## **Source** Chemical fractionation of non-process elements in slaker grits for environmental risks assessment

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## ABSTRACT

Aim: The non-process elements (NPEs) in slaker grits, which are solid residues from the causticizing process of a pulp mill, were sequentially extracted with water (H<sub>2</sub>O), ammonium-acetate (CH<sub>2</sub>COONH<sub>2</sub>) and hydrochloride acid (HCI) in order to evaluate their mobile forms and their release potential from the sample matrix under changing environmental conditions. Materials and Methods: The slaker grits investigated in this study were sampled on November 2013 from a sulfate (kraft) pulp mill located in Finland. The slaker grits were extracted as follows: (1) once in 30-50 mL ultra-pure H<sub>2</sub>O for 24 h under stirring (65 rpm), (2) 3 times in 3 mL  $\times$  25 mL 1.0 M CH<sub>2</sub>COONH, (aq) for 3 h  $\times$  24 h under stirring, and (3) twice in 2 mL  $\times$  25 mL 1.0 M HCl (aq) for 2 h  $\times$  24 h under stirring and heating (80°C). **Results:** Compared with the total NPE concentrations, the efficiencies of H<sub>2</sub>O in extracting S (6020 mg/kg; dry weight [d.w.]) and Na (17200 mg/kg; d.w.) were highest, being 92.6% and 88.7%, respectively. Compared with the total NPE concentrations, the efficiencies of CH<sub>2</sub>COONH, in extracting Mg (4010 mg/kg; d.w.) and B (5.0 mg/kg; d.w.) were highest, being 39.7% and 31.3%, respectively. Conclusion: From the environmental and utilization perspectives the greatest hazards to the environment are those metals, which leach out as a result of contact with H<sub>2</sub>O or CH<sub>2</sub>COONH<sub>4</sub>. Therefore, it is worth noting the ability of H<sub>2</sub>O and CH<sub>2</sub>COONH<sub>4</sub> to release high concentrations of alkali metals (Na, K), alkaline earth metals (Mg, Ca), and sulfur (S) from slaker grits, and the need to apply for an environmental permit if this residue is to be utilized.

KEY WORDS: Causticizing, extraction, leaching, heavy metals, non-process elements

### INTRODUCTION

In pulp and paper mills water represents one of the key components of the process being used as a transport medium and in cooling, as a diluter of paper stock, as a solvent for process chemicals, in the form of steam for energy transfer, and as a cleaning medium for all kinds of washing and cleaning operations [1]. Wastewater reduction and water conservation are becoming increasingly important issues in the pulp and paper industry. More stringent environmental regulations and the process integration techniques initially developed for energy integration have been the main factors driving efforts toward improvements in water conservation and wastewater reduction in pulp and paper manufacturing industry [2,3].

One major concern in the development of technology for achieving closed cycle operations in pulp and paper mills is the accumulation of metal ions, commonly referred to as nonprocess elements (NPEs) in process liquors due to the usage of different process chemicals in various stages, e.g. bleaching stages, stock preparation and paper machine operations [4-6]. NPEs are loosely described as materials (metals), which are not needed in the pulping process [7,8]. Therefore, there is some disagreement amongst researchers on the exact definition of NPEs since Grace and Tran [9] regard neither sodium (Na) nor sulphur (S) as NPEs, whereas according to Matilainen and Tummavuori [10], sulphur is to be considered an NPE. However, Emunds *et al.* [11], consider both sodium (Na) and calcium (Ca) to be NPE, because Na becomes an NPE when it is admitted into the calcium cycle, while Ca becomes an NPE when it is admitted into the sodium cycle [12].

In terms of inputs, NPEs enter the mill mainly with the wood raw materials, in fresh process water and make-up chemicals and are not required in the distinct pulp production stages. The accumulation of NPEs in a pulp mill may cause deposits and corrosion in the liquor recovery cycle and in various parts of the bleach plant, such as washer screens, filtrate tanks, nozzles,

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Received: December 15, 2014 Accepted: January 14, 2015 Published: February 03, 2015 repulpers, pumps, piping and instrumentation. The presence of NPEs may also affect bleaching reagent consumption, especially when hydrogen peroxide  $(H_2O_2)$  is used [13]. In order to stop the accumulation of such NPEs, different processes to remove them need to be introduced into the system. Processes that remove NPEs from a pulp mill's cycles are referred to as kidneys [14]. Some water soluble NPEs can be purged via effluent streams. For other non-soluble NPEs, filtration or screening processes are natural process kidneys. One important kidney in the pulp mill is the causticizing process and the removal of slaker grits [15]. The purged slaker grits are solid waste fractions typically disposed of to landfills. To achieve the maximum protection of the environment against hazards associated with slaker grits waste management via landfilling, all potential hazards must be identified, and the risks associated with them analyzed [16,17].

Environmental studies are often based on information obtained from leaching or extraction procedures for evaluating the fraction of total, mobile forms of metals, which are in most instances sufficient for environmental risk assessment [18]. The need to assess the environmental impacts of solid residues and wastes when they are utilized or disposed of to landfill has led to the development of numerous leaching procedures [19]. The chemical forms of heavy metals in the solid phase can strongly influence their behavior, in terms of their mobility, toxicity, bioavailability and chemical interactions. The total content of metals determined by dissolution of strong acids may be useful as a gross index of contamination. However, this provides little insight into the potential mobility of metals under field conditions [20]. In view of this, methods using the sequential extraction approach allow for a wider assessment of the potential behavior of heavy metals in the environment. Chemical fractionation enables the separation of metals from solid samples into forms which can be released into a solution under different conditions of increasing activity [21].

The aim of this study was to extract and fractionate the NPEs in slaker grits between the increasingly aggressive solvents of water-soluble (H<sub>2</sub>O), ammonium-acetate (CH<sub>2</sub>COONH<sub>4</sub>) soluble and hydrochloride acid (HCl) soluble fractions [22]. This chemical fractionation technique distinguishes different types of inorganic matter in the waste material based on their solubility in different solvents and predicts the leaching behavior of NPEs in slaker grits thereby indicating the potential release of elements from the grits under changing environmental conditions e.g., in landfills, where the pH may change due to sulfide oxidation, acid rain and atmospheric CO<sub>2</sub> for example [23]. This study is the sequel to our previous publication [24], which focused on the occupational safety aspects and bio-accessible concentrations of NPEs in slaker grits. In this context, it is worth noting that when slaker grits are to be utilized for example in earth works, the main human exposure parthway is the inhalation of dust, dermal contact and ingestion of this residue. Once the slaker grits material enters the body through respiratory and gastrointestinal tracts, it mixes with biological fluids and hence has an opportunity to be dissolved and absorbed [24].

#### MATERIALS AND METHODS

#### **Sampling Procedure**

The slaker grits investigated in this study were sampled from the causticizing process of the chemical recovery circuit of a sulfate (kraft) pulp mill located in Finland [24]. In the causticizing process, calcium hydroxide (Ca[OH]<sub>2</sub>) reacts with the sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) formed during combustion of black liquor in the recovery boiler that has been quenched with water to form green liquor. This reaction generates sodium hydroxide (NaOH) and calcium carbonate (CaCO<sub>2</sub>). The objective of the causticizing process is to turn inactive Na,CO, back into the active cooking chemical NaOH and to make sure that the conversion efficiency of carbonate into hydroxide is as high as possible. The sampling was carried out on November 2013 over a period of 3 days. Six individual daily samples were combined to give one composite sample with a weight of 10 kg (wet weight). The sampling was carried out during a period during which the causticizing process operating conditions were normal for the mill. After sampling, the individual samples were stored in polyethylene bottles under dark and cool (+4°C) conditions in the laboratory.

# Determination of the Total NPE Concentrations in the Grits

For the determination of the total NPE concentrations in the grits, the dried sample was digested with aqua regia (3 mL HCl and 9 mL HNO<sub>2</sub>). The cooled solution was transferred to a 100 mL volumetric flask and subsequently diluted to volume with ultrapure water. The ultrapure water was generated by an Elgastat Prima reverse osmosis and Elgastat Maxima ion exchange water purification system (Elga, Ltd; Bucks, United Kingdom). All reagents and acids were suprapure or pro analysis quality. The total NPE concentrations in the grits 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 grits was determined with a Perkin Elmer AAnalyst 700 cold-vapor atomic adsorption spectrometer (Norwalk, USA) equipped with a Perkin Elmer FIAS 400 and AS 90 plus autosampler. A comprehensive review of the standards, analytical methods, instrumentation and quality control is given in our previous paper [24].

#### **Chemical Fractionation of NPEs in the Grits**

The chemical fractionation of NPEs in the slaker grits was carried out in accordance with the approach of Zevenhoven-Onderwater *et al.* [22]. In this fractionation scheme, the sample is dried (105°C) and the ground to a particle size of <5 mm. The sample is then subjected to three successive extractions using different solvents, i.e. ultrapure water (H<sub>2</sub>O), 1 M ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>) and finally 1 M hydrochloric acid (HCl). The NPEs were extracted in the following way: (1) Once in 30-50 mL ultra-pure H<sub>2</sub>O for 24 h under stirring (65 rpm), (2) three times in 3 mL  $\times$  25 mL 1.0 M CH<sub>3</sub>COONH<sub>4</sub> (aq) for 3 h  $\times$ 24 h under stirring, and (3) twice in 2 mL  $\times$ 25 mL 1.0 M HCl (aq) for 2 h  $\times$ 24 h under stirring and heating (80°C). A comprehensive review of the extraction procedure is given in the publication [22].

After each extraction step, the solids were rinsed twice for 2 min ×10 min with 2 mL ×25 mL ultra-pure H<sub>2</sub>O. After each extraction step, the extractants were separated from the solid residue by filtration through a 0.45  $\mu$ m membrane filter (47 mm diameter; Schleicher and Schuell, Dassel, Germany). In order to avoid losses between the extraction stages, the filters and adhering grit particles from the previous extraction stage were also included in the next stage. After adding 200  $\mu$ L of 65% HNO<sub>3</sub> to the supernatant phase, it was stored under dark and cool (+4°C) conditions in the laboratory. The NPE concentrations in the extracts were determined with ICP-OES.

#### RESULTS

#### **Total NPE Concentrations in the Grits**

The total (3 mL HCl and 9 mL HNO,) and literature values [25,26] for NPEs in slaker grits with concentrations expressed on a dry weight (d.w.) basis are shown in Table 1. The literature values from the reference [26] are average of triplicate samples including the standard deviation. If we compare the total NPE concentrations in the sample grits to those reported in the literature, it can be seen that except for Al, Fe, Ti, Ca and Mg, the concentrations of other NPEs in the sample grits agree relatively well with the NPE concentrations observed in grits in other pulp mills. In general, the characteristics of the slaker grits, e.g., the NPE concentrations, are dependent on the process conditions and activities applied in each specific mill, as well as on the wood species and make-up chemicals used in the mills [27,28]. Furthermore, one important NPE incorporating agent is the quality of process water used in the mill [11]. The elevated Na concentration (19400 mg/kg; d.w.) observed in the sample grits is reasonable, since sodium in the forms of NaOH, Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>S are principal cooking chemicals employed in the sulfate pulping process [29]. This phenomenon, as well as the fact that the source of sulfur introduction to the chemical recovery system is closely linked to the fuel used to power the lime kiln for Ca(OH), production, explains the high S concentrations of 6500 mg/kg (d.w.) in the grits. The very high Ca concentration (378000 mg/kg; d.w.) in the slaker grits is due to the fact that calcium is an element used in the causticization and calcinations processes of the mill. The high Mg (10100 mg/kg; d.w.) concentration in the grits is derived from the use of magnesium sulfate as an inhibitor during an oxygen delignification process step at the mills

#### Fractionated NPE Concentrations in the Grits

The fractionated concentrations of NPEs in the slaker grits expressed on a d.w. basis are shown in Table 1. According to the X-ray diffraction study results, published in our previous paper [24], calcium carbonate (CaCO<sub>3</sub>) was the only crystalline

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Table 1: Total (3 mL HCl and 9 mL HNO<sub>3</sub>) and extractable concentrations (mg/kg; d.w.) of NPEs in slaker grits using H<sub>2</sub>O, CH<sub>3</sub>COONH<sub>4</sub> (abbr. NH<sub>4</sub>Ac) and HCl extraction, their sum ( $\Sigma$ ), as well as the variation of NPE concentrations in slaker grits according to literature [25,26]

NPEs	Total o	Extractable concentration				
	This study	Literature value <sup>a</sup>	H <sub>2</sub> 0	NH <sub>4</sub> Ac	HCI	Σ
AI	6500	1540±43.6	130	<15	<15.0	<160
As	<3.0	<3.0	<0.2	< 0.5	<0.5	<1.2
В	16.0	13.0	5.0	5.0	4.5	14.5
Ba	230	228.7±4.2	<0.1	37.0	78.0	<115.1
Cd	<0.3	0.3	< 0.02	< 0.05	0.07	<0.14
Co	1.8	1.1±0.1	<0.1	<0.2	0.6	<0.9
Cr	15.0	12.6±0.4	<0.2	<0.4	<0.4	<1.0
Cu	2.6	23.0	<0.2	<0.4	<0.4	<1.0
Fe	7470	2390	<3.0	<5.0	73.0	<78.0
Mn	180	273.3±5.8	<0.4	2.0	93.0	<95.4
Mo	<1.0	<10.0	0.4	0.1	<0.2	<0.7
Ni	33.0	23.9±1.2	<0.1	7.7	8.7	<16.5
Pb	4.7	11.0	<0.2	<0.5	<0.5	<1.2
S	6500	9630±102	6020	170	310	6500
V	40.0	39.0±0.6	1.9	1.3	<0.4	<3.6
Zn	33.0	9.9±0.3	<0.2	0.6	6.3	<7.1
Ti	450	113.3±5.8	<5.0	<10.0	<10.0	<25.0
Ca	378000	331333±3786	30.0	21500	231000	252530
Na	19400	35033±586	17200	900	1300	19400
Mg	10100	4910±114	<2.0	4010	6100	10130
Ρ	2680	4217±71	<2.0	6.8	<3.0	<11.8
К	3120	3073±32	1640	150	1200	2990
Нg	<0.04	<0.03	n.d.	n.d.	n.d.	n.d.

<sup>a</sup>The literature values for B, Cu, Fe, Mo and Pb are from reference [25] and the values for other NPEs are from reference [26], NPEs: Non-process elements, d.w.: Dry weight

phase observed in the slaker grits. In the first extraction step, ultrapure water ( $H_2O$ ) was used as an extractant. Water is a suitable extraction solvent if we wish to determine the bioavailability of the components in the environment since water is the medium for the transfer of substrate and nutrients for example within landfills [30]. Although the water is a weak extractant [31], it is a commonly used extraction liquid for solid samples, and it dissolves the most easily water soluble fraction is generally considered to be metals, which are the most available metal forms for plant uptake [33]. Compared with the total NPE concentrations, the efficiencies of water in extracting S and Na were 92.6% and 88.7%, respectively. For K, the extraction efficiency of water was 52.6%. Thus, S, Na and K in the slaker grits were the NPEs released most easily using water extraction.

In the second extraction step, 1 M ammonium acetate  $(CH_3COONH_4)$ , which is a salt of a weak acid (acetic acid) [33]

and a weak base of ammonia [34], was used as extractant. Ammonium acetate releases metals which are weakly bound to the sample matrix [23]. According to ion exchange theory, the ammonium ion  $(NH_4^+)$  can exchange or replace a small proportion of the heavy metals in the sample [35]. The use of  $CH_3COONH_4$  as extractant is reasonable, because during the anerobic degradation of organic matter (e.g., forest products in landfills), volatile fatty acids and ethanol are produced and transformed for instance into acetate by bacteria [36]. Compared to the total NPE concentrations, the efficiencies of ammonium acetate in extracting Mg and B were 39.7% and 31.3%, respectively. For Ni, the extraction efficiency of ammonium acetate was 23.3%. Thus, Mg, B and Ni in the slaker grits were the NPEs released most easily using ammonium-acetate extraction.

In the third extraction step, dilute hydrochloride acid (1 M HCl) was used as an extractant. Dilute HCl is one of the most widely used reagents, in techniques which employ acid solutions to isolate the non-residual phase, in a variety of solid environmental media, and it is assumed to extract metals on exchange sites due to its acidic properties [35]. The main mechanisms for metal removal under HCl are the desorption enhanced by low pH, the dissolution of discrete metal compounds and the dissolution of specific matrix components containing metals (e.g., Fe-Mn oxides) [37]. Compared to strong HCl, which attacks and degrades the matrix crystalline structure on extended contact time, dilute HCl has a sufficient buffering capacity to dissolve carbonates and sulfates, without attacking silicates [22,38-41]. Compared to the total NPE concentrations, the efficiencies of HCl in extracting Ca and Mg were 61.1% and 60.4%, respectively. For K, the extraction efficiency of HCl was 38.5% and for B it was 33.9%. Thus, Ca and Mg in the slaker grits were the NPEs released most easily using HCl extraction.

#### DISCUSSION

It is evident from the results of the extraction study that the NPEs in the slaker grits investigated in this study are bound to different fractions with different strengths. From the environmental and utilization perspectives, it is worth noting the ability of  $H_2O$  and  $CH_3COONH_4$  to release high concentrations of alkali metals (Na, K) alkaline earth metals (Mg, Ca) and sulphur (S) from the grits. Therefore, if slaker grits are to be utilized as a fertilizer, according to Samoraj *et al.* [42], the easy release of metals in  $H_2O$  and  $CH_3COONH_4$  extraction fractions can lead to possible soil contamination.

According to Wielgosiński *et al.* [21], the greatest hazards to the environment are metals which leach out as a result of contact with water, since  $H_2O$  is the main carrier of contaminants in field conditions. The risk is based on the fact that water soluble metal ions can easily be mobilized, and may thus be considered as highly "bioavailable" [43]. If we disregard NPEs whose concentrations were lower than the detection limit, the extractable concentrations in the water-soluble fraction followed the order: Na (17200 mg/kg; d.w.), S (6020 mg/kg; d.w.), K (1640 mg/kg; d.w.), Al (130 mg/kg; d.w.), Ca (30.0 mg/kg; d.w.) and negligible concentrations of B, V and Mo.

Futhermore, Wielgosiński *et al.* [21] concluded that the heavy metals extracted in the CH<sub>3</sub>COONH<sub>4</sub> fraction also pose potential hazards to the environment. The risk here is based on the fact that CH<sub>3</sub>COONH<sub>4</sub> soluble metal ions are believed to be plant-available or readily mobile metal forms [20]. If we disregard NPEs whose concentrations were lower than the detection limit, the extractable concentrations in the CH<sub>3</sub>COONH<sub>4</sub> fraction followed the order: Ca (21500 mg/kg; d.w.), Mg (4010 mg/kg; d.w.), Na (900 mg/kg; d.w.) and negligible concentrations of B, Mn, Mo, Ni, V, Zn and P. According to Pettersson *et al.* [32], the highly elevated concentrations of Ca, Mg and Na in the CH<sub>3</sub>COONH<sub>4</sub> fraction are reasonable considering that they are replaced with ammonium ions and are thus released to the liquid phase.

As expected, the highest extractable concentrations of NPEs were observed in the HCl soluble fraction and they followed the order: Ca (231000 mg/kg; d.w.), Mg (6100 mg/kg; d.w.), Na (1300 mg/kg; d.w.), K (1200 mg/kg; d.w.) and S (310 mg/kg; d.w.). The strongly acidic extraction (1 M HCl), which was used in the last step, is not likely to occur under normal conditions in nature. However, in landfills there are numerous physical, chemical and biological processes, which may influence the pH, and so acidic conditions may exist in the leachate [44]. According to Bolton and Evans [45], landfill leachates contain many organic and inorganic complexant ligands, particularly chloride-ions, which also exist in the HCl. Therefore, we conclude that the NPEs in slaker grits may also become soluble in these kinds of conditions and this phenomenon need to be taken into account if slaker grits are to be utilized.

#### CONCLUSION

From an environmental and utilization perspective, the greatest hazards to the environment are metals, which leach out from slaker grits as a result of contact with  $H_2O$  or  $CH_3COONH_4$ . Compared to the total NPE concentrations, the efficiencies of water in extracting S and Na were 92.6% and 88.7%, respectively. Thus, S and Na were the NPEs released most easily using water extraction following the order: Na (17200 mg/kg; d.w.) and S (6020 mg/kg; d.w.). Compared to the total NPE concentrations, the efficiencies of  $CH_3COONH_4$  in extracting Mg and B were 39.7% and 31.3%, respectively. Thus, Mg and B in the slaker grits were the NPEs released most easily using  $CH_3COONH_4$  extraction following the order: Mg (4010 mg/kg; d.w.) and Ba (37 mg/kg; d.w.).

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