence of pirssonite (CaNa₂(CO₃)₂ × 2H₂O), portlandite (Ca(OH)₂) or wustite (FeO) as reported by Martins *et al.* (2007). One reason for the differing detection of minerals in the grits may be the differences between the causticizing processes at our mill and those at the mills investigated by Castro *et al.* (2009) and Martins *et al.* (2007), since according to Martins *et al.* (2007), the physical and chemical properties of slaker grits vary significantly depending on the process conditions in which the grits are formed. In pulp mill systems, the level of metals in process streams depends e.g., on the intake of metals, process configuration and equipment operating conditions, as well as on the type of raw materials and the degree of closure. Thus, the concentrations of non-process elements vary from one mill to another (Jemaa *et al.*, 1999; Gu and Edwards, 2004).

In this context it is worth noting that, the XRD spectrometer is unable to identify the amorphous phase (i.e., non-crystalline matter), and its detection limit is normally 1-2 % (w/w). This is probably one reason why we could not identify all the minerals observed by Castro *et al.* (2009) and Martins *et al.* (2007), and why elements other than calcium were not identified by XRD, despite the fact that the many other elements were measured quantitatively by ICP-OES (Table 2).

Total element concentrations in the slaker grits: The total element concentrations in the grits are shown in Table 2. The elevated sodium and sulfur concentrations are reasonable in the light of the fact that sodium in the form of Na₂S, NaOH and Na₂SO₄ are cooking chemicals employed in the sulfate pulping process. Sodium also enters the system in moderate quantities in the wood raw materials and from make-up and bleaching chemicals. The elevated magnesium concentration in the grits is derived from the use of magnesium sulfate as an inhibitor during an oxygen delignification process step employed in the bleaching step at the particular mill investigated in this study. The elevated calcium concentration is reasonable since slaker grits are produced during the slaking process which is a reaction of quick lime (i.e., calcium oxide) with green liquor (i.e., aqueous sodium hydroxide, sodium sulfide, and sodium carbonate) in the slaker unit (Castro *et al.*, 2009). Furthermore, calcium is also the most abundant mineral nutrient in wood. Copper and zinc are trace elements in the wood raw material, but they can also originate from equipment corrosion in the chemical recovery process and from process chemicals (Nurmesniemi *et al.*, 2005).

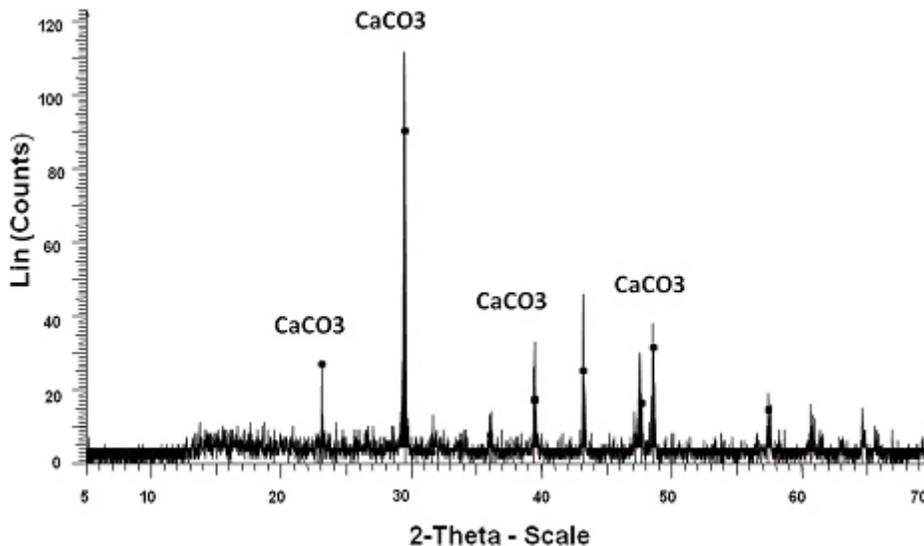


Fig. 2: XRD data of the slaker grits

Table 3: Leachable concentrations of heavy metals, chloride, fluoride, sulfate, dissolved organic carbon (DOC) and total dissolved solids (TDS) at a liquid-to-solid (L/S) ratio of 10 L/kg (mg/kg; d.w., n = 1) in the slaker grits and the current Finnish limit values (mg/kg; d.w.) of these compounds for acceptance as waste at landfills (EC, 1999), as well as current Finnish limit values (mg/kg; d.w.) for these compounds for unpaved and paved materials (i.e., coal, peat and biomass-derived ash) used as an earth construction agent (Vna, 2006)

Compound	Slaker grits	Inert waste landfill	Non-hazardous waste landfill	Hazardous waste landfill	Limit Value (unpaved)	Limit Value (paved)
As	< 0.15	0.5	2.0	25	0.50	0.50
Ba	0.58	20	100	300	20	20
Cd	< 0.01	0.04	1.0	5.0	0.04	0.04
Cr	< 0.1	0.5	10	70	0.50	0.50
Cu	< 0.1	2.0	50	100	2.00	2.00
Hg	< 0.005	0.3	10	30	0.01	0.01
Ni	< 0.1	0.4	10	40	0.40	0.40
Pb	< 0.15	0.5	10	50	0.50	0.50
Sb	< 0.05	0.06	0.7	5.0	0.06	0.06
Mo	0.19	0.5	10	30	0.50	0.50
V	7.3				2.00	3.00
Se	< 0.075	0.1	0.5	7.0	0.10	0.10
Zn	< 0.1	4.0	50	200	4.00	4.00
Cl ⁻	181	800	15.000	25.000	800	2400
F ⁻	< 5	10	150	500	10	50
SO ₄ ²⁻	5250	1000	20.000	50.000	1000	10.000
DOC	80	500	800	1000	500	500
TDS ^(a)	88500	4000	60.000	100.000		

^(a): The value for total dissolved solids (TDS) can be used alternatively to the values for sulfate (SO₄²⁻) and chloride (Cl⁻).

Table 2 shows that the heavy metal concentrations in the slaker grits compare well with those in Finnish soils (Laine-Ylijoki *et al.*, 2005; Sorvari, 2008), except for the sodium concentration. The very low metal concentrations support its beneficial utilization instead of final disposal to landfill, since it would be economically and ecologically preferable if solid industrial residues and by-products could be utilized e.g., as an earth construction agent. Such an approach conserves virgin raw materials and the utilization of solid wastes and residues in activities such as land-spreading and as an earth construction agent, allows industry to implement the 3R principles of the reduction, reuse and recycling through

the use of residue materials as beneficial products (Yoshida *et al.*, 2007).

In order to obtain information about the concentrations of hazardous compounds in slaker grits and to promote their utilization, we compared the total (Table 2) and leachable (Table 3) concentrations of hazardous compounds in slaker grits to the limit values for coal, peat and biomass-derived ash used as an earth construction agent (Vna, 2006). The total concentrations of As, Ba, Cd, Cr, Cu, Mo, Pb, V and Zn in slaker grits are clearly lower than the maximum allowable concentrations of these compounds in coal, peat and biomass-derived ash used as an earth construction agent

(Table 2). This indicates that slaker grits are potential industrial residues for utilization in earth construction. However, according to the results in Table 3, the leachable concentrations of vanadium (7.3 mg/kg; d.w.) and sulfate (5250 mg/kg; d.w.) in slaker grits exceeded the limit values set for coal, peat and biomass-derived ash used as an earth construction agent. The limit values are 2.0 mg/kg (d.w.) and 3.0 mg/kg (d.w.) for vanadium in unpaved materials and in paved materials, respectively, and 1000 mg/kg (d.w.) for sulfate in unpaved materials. Although the limit values given in Table 3 are not applied for slaker grits, this comparison will help the environmental authorities to assess the leachability of hazardous compounds from slaker grits.

Legislative requirements for the use of slaker grits as an earth construction agent in Finland:

In Finland, industrial residues such as ash, blast furnace slag, concrete, used tyres, crushed glass, paving materials and ferrosulfate gypsum, have been used in earth construction for decades (Mroueh and Wahlström, 2002; Sorvari, 2003). The most extensively utilized materials in earth construction are blast-furnace slag, concrete debris from demolition work, and power plant ash. At the present time, the Finnish environmental legislation sets limit values for both the total and leachable concentrations of certain heavy metals, and/or of chloride, fluoride, sulfate and Dissolved Organic Carbon (DOC) and Total Organic Carbon (TOC), if a waste material such as coal, peat and biomass-derived ash or crushed concrete are used as an earth construction agent. However, if coal, peat and biomass-derived ash are applied as an earth construction agent, then the limit value for both the total and leachable concentrations of Polychlorinated Biphenyls (PCB) and Polycyclic Aromatic Hydrocarbons (PAH) are also applied. These limit values, which are presented in this study (Table 3) for coal, peat and biomass-derived ash, came into force in July 2006 and are applied if the ash is used as an earth construction agent e.g. in roads, cycling paths, pavements, car parks, sport fields etc., (Vna, 2006).

Finnish environmental legislation currently does not recognize the concept of a “by-product” and thus, if industrial residues other than coal, peat and biomass-derived ash or crushed concrete materials are used as an earth construction agent, then the environmental permit is required (Mroueh and Wahlström, 2002; Sorvari, 2003). According to the Finnish environmental legislation, all industrial by-products and residues are actually classified as waste and normally anyone who intends to reprocess, reuse, or recycle on a large scale has to apply for an environmental permit. However, the new WFD “end-of-waste” criteria describe above, will make it possible for EU member states to define in an environmental licence or general binding norm that certain by-products have no

adverse environmental or human health impacts (new WFD preamble 22). This means that end-of-waste criteria can to some extent be decided on national level and domestic legislation could be forthcoming on this.

In Finland, the environmental permit is granted by the local municipal environmental authority if the amount of waste to be used is lower than 5000 tonnes. For amounts large than 5000 tonnes, the permitting authority is the regional environmental centre. In the case of experimental projects, however, an environmental permit is not necessarily required and a notification to the authorities is usually sufficient (Mroueh and Wahlström, 2002; Sorvari, 2003). However, an environmental permit is also required for the utilization of coal, peat and biomass-derived ash or crushed concrete materials in cases where the total and the leachable concentrations of hazardous compounds in these residues exceed the maximum Finnish limit values set for their utilization. Therefore, on the grounds of the above-mentioned Finnish legislation requirements, grits cannot be utilized freely as an earth construction agent, and an environmental permit is required for their utilization.

Classification of slaker grits for landfill disposal: The European Council Landfill Directive 1999/31/EC classifies all waste into one of three classes: hazardous waste, non-hazardous waste, and inert waste (EC, 1999; Pöykiö *et al.*, 2009). In the European Union (EU), a hazardous classification of waste should be performed before decisions are made on waste landfill disposal. The leachable concentrations of heavy metals (As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se and Zn), as well as the concentrations of chloride, fluoride, sulfate, dissolved organic carbon (DOC) and Total Dissolved Solids (TDS), in slaker grits are shown in Table 3. In this context it is worth noting that, when the decision about waste acceptance is made, the value for TDS can be used as an alternative to the values for sulfate and chloride (Vna, 2006).

According to the results in Table 3, the leachable concentrations of all heavy metals, chloride, fluoride and DOC in slaker grits were lower than the current EU limit values for these compounds for acceptance of as waste at inert waste landfills. However, the leachable concentration of sulfate (5250 mg/kg; d.w.) in slaker grits clearly exceeded the limit value for inert waste landfill (1000 mg/kg; d.w.), but was lower than that for non-hazardous landfill (20.000 mg/kg; d.w.). Furthermore, the leachable concentration of TDS (88.500 mg/kg; d.w.) in slaker grits clearly exceeded both the limit value for inert waste landfill (4000 mg/kg; d.w.) and for non-hazardous waste landfill (60.000 mg/kg; d.w.), but was lower than the limit value for hazardous waste landfill (100.000

mg/kg; d.w.). However, due to the fact that the value for TDS can be used as an alternative to the value for sulfate (EC, 1999), the slaker grits investigated in this study can even be deposited in a non-hazardous waste landfill. In this context it is worth noting that, although the leached concentration of sulfate (5250 mg/kg; d.w.) exceeded the limit value for inert waste landfill, according to the Finnish legislation, which is based on EU directives and regulations, the competent environmental authority may decide that the maximum limit values can be up to three times higher than those given in Table 3 on the basis of the local environmental conditions in a landfill (EC, 1999). In spite of this possibility for the environmental authorities to relax the maximum limit values for sulfate, the slaker grits investigated in this study cannot be deposited in inert waste landfill according to local policy decisions with respect to relaxation. However, the classification of slaker grits as non-hazardous waste does not restrict the use of the residue as an earth construction agent e.g. at landfills themselves, because, according to Sorvari (2003), a by-product that is used in earth construction may not have the properties of a hazardous waste. Future changes to Finnish waste management laws in response to the new provisions introduced by the EU Waste Framework Directive (EC, 2006) might also allow for wider utilization of slaker grits for beneficial purposes if end-of-waste status criteria could be complied with.

CONCLUSION

At the present time, Finnish environmental legislation sets the limit values for both the total and leachable concentrations of certain heavy metals, and/or of chloride, fluoride, sulfate and Dissolved Organic Carbon (DOC) and Total Organic Carbon (TOC), if a waste material such as coal, peat and biomass-derived ash or crushed concrete material is used as an earth construction agent. However, there are no such maximum allowable concentrations specified for slaker grits used as an earth construction agent in Finland and, therefore, the utilization of slaker grits always requires an environmental permit. The very low metal concentrations in slaker grits support its beneficial utilization instead of final disposal in a landfill because it would be economically and ecologically preferable if solid industrial residues and by-products could be reused, e.g., as an earth construction agent.

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REFERENCES

- Cabral, F., H.M. Ribeiro, L. Hilário, L. Machado and E. Vasconcelos, 2008. Use of pulp mill inorganic wastes as alternative liming materials. *Bioresour. Technol.*, 99(17): 8294-8298.
- Castro, F., C. Vilarinho, D. Trancoso, P. Ferreira, F. Nunes and A. Miragaia, 2009. Utilisation of pulp and paper industry wastes as raw materials in cement clinker production. *Int. J. Materials Eng. Innov.*, 1(1): 74-90.
- EC, 1991. European Council Directive 91/156/EEC of 18 March 1991 amending directive 75/442/EEC on Waste. *Official J. Eur. Comm. L*, 78: 32-37.
- EC, 1999. Directive 1999/31/EC of 26 April 1999 on the landfill of waste. *Official J. Eur. Comm. L*, 135: 32-34.
- EC, 2006. Directive 2006/12/EC of the European Parliament and of the council of 5 April 2006 on waste (Text with EEA relevance). *Official J. Eur. Comm. L*, 114: 9-21.
- EC, 2008. Directive 2008/98/EC of the European Parliament and of the council of 19 November 2008 on waste and repealing certain directives (Text with EEA relevance). *Official J. Eur. Comm. L*, 312: 3-30.
- Gerlach, R.W., D.E. Dobb, D.A. Raab and J.M. Nocerino, 2002. Gy sampling theory in environmental studies. 1. Assessing soil splitting protocol. *J. Chemometr.*, 16(7): 321-328.
- Gu, X. and L. Edwards, 2004. Prediction of metals distribution in mill process, Part 2: Fiber line metal profiles. *Tappi J.*, 3(2): 13-20.
- Heiri, O., A.F. Lotter and G. Lemcke, 2001. Loss on ignition as method for estimating organic and carbon content in sediments: Reproducibility and comparability of results. *J. Paleolim.*, 25(1): 101-110.
- Jemaa, N., R. Thompson, M. Paleologou and R.M. Berry, 1999. Non-process elements in the kraft cycle, Part I: sources, levels and process effects. *Pulp Pap. Can.*, 100(9): 47-51.
- Järvensivu, M., K. Saari and S.L. Jämsä-Jounela, 2001. Intelligent control system of an industrial lime kiln process. *Control Eng. Pract.*, 9(6): 589-606.
- Laine-Ylijoki, J., U.M. Mroueh, P. Vahanne, M. Wahlström, E. Vestola, S. Salonen and J.C. Havukainen, 2005. Current international status of MSW ashes and slags. VTT Research Notes 2291-TIED-2291 (in Finnish, abstract in English).
- Martins, F.M., J.M. Martins, L. C. Ferracin and C.J. da Cunha, 2007. Mineral phases of green liquor dregs, slaker grits, lime mud and wood ash of a Kraft pulp mill. *J. Hazard. Mater.*, 147(1-2): 610-617.
- Monte, M.C., F. Fuente, A. Blanco and C. Negro, 2009. Waste management from pulp and paper production in the European Union. *Waste Manage.*, 29(1): 293-308.

- Mroueh, U.M. and M. Wahlström, 2002. By-products and recycled materials in earth construction in Finland - an assessment of applicability. *Resour. Conserv. Recy.*, 35(1-2): 117-129.
- Nurmesniemi, H., R. Pöykiö, P. Perämäki and T. Kuokkanen, 2005. The use of a sequential extraction procedure for heavy metal fractionation in green liquor dregs from a causticizing process at a pulp mill. *Chemosphere*, 61(10): 1475-1484.
- Nurmesniemi, H., R. Pöykiö and R.L. Keiski, 2007. A case study of waste management at the Northern Finnish pulp and paper mill complex of Stora Enso Veitsiluoto mills. *Waste Manage.*, 27(12): 1939-1948.
- Nurmesniemi, H., R. Pöykiö, R.L. Keiski and T. Matsuto, 2008. Total and extractable heavy metal and sulfur concentrations in fly ash from a large-sized (90 MW) fluidized bed boiler at a pulp mill incinerating biofuels. *J. Residuals Sci. Technol.*, 5(4): 171-179.
- Nurmesniemi, H., R. Pöykiö, G. Watkins and O. Dahl, 2010a. Total and extractable heavy metal, phosphorous and sulfur concentrations in slaker grits from the causticizing process of a pulp mill for use as soil amendment. *Chem. Spec. Bioavail.*, 22(2): 87-97.
- Nurmesniemi H., O. Dahl, G. Watkins and R. Pöykiö, 2010b. Slaker grits from the causticizing process of a pulp mill - a potential fertilizer and liming agent material for use in agriculture and forestry. *Int. J. Mat. Eng. Innovat.*, 1(3/4): 312-324.
- Parthasarathy, G. and G. Krishnagopalan, 1999. Effluent reduction and control of non-process elements towards a cleaner Kraft pulp mill. *Clean Prod. Process.*, 1(4): 264-277.
- Pöykiö, R., H. Nurmesniemi, T. Kuokkanen and P. Perämäki, 2006. Green liquor dregs as an alternative neutralizing agent at a pulp mill. *Environ. Chem. Lett.*, 4(1): 37-40.
- Pöykiö, R., H. Nurmesniemi and R.L. Keiski, 2008. Chemical, physical and leaching studies of bottom ash from a medium-sized (32 MW) municipal district heating plant for assessing its suitability for an earth construction agent and for a fertilizer used in agriculture and in forestry. *J. Residuals Sci. Technol.*, 5(1): 27-35.
- Pöykiö, R., H. Rönkkömäki, H. Nurmesniemi, P. Perämäki, K. Popov, I. Välimäki and T. Tuomi, 2009. Chemical and physical properties of cyclone ash from the grate-fired boiler incinerating forest residues at a small municipal district heating plant (6 MW). *J. Hazard. Mater.*, 162(1): 1059-1064.
- Sorvari, J., 2003. By-products in earth construction: Environmental assessments. *J. Environ. Eng.*, 129(10): 899-909.
- Sorvari, J., 2008. Developing environmental legislation to promote recycling of industrial by-products - An endless story? *Waste Manage.*, 28(3): 489-501.
- Vna, 2006. The Government Decree (591/2006) Recovery of Certain Wastes in Construction, (In Finnish). Retrieved from: <http://finlex.fi>, (Accessed on: September 2009).
- Yafa, C. and J.G. Farmer, 2006. 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(1-2): 296-303.
- Yoshida, H., K. Shimamura and H. Alzawa, 2007. 3R strategies for the establishment of an international sound material-cycles society. *J. Mater. Cycles Waste Manage.*, 9(2): 101-111.