



# Evaluation of the bio-accessible non-process element concentrations in slaker grits by synthetic sweat and gastric fluids extraction

Risto Pöykio<sup>1</sup>, Hannu Nurmesniemi<sup>2</sup>, Olli Dahl<sup>3</sup>, Gary Watkins<sup>3</sup>, Kati Manskinen<sup>4</sup>

## ABSTRACT

**Aim:** The non-process elements (NPEs) or more correctly inorganic process contaminants are compounds that are not necessary for the chemistry of kraft pulping, e.g. heavy metals. The aim of this study was to determine the extractability of NPEs in the slaker grits using artificial sweat and gastric fluids (GFs) to assess the potential occupational risk from grits handling. **Methods:** The slaker grits investigated in this study were sampled in November 2013 from the outlet of the causticizing process at a pulp mill located in Finland. The bio-accessible concentrations of NPEs in the slaker grits were determined using their solubility (extractability) in synthetic sweat (pH = 6.4) and gastric (pH = 1.5) fluids. **Results:** The highest bio-accessible concentration of NPEs in the synthetic sweat fluid was observed for Al (14.0 mg/kg; d.w.), and in the synthetic GF for Al (4920 mg/kg; d.w.) and Ba (163 mg/kg; d.w.). If we disregard the NPEs whose concentrations were lower than the detection limits, the synthetic GF was able to release between 42.6% (Pb) and 81.8% (Ni) of the total element concentrations of NPEs in the slaker grits. **Conclusion:** We conclude that due to the very high bio-accessible concentration of certain NPEs in the synthetic GF, it is necessary to prevent the ingestion and penetration of slaker grits particles across the human gastrointestinal tract.

<sup>1</sup>Environmental Research Unit, City of Kemi, Valtakatu 26, Kemi, Finland, <sup>2</sup>Environmental Research Unit, Stora Enso Oyj Veitsiluoto Mill, Kemi, Finland, <sup>3</sup>Department of Forest Products Technology, Aalto University, School of Chemical Technology, Aalto, Finland, <sup>4</sup>Materials Technology and Environmental Safety, Mikkeli University of Applied Sciences, Mikkeli, Finland

### Address for correspondence:

Dr. Risto Pöykio,  
City of Kemi, Valtakatu 26,  
FI-94100 Kemi, Finland.  
E-mail: risto.poykio@kemi.fi

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## INTRODUCTION

In chemical pulping, fibres are separated from the wood matrix as the lignin is dissolved and removed by cooking at a high temperature. At present, the kraft (sulphate) pulping process, where sodium hydroxide (NaOH) and sodium sulphide are the active cooking chemicals, is the dominating chemical pulping process worldwide due to better pulp quality, its applicability to most wood species, efficient chemical recovery, and low environmental hazardousness compared to other systems [1]. Causticizing system is an important part of the recuperation cycle of the kraft pulp production process. In this system, sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) in green liquor from the recovery boiler is converted in NaOH, which is a component of the digester cooking liquor [2].

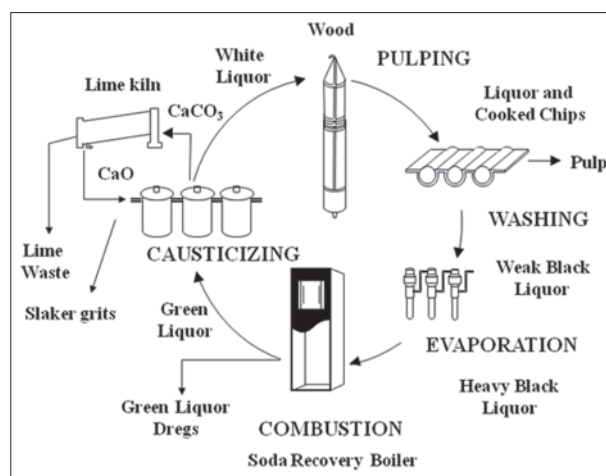
Different processes in the pulp and paper industry result in the formation of different solid wastes and sludges. Solid waste is mainly generated from pulping and wastewater treatment. The amount and composition of the solid wastes depend on the pulp and/or paper produced, the raw materials used, the process techniques applied, and the pulp and/or paper properties to be achieved. The significant residual waste streams from a pulp and paper mill include wastewater treatment sludges, lime mud, slaker grits, green liquor dregs, boiler and furnace ash, and wood processing residuals [3].

Slaker grits are one of the waste by-products from the recovery circuit of a kraft pulp mill. Slaker grits are generated during the hydration, i.e., slaking, of calcium oxide (CaO) generated by the calcining of calcium carbonate (CaCO<sub>3</sub>) in the lime

kiln. Slaker grits are the insoluble material from the reaction of CaO and clarified green liquor to produce calcium hydroxide  $[\text{Ca}(\text{OH})_2]$ . Slaker grits primarily consist of CaO and  $\text{CaCO}_3$ , as well as of non-process elements (NPEs). The NPEs, or more correctly inorganic process contaminants, are compounds that are not necessary for the chemistry of kraft pulping, e.g., heavy metals [4,5]. Carbon, hydrogen, and oxygen form the organic material and are not regarded as NPEs [6]. The NPEs enter the process mainly in raw materials, water and make-up chemicals, and through recycling with bleach plant systems. When NPEs accumulate in process streams through their enrichment in the chemical cycles of a modern kraft pulp mill, they cause various operating problems in the bleach plant. In order to remove NPEs from the process, natural (kidneys) and artificial purges must both be applied. Some water soluble NPEs can be purged along with effluent streams. For other NPEs, filtration or screening process are natural kidneys. The main kidneys associated with the removal of NPEs given rise to residues such as green liquor dregs, slaker grits, lime mud or recovery boiler and lime kiln electrostatic precipitator dust [6,7].

Occupational health and safety risk is posed when industrial by-products are used. The most significant activities that cause potential occupational risks to humans when industrial by-products are used in earthworks are: (1) Transportation of the by-product, (2) intermediate storage in a stockpile, (3) pre-processing of by-products, (4) construction, (5) use of a construction, (6) structural maintenance and repairs, and (7) accident risks. The main human exposure pathways in these work activities are the inhalation of dust or volatile compounds, dermal contact, and ingestion [8]. In terms of human health risk assessment, the main area of concern is the oral/ingestion pathway, followed by respiratory and dermal exposure routes. Once the material enters the body through respiratory and gastrointestinal tracts, it mixes with biological fluids and hence has an opportunity to be dissolved and absorbed [9].

The bio-accessibility of a metal indicates the upper level estimate of risk assessment and is defined as the value representing the availability of metal for absorption when dissolved in synthetic body fluids or juices *in-vitro* [10]. Synthetic (artificial) sweat is an *in-vitro* chemical test model that is used for assaying metal released from products intended to be in close contact with the skin [11]. Synthetic gastric fluid (GF) is the most acidic digestive juices and is therefore likely to yield the greatest fractions of soluble metal compounds or complexes [12]. Although *in-vitro* test by synthetic fluids have been reported to have limitations, e.g., due to the fact that they cannot contain all the constituents of human fluids (e.g., proteins, enzymes, etc.), they provide an appropriate means of determining the bio-accessibility of heavy metals in various materials such as airborne particulate matter [12], ash [13], contaminated soil [14], and waste rock [15]. The aim of this study was to determine the extractability of NPEs in the slaker grits using artificial sweat and GFs to assess the potential occupational risk from grits handling.



**Figure 1:** The causticizing process as part of the pulp mill chemical recovery circuit

## METHODS

### Sampling Procedure

The slaker grits investigated in this study were sampled in November 2013 from the outlet of the causticizing process at a pulp mill located in Finland [Figure 1]. 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 [16]. The sampling was carried out over a period of 3 days, where individual daily samples of 1 kg were combined to give one composite sample with a weight of 3 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 ( $+4^{\circ}\text{C}$ ). A coning and quartering method was applied repeatedly to reduce the grits sample to a size suitable for conducting laboratory analyses [17].

### Determination of the Mineral Composition and Physical and Chemical Properties of the Grits

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  $\text{CuK}\alpha$  radiation. The scan was run from  $5^{\circ}$  to  $80^{\circ}$  ( $2\theta$ -scale), with increments of  $0.02^{\circ}$  and a counting time of 1.0 s/step. The 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 (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 (DMC) 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  $105^{\circ}\text{C}$ . 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 500°C. The total organic carbon (TOC) content was determined according to European standard SFS-EN 13137 using a Leco CHN-600 analyzer (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, instrumentation and quality control is given in our previous paper [16].

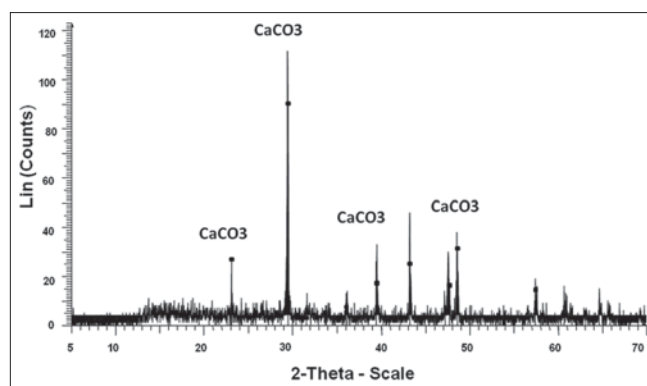
For the determination of the NPEs in different particle size fractions, the slaker grits material was dry sieved on an automatic sieve shaker (Retsch Vibro, Haan, Germany) through stainless-steel sieve sieves using a stack of nested sieves (DIN 4188, Retsch 5657, Haan, Germany) with the following particle size fractions: 63-32 mm, 32-16 mm, 16-8 mm, 8-4 mm, 4-2 mm, 2-1 mm, 1-0.5 mm, 0.5-0.25 mm, 0.25-0.125 mm, 0.125-0.074 mm, 0.074-0.045 mm and <0.045 mm. The weight of each fraction was recorded, and the percent distribution of weight in each fraction was calculated.

### Determination of Total Element Concentrations in the Grits

For the determination of total element concentrations in the grits, the dried samples were digested with a mixture of HCl (3 mL) and HNO<sub>3</sub> (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 [16]. The cooled solutions were transferred to 100 mL volumetric flasks and diluted to volume with ultrapure water. All reagents and acids were suprapure or pro analysis quality. The total element concentrations in the grits were determined with a Thermo Fisher Scientific Inc., iCAP6500 Duo Cambridge (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES). A comprehensive review of analytical methods, instrumentation and quality control is given in our previous paper [16].

### Procedure for Determining the Bio-accessible of NPEs in Slaker Grits using Synthetic Sweat and GFs

Synthetic sweat was prepared by dissolving 5 g NaCl, 1 g lactic acid and 1 g urea in 1 L of deionized water and adjusting the pH to a value of 6.4 with ammonia [18]. Synthetic GF was prepared by dissolving 60.06 g glycine in 2 L of deionized water and adjusting the pH to a value of 1.5 with HCl [19]. The extraction was carried out in polypropylene bottles by shaking 1 g of grits on a dry weight (d.w.) basis with 100 mL of the extract (i.e., synthetic sweat or GF) for 1 h by end-over-end mixing at 37°C. Thus, the liquid-to-solid ratio (L/S 100 L/kg) in our procedure was the same as that of Wang *et al.* [19]. In order to minimize possible chemical and/or microbiological changes in the grits during the extraction procedure, extraction was carried out using an undried grits sample instead of a dried sample, since according to Kosson *et al.* [20], it is preferable to avoid sample drying before extraction. After extraction, the extract was separated from the solid residue



**Figure 2:** X-ray diffraction data of the slaker grits

(i.e., the undissolved grits) by filtration through a 0.45  $\mu$ m membrane filter. The pH of the extract was then measured, and the metal concentrations were determined with a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) ICP-OES.

## RESULTS AND DISCUSSION

### Mineral Composition and Physical and Chemical Properties of the Slaker Grits

According to the X-ray diffraction (XRD) spectra in Figure 2, only calcite (CaCO<sub>3</sub>), which is a silicate mineral, could be identified in our slaker grits. The existence of CaCO<sub>3</sub> in the slaker grits has also been reported by Castro *et al.* [21] and Martins *et al.* [22]. However, Castro *et al.* [21] could detect the existence of (Na<sub>2</sub>CO<sub>3</sub> × H<sub>2</sub>O) in the grits. Furthermore, Martins *et al.* [22] also reported the existence of pirssonite (CaNa<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> × 2H<sub>2</sub>O), portlandite (Ca(OH)<sub>2</sub>) and wustite (FeO) in the grits. One reason for the different detection of minerals in the grits may be differences between the causticizing processes of our mill and those at the mills investigated by Castro *et al.* [21] and Martins *et al.* [22], since according to Martins *et al.* [22], the physical and chemical properties of slaker grits vary significantly depending on the process conditions in which the grits are formed. 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 also one reason why we could not detect all the minerals observed by Castro *et al.* [21] and Martins *et al.* [22], and why elements other than calcium were not identified by XRD, despite the fact that many other elements were measured quantitatively by ICP-OES [Table 1].

Table 2 presents the main important physical and chemical properties of the slaker grits investigated in this study. As seen in Table 2, the pH of the grits was strongly alkaline (pH 12.5). According to van Herck and Vandecasteele [23], the alkaline pH is due to the fact that the proportion of soluble basic metal salts, oxides, hydroxides and carbonates in the waste material outweighs the proportion of soluble acidic components, and thus, the slaker grits subsequently generate an alkaline pH. From the occupational risk point of view, the strongly alkaline nature of the grits (pH = 12.5) is worth noting since the careless handling of this residue may cause skin irritation. According to the EC value (1970 mS/m),

**Table 1: Total (3 mL HCl and 9 mL HNO<sub>3</sub>) and bio-accessible non-process element concentrations (mg/kg; dry weight) in the slaker grits using synthetic sweat and gastric fluids extraction as well as the pH of the extracts before (i.e., only extract) and after (i.e., extract+grits) extraction and the extraction recovery (R%) values for the synthetic body fluids**

| pH and NPE  | Total concentration | Bio-accessible concentration in the synthetic body fluid |       | R% (SF) | R% (GF) |
|-------------|---------------------|----------------------------------------------------------|-------|---------|---------|
|             |                     | SF                                                       | GF    |         |         |
| pH (before) |                     | 6.4                                                      | 1.5   |         |         |
| pH (after)  |                     | 8.8                                                      | 2.5   |         |         |
| Al          | 6500                | 14.0                                                     | 4920  | 0.2     | 75.7    |
| As          | <3.0                | <1.5                                                     | <1.5  |         |         |
| Ba          | 230                 | 6.0                                                      | 163   | 2.6     | 70.9    |
| Cd          | <0.3                | <0.15                                                    | <0.15 |         |         |
| Co          | 1.8                 | <0.5                                                     | 1.1   | <27.8   | 61.1    |
| Cr          | 15.0                | <1.0                                                     | 12.0  | <6.7    | 80.0    |
| Cu          | 2.6                 | <1.0                                                     | <1.0  | <38.5   | <38.5   |
| Mo          | <1.0                | <0.5                                                     | <0.5  |         |         |
| Ni          | 33.0                | <0.5                                                     | 27.0  | <1.5    | 81.8    |
| Pb          | 4.7                 | <1.5                                                     | 2.0   | <31.9   | 42.6    |
| V           | 40.0                | 2.3                                                      | 30.0  | 5.8     | 75.0    |
| Zn          | 33.0                | <1.5                                                     | 21.0  | <4.5    | 63.6    |

SF: Sweat fluid; GF: Gastric fluid; NPE: Non-process element

**Table 2: Physical and chemical properties of the slaker grits**

| Parameter                         | Unit        | Slaker grits |
|-----------------------------------|-------------|--------------|
| pH (1:5)                          |             | 12.5         |
| Electrical conductivity (1:5)     | mS/m        | 1970         |
| Loss-on-ignition (550°C)          | % (d.w.)    | 0.7          |
| TOC                               | g/kg (d.w.) | 0.1          |
| <b>Dry matter content (105°C)</b> | <b>%</b>    | <b>78.8</b>  |
| 32 ≤ size < 63 (mm)               | Weight (%)  | 0            |
| 16 ≤ size < 32 (mm)               | Weight (%)  | 1.8          |
| 8.0 ≤ size < 16 (mm)              | Weight (%)  | 4.6          |
| 4.0 ≤ size < 8.0 (mm)             | Weight (%)  | 4.9          |
| 2.0 ≤ size < 4.0 (mm)             | Weight (%)  | 11.3         |
| 1.0 ≤ size < 2.0 (mm)             | Weight (%)  | 19.1         |
| 0.5 ≤ size < 1.0 (mm)             | Weight (%)  | 23.6         |
| 0.25 ≤ size < 0.5 (mm)            | Weight (%)  | 23.3         |
| 0.125 ≤ size < 0.25 (mm)          | Weight (%)  | 4.7          |
| 0.074 ≤ size < 0.125 (mm)         | Weight (%)  | 1.0          |
| 0.045 ≤ size < 0.074 (mm)         | Weight (%)  | 3.4          |
| Size < 0.045 (mm)                 | Weight (%)  | 2.2          |
| Sieving loss                      | Weight (%)  | 0.1          |

pH: Phosphate; d.w.: Dry weight; TOC: Total organic carbon

which is an index of the total dissolved electrolyte concentrations, the extraction solution of the slaker grits material have a very high ionic value, which also indicates that part of the dissolved NPEs occur in the grits as dissolved basic metal salts. The very low TOC value (0.1 g/kg; d.w. = 0.01%; d.w.) and low LOI value (0.7 %; d.w.) indicate that the organic matter content in the grits is low. The relatively low DMC (78.8 %) of slaker grits is an advantage, since dust problems during handling are not very likely.

According to Table 2, no particles of diameter range between 32 and 63 mm existed in the slaker grits material. The particle size 0.5-1.0 mm accounted for 23.6 weight percent. The slaker

grits material consists of particles with a relatively large diameter, since the particles in the diameter range smaller than 0.074 mm accounted for only 5.6 weight percent. However, from the utilization point of view, the smallest particles are of the greatest concern for dust generation potential when industrial residues are handled at landfill sites.

### Total and Bio-accessible NPE Concentrations in the Slaker Grits

According to Mroueh *et al.* [8], the most significant activities that cause potential occupational risks to humans when industrial by-products are used are: (1) Transport of the by-product, (2) intermediate storage in a stockpile, (3) pre-processing of by-products, (4) construction, (5) use of a construction, (6) structural maintenance and repairs, and (7) accident risks. According to Mroueh and Wahlström [24], the main human exposure pathway during these work activities is the inhalation of dust or volatile compounds, dermal contact and ingestion. In addition, the typical exposure pathways in the environment affect the flora and fauna of the site, as well as ground and surface waters [8].

In terms of human health risk assessment, the main area of concern is the oral/ingestion pathway, followed by respiratory and dermal exposure routes [9,24]. Although the skin provides a large surface area, according to Twining *et al.* [9], it is relatively impervious to solids such as ash particles. However, the highly alkaline nature of the Slaker grits [pH = 12.5; Table 2] may cause skin irritation. Once the material enters the body through the respiratory and gastrointestinal tracts, it mixes with biological fluids and hence has an opportunity to be dissolved and absorbed [9].

Although the NPEs in the slaker grits investigated in this study were extractable in the synthetic sweat and GFs, this does not necessarily mean that humans working in landfill areas or in earthworks are exposed to the heavy metals in grits. The extractable concentrations of NPEs in the synthetic sweat and GFs cannot be used for assessing the level of human exposure, because we have not carried out any experiments to determine the dose of grits for humans. As human exposure assessment associated with grits handling is complex, in this context, we only discuss the extractability of certain NPEs in slaker grits by synthetic sweat and GFs. However, the extractability (solubility) of NPEs in synthetic body fluids should be determined in order to understand the possible occupational risks associated with grits handling.

Table 1 presents the total and bio-accessible concentrations of NPEs in the slaker grits. The highest individual total concentration for NPEs was observed for Al (6500 mg/kg; d.w.), following by Ba (230 mg/kg; d.w.), V (40.0 mg/kg; d.w.), as well as equal concentrations of 33.0 mg/kg (d.w.) for Ni and Zn. If we disregard the NPEs whose concentrations were lower than the detection limits, the bio-accessible concentrations of NPEs in the synthetic GF were higher than those in the artificial sweat fluid (SF). These results are reasonable in the light of the fact that the pH of the synthetic GF was extremely acidic both before



(pH = 1.5) and after (pH = 2.5) extraction, whereas the pH of the synthetic SF was slightly alkaline before (pH = 6.4) and after extraction (pH = 8.8). Except for Al (14.0 mg/kg; d.w.), Ba (6.0 mg/kg; d.w.) and V (2.3 mg/kg; d.w.), the bio-accessible concentrations of other NPE concentrations in the synthetic sweat were lower than the detection limits. The bio-accessible concentration of Ba (6.0 mg/kg; d.w.) in the synthetic sweat is reasonable, since Ba is able to form oxyanions, which means that its extractability clearly increases from acidic pH values to neutral and alkaline conditions [25].

The highest bio-accessible concentrations of NPEs in the synthetic GF were observed for Al (4920 mg/kg; d.w.) and Ba (163 mg/kg; d.w.). These concentrations are correspondingly ca. 351 and 27 times higher than those in the synthetic SF. The bio-accessible concentrations of V (30.0 mg/kg; d.w.), Ni (27.0 mg/kg; d.w.), Zn (21.0 mg/kg; d.w.) and Cr (12.0 mg/kg; d.w.) in the synthetic GF were moderate. These results are reasonable considering that the pH of the GF was extremely acidic both before (i.e., pH = 1.5) and after (i.e., pH = 2.5) extraction. According to our previous study [26], the heavy metals such as Al, Cd, Co, Cr, Cu, Ni, Pb, and Zn, have highest solubility in extreme or strongly acidic conditions, although metals such as Cr, Zn, Cu, As and Pb, are reported to be amphoteric metals, which means that they are clearly soluble also in alkaline conditions, but are relatively insoluble at neutral pH values. In this context, it is worth noting that according to Ludwig *et al.* [27], the element release from waste material depends not only on the extraction method and the type of extractant used, but also on the element, type of matrix and the chemical and mineralogical characteristics of the waste matrix.

The extraction recovery (R%) values for NPEs in Table 1 indicate the ability of synthetic body fluid to release metals from the slaker grits matrix. The R% values were determined at the ratio of the NPEs concentration extracted with the synthetic body fluid. The abbreviation R% (SF) in Table 1 means the extraction recovery value for NPEs when synthetic SF was used as extractant. Correspondingly, the R% (GF) means the extraction recovery value for NPEs when synthetic GF was used as extractant. The R% values for NPEs in Table 1 have not been calculated in those cases in which the total or the extractable concentrations of a NPE was lower than the limit of detection by ICP-OES. If we disregard the NPEs whose concentrations were lower than the detection limits, according to Table 1, the highest extraction recovery value of 5.8% in the synthetic SF was observed for V. Furthermore, if we disregard the NPEs whose concentrations were lower than the detection limits, the highest extraction recovery value of 81.8% in the synthetic GF was observed for Ni. The R%-values in Table 2 indicate that the synthetic GF was able to release NPEs more effectively from the slaker grits matrix than the synthetic SF. Therefore, taking into consideration the toxicity properties of many of the NPEs in the slaker grits and the relatively high bio-accessible concentrations of certain NPEs in synthetic GF, we conclude that, careful handling of this residue is recommended to minimize human health risks, especially if it causes dusting.

## CONCLUSIONS

The bio-accessible concentrations of NPEs in the synthetic SF were relatively low, since the highest individual concentration of 14.0 mg/kg (d.w.) was observed for Al, following by Ba (6.0 mg/kg; d.w.) and V (2.3 mg/kg; d.w.). From the human health risk assessment point of view, the careful handling of this residue is recommended. The strongly alkaline nature of the grits (pH 12.5) is worth noting since dermal contact of this residue may cause skin irritation. The highest bio-accessible concentrations of NPEs in the synthetic GF were observed for Al, which was 4920 mg/kg (d.w.). This is 75.7% of the total concentration of Al (6500 mg/kg; d.w.) in the slaker grits. Furthermore, the bio-accessible concentration of Ba (160 mg/kg; d.w.) in the slaker grits using synthetic GF was elevated, and the concentrations of V (30.0 mg/kg; d.w.), Ni (27.0 mg/kg; d.w.) and Zn (21.0 mg/kg; d.w.) moderate. Therefore, in terms of human health risk assessment, we conclude that careful handling of slaker grits is recommended in order to prevent particle dusting and the penetration of particles across the human gastrointestinal tract, e.g., through inadvertent wiping of the mouth with dirty hands or through the inhalation of air-borne particles.

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