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NOVEL TREATMENT METHODS FOR GREEN LIQUOR DREGS AND ENHANCING CIRCULAR ECONOMY IN KRAFT PULP MILLS

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Thesis for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in the auditorium of the student union building at Lappeenranta University of Technology, Lappeenranta, Finland on the 17th of December, 2018, at noon.

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Supervisors Professor Antti Häkkinen
LUT School of Engineering Science
Lappeenranta University of Technology
Finland

D.Sc. Teemu Kinnarinen
LUT School of Engineering Science
Lappeenranta University of Technology
Finland

Reviewers Assoc. Prof. Morten Lykkegaard Christensen
Department of Chemistry and Bioscience
Aalborg University
Aalborg, Denmark

Prof. Hans Theliander
Department of chemistry and chemical engineering
Chalmers University of Technology
Göteborg, Sweden

Opponent Assoc. Prof. Morten Lykkegaard Christensen
Department of Chemistry and Bioscience
Aalborg University
Aalborg, Denmark

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Abstract

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Green liquor dregs (GLD) are known to be the largest fraction of inorganic residue in the kraft pulping process, or even in virgin pulp production. GLD originates from the chemical recovery cycle where effective cooking chemicals sodium hydroxide and sodium sulfide are regenerated from black liquor. Black liquor is the mixture of spent cooking chemicals and dissolved wood components which is resulted from delignification process where lignin is removed from wood chips. Unfortunately, GLD is still landfilled, while converting this residue to sustainable products would be considered as an achievement as regards material utilization in circular economy.

The main obstacle in converting this inorganic residue to sustainable products, i.e. fertilizing products, is the level of some metals with environmental pollution effects. Of the inorganic residues generated in the kraft pulping process, GLD is not the most enriched one by nutrient elements, but it could be suitable for soil fertilizing usages. However, removal of environmentally hazardous metals from GLD still remains as a challenge for currently applied separation techniques.

The present study is divided to two parts: in the first part the filtration characteristics of GLD are studied, and in the second part, practical methods for the separation of target hazardous trace metals such as Cd, Ni, Pb and Zn are studied. The results of the first part reveal that the filterability of GLD sludge can be improved by optimized filtration parameters without a need for filter aids such as a lime mud precoat.

In the second part of the study, the separation of hazardous metals by the use of chelating agents as the extractant and mechanical classification are investigated. The chelating agent EDTA is utilized successfully in the extraction of the target hazardous metals, especially Cd from GLD, while keeping most of Ca, which is the main mineral nutrient present in GLD. Hydrocyclone classification of GLD reveals that the target hazardous metals are mainly accumulated in the finer fraction of GLD separated into the overflow. The coarser underflow fractions containing a larger share of GLD and its Ca content are assessed regarding categorizing them as CE-marked fertilizing products. The results prove that the concentration of hazardous metals in GLD is reduced in the underflow fractions to a level lower than the maximum allowed concentrations in CE-marked fertilizing products.

This study is the first in which chemical and mechanical treatment methods are implemented successfully by novel methods in the separation of hazardous metals from GLD. The outcome of this thesis can be used for developing novel treatment processes in kraft pulp mills to reduce the amount of inorganic solid wastes, and to separate toxic metals from GLD while keeping its main nutrients.

Keywords: Kraft pulp mill, Green liquor dregs, Hazardous trace metals, Filtration characteristics, Chelating agents, Hydrocyclone classification, Circular economy

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Lappeenranta, Finland, December 2018

Mohammad Golmaei

Contents

Publications

List of publications

This thesis is based on the following papers. Rights have been granted by the publishers to include the papers in a doctoral dissertation.

I Kinnarinen, T., Golmaei, M., Jernström, E., Häkkinen, A., 2016. Separation, treatment and utilization of inorganic residues of chemical pulp mills. *J. Clean. Prod.*, 133, 953–964.

II Golmaei, M., Kinnarinen, T., Jernström, E., Häkkinen, A., 2017. Study on the filtration characteristics of green liquor dregs. *Chem. Eng. J.*, 317, 471–480.

III Golmaei, M., Kinnarinen, T., Jernström, E., Häkkinen, A., 2018. Extraction of hazardous metals from green liquor dregs by ethylenediaminetetraacetic acid. *J. Environ. Manage.*, 212, 219-227.

IV Golmaei, M., Kinnarinen, T., Jernström, E., Häkkinen, A., 2018. Efficient separation of hazardous trace metals and improvement of the filtration properties of green liquor dregs by a hydrocyclone. *J. Clean. Prod.*, 183, 162-171.

Author's contribution

The author has been responsible for planning the research, performing the experimental work, processing the data, part of the chemical analyses, and writing journal papers II, III and IV. In Paper I, which is a review article, the author made significant contribution to collecting and analyzing the information available in the current literature. The SEM images and ICP analyses of the samples were carried out by others.

Related Publications

M. Golmaei, T. Kinnarinen, Eeva Jernström, A. Häkkinen. Effect of hydrocyclone classification on the filtration characteristics of green liquor dregs. FILTECH conference (Cologne, Germany), March 2018.

Nomenclature

Latin alphabet

A	Filtration area	m^2
A_c	Surface area of cake	m^2
a	Slope of t/V vs. V line	$s\ m^{-6}$
b	Intersection of t/V vs. V line and y-axis	$s\ m^{-3}$
C_P	Corrected partition number	–
c	Filtration concentration	$kg_{cake}\ m^{-3}{}_{filtrate}$
D	Diameter of particle	µm
D_C	Hydrocyclone diameter	m
d	Particle size	µm
E_t	Total separation efficiency of hydrocyclone	–
F	Distribution function for the particle	–
f	Weight fraction of particles in the feed of hydrocyclone	–
m_i	Mass of solids in the feed flow of hydrocyclone	kg
m_u	Mass of collected solids in the underflow of hydrocyclone	kg
n	Compressibility index	–
n_R	Uniformity index	–
Q	Volumetric flow rate of feed suspension	$m^3\ s^{-1}$
q	Volumetric flow rate of liquid	$m^3\ s^{-1}$
P	Partition number	–
ΔP	Pressure drop in hydrocyclone	Pa
Δp	Total pressure difference	Pa
Δp_c	Pressure difference through cake	Pa
Δp_m	Pressure difference through filter medium	Pa
L	Thickness of porous medium or filter cake	m
K	Permeability	m^2
K_0	Kozeny constant	–
S_0	Volume-specific surface of the bed	$m^2\ m^{-3}$
R	Total filtration resistance	m^{-1}
r	Weight fraction of particles bypassing hydrocyclone	–
R_c	Cake resistance	m^{-1}
R_m	Medium resistance	m^{-1}
w	Mass of cake per unit of filtration area	$kg\ m^{-2}$
V	Volume of filtrate	m^3
V_s	Volume of filtrate at filtration pressure stabilization point	m^3
t	Time	s
t_s	Filtration pressure stabilization time	s
u	Weight fraction of particles in the underflow of hydrocyclone	–

Greek symbols

α	Specific cake resistance	m kg^{-1}
α_0	Specific cake resistance at specific pressure drop	m kg^{-1}
α_{av}	Average specific cake resistance	m kg^{-1}
ε	Voidage of the bed or local porosity	–
ρ	Density of liquid	kg m^{-3}
μ	Dynamic viscosity of liquid	Pa s

Abbreviations

APAM	Anionic polyacrylamide
ARD	Acid rock drainage
DCyTA	Diaminocycloexanetetraacetic acid
DTPA	Diethylenetriamine pentaacetic acid
ECF	Elemental chlorine-free
EDDS	Ethylene diamine tetraacetate
EDTA	Ethylenediaminetetraacetic acid
EGTA	Ethyleneglycol tetraacetic acid
ESP	Electrostatic precipitator
GLD	Green liquor dregs
ICP-OES	Inductively coupled plasma optical emission spectrometer
ICP-MS	Inductively coupled plasma mass spectrometer
IDSA	Iminodisuccinic acid
MGDA	Methylglycine diacetic acid
NPEs	Non-process elements
NTA	Nitrilotriacetic acid
PFC	Product function category
PPB	Parts per billion
TDS	Total dissolved solids
TSS	Total suspended solids
REE	Rare earth elementIntroduction

1 Introduction

1.1 Background

The world’s largest share of virgin pulp is produced by the kraft pulping process, while the largest inorganic waste fraction of this process, the so-called green liquor dregs (GLD), is still disposed to landfill areas (Mäkitalo et al., 2012; Tran and Vakkilainen, 2007). GLD, together with the other inorganic solid residues such as lime mud, chemical recovery boiler fly ash and slaker grits originate from the chemical recovery cycle which is mainly responsible for kraft cooking chemical recovery. Before landfilling, GLD is washed and dried by different methods of cake filtration, cross-flow filtration or centrifugation to recover the remaining green liquor after the purification stage. Green liquor contains valuable sodium which can be converted to cooking chemicals, so its recovery is highly important for the kraft pulping process from the economical point of view. In addition, the recovery of green liquor from the dregs is a way to prohibit their release into the soil and their further environmental contaminating effects (Tikka, 2008). Non-process elements (NPEs) such as Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Ti, V, and Zn are accumulated in the dregs (Nurmesniemi et al., 2005), and therefore NPEs are also purged out of the chemical recovery cycle together with GLD. For this reason the GLD separation stage is considered as the ’’kidney’’ in the chemical recovery cycle.

The currently applied filtration and washing techniques for GLD treatment are somehow capable to recover the soluble sodium, while the level of insoluble NPEs remains unchanged in the dregs after treatment. Apart from the comprehensive studies done by Nurmesniemi et al. (2005) and Manskinen et al. (2011) on the extractability of NPEs from GLD, a practical method for separating the hazardous metals from this residue has not been introduced yet. This residue can be converted to a valuable raw material for producing new sustainable materials, after reducing the level of the hazardous metals in it. GLD is a suitable raw material for producing fertilizers, as it is enriched by base cations such as K, Ca and Mg (Rothpfeffer, 2007). In addition, producing forest fertilizers from GLD is a practical method to recycle the lost nutrients to the ecosystem as well (Mahmoudkhani et al., 2004). On the other hand, producing new sustainable materials from the main inorganic solid residue of kraft pulp mills would be a great attempt to achieve circular economy in the pulp industry. In the first part of the current study, the filtration characteristics of GLD are discussed. In the second part, the separation of the NPEs from the dregs by leaching and mechanical classification is investigated.

1.2 Objectives and outline of the thesis

The main target of this study is to find industrially applicable techniques for efficient removal of NPEs from GLD. In order to use GLD to produce environmentally non-hazardous fertilizers, it is necessary to find a treatment method to remove NPEs from

GLD while keeping its nutrient content. Therefore, the extractability of Ca, which is the most abundant nutrient element in GLD, with the investigated techniques was studied as well. Of the NPEs present in GLD, Cd, Ni, Pb and Zn were considered as hazardous target metals in this study. The two micronutrient elements of Ni and Zn were classified as target hazardous metals due to their high level in GLD. Prior to investigating new treatment methods for the GLD, the filtration properties of GLD sludge were studied. The main objectives and the outlines of this study can be divided to main bullet points as listed below:

- *Literature review on the origin of green liquor dregs and their chemical properties*

  As the first step of the study, a comprehensive literature review was done to collect information from previous studies about the origin, commonly applied treatment methods and chemical properties of GLD. In addition, possible methods for the extraction of NPEs from green liquor dregs were looked for. This study was published together with the study done on the other inorganic residues of kraft pulp mills by Kinnarinen et al. (2016) (*Paper I*).

- *The effect of the filtration operating variables on the filtration characteristics of green liquor dregs, and the extractability of sodium and NPEs*

  Purification of green liquor from dregs is still a major challenge in kraft pulping process due to the formation of a highly resistant dregs cake in the filtration equipment. The effects of filtration variables, such as filter cloth permeability, temperature and pressure on the filterability of the GLD sludge and the characteristics of the dregs cake were studied. The filtration experiments were carried out without using a lime mud precoat. The effect of filtration temperature on the recovery of sodium and some of the NPEs from the dregs were investigated as well. In this study, it was found that the NPEs were mostly accumulated in the dregs, and the filtration temperature had no tangible effect on their mobilization. The outcome of this study was published by Golmaei et al. (2017) (*Paper II*).

- *Extraction of non-process elements from green liquor dregs by leaching*

  The outcome of primary studies on the filtration characteristics of GLD sludge revealed that hazardous metals were accumulated in the dregs. So, the extractability of hazardous metals and some of the other non-process elements (NPEs) from the dregs cake by utilizing chelating agents was studied in next level of the research. Through primary leaching experiments on the extractability of NPEs from the dregs cake by the use of ethylenediaminetetraacetic acid (EDTA) and ethylene glycol-bis(β-aminoethyl ether)-N,N,N',N'-tetraacetic acid (EGTA) as chelating agents, EDTA was selected for further study. The result of this study showed efficient extraction of two hazardous metals, Cd and Pb, from the dregs by the use of EDTA in a relatively fast reaction, while most of Ca remained in the dregs after leaching. In addition, the results showed that EDTA could be a suitable extractant also for the removal of other NPEs from the dregs. It should be mentioned that the treatment of the resulting supernatant solution will remain as a challenge in the process. The outcome of this study was published by Golmaei et al. (2018) (*Paper III*).

- *Efficient separation of Ca and non-process elements from green liquor dregs by mechanical classification*

  As the final treatment method, the separation of Ca and non-process elements (NPEs) by mechanical classification of the dregs was investigated by using a hydrocyclone. In the hydrocyclone, dregs are classified into a coarser underflow fraction and a finer overflow fraction according to their size and density. The results showed that hazardous metals Cd, Ni, Pb and Zn accumulated mostly in the finer overflow fraction, while Ca was mostly concentrated in the coarser underflow fraction. Furthermore, the effect of dregs classification by hydrocyclone on the filtration characteristics of GLD sludge was studied. The outcome of this study was published by Golmaei et al. (2018b) (*Paper IV*).

2 Chemical recovery cycle

The chemical recovery cycle is mainly responsible for the recovery of kraft cooking chemicals, such as sodium sulphide (Na_2S) and caustic sodium hydroxide (NaOH) from black liquor. In kraft pulp mills, the mixture of kraft cooking chemicals, which is so-called white liquor is utilized in the chemical delignification of wood chips. During kraft pulping, degradation and dissolution of lignin happens in a series of chemical reactions at elevated temperatures (Ek et al., 2009; Sixta, 2006a). The recovery and reuse of white liquor is necessary for an economically efficient kraft pulping process, due to the high cost of sodium hydroxide and sulfide. Kraft cooking chemicals are recirculated through the chemical recovery cycle. In recent years, the efficiency of this process has been improved considerably not only from economical aspects, but also for environmental issues (Tikka, 2008; Zumoffen and Basualdo, 2008). A schematic view of the kraft chemical recovery cycle is illustrated in Figure 2.1.

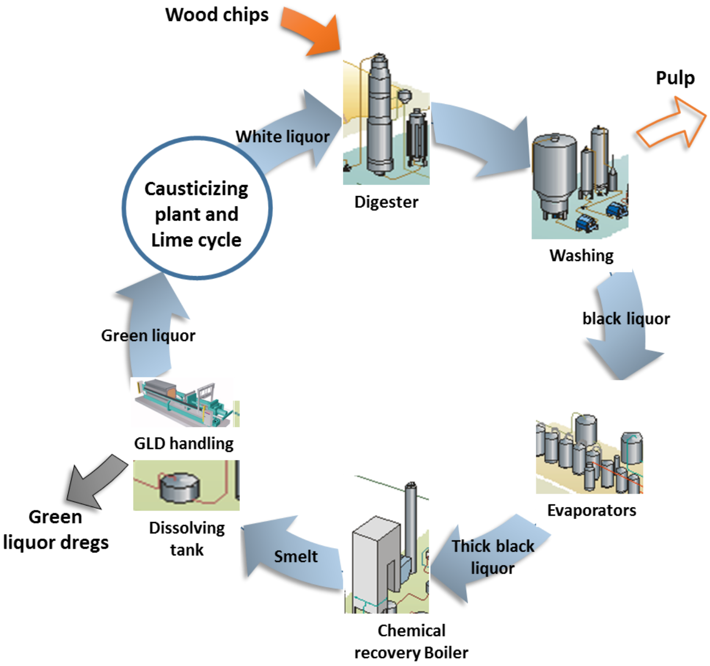


Figure. 2.1. A schematic view of the chemical recovery cycle of kraft pulp mills.

Prior to the kraft pulping process, the received logs and chips are processed through wood yard operations to have a homogeneous feed for the pulping process. As can be seen in Figure 2.1, the wood chips are firstly delignified in a digester by utilizing white liquor, and then the resulted mixture of pulp and black liquor is sent to the washing stage. The black liquor contains dissolved lignin and spent cooking chemicals. At the brown stock washing stage, the black liquor is separated from the pulp (Sixta, 2006b; Tikka, 2008).

The postdelignification of separated pulp is done in a bleaching tower to obtain a certain brightness coefficient (Castro and Doyle, 2002; Klugman et al., 2007). As shown by Figure 2.1, the resulting black liquor from the washing stage is sent to evaporators to increase its net heating value by the removal of excess water. Then the thick black liquor is combusted in a chemical recovery boiler to produce a sodium-enriched inorganic smelt and high-pressure steam for the generation of electricity and medium and low pressure steam for process needs. At the next stage, GLD sludge is formed by mixing the smelt with weak white liquor in a dissolving tank. Undissolved content of smelt remains in the sludge in the form of solid particles, which are so-called dregs. The dregs are separated from the green liquor in the purification stage, and sent for further treatment by washing and dewatering before landfilling. Finally, the purified green liquor is sent to the causticizing plant to convert its sodium carbonate content to sodium hydroxide, which is the main component of white liquor (Sixta, 2006b; Tikka, 2008).

2.1 Evaporation

The black liquor obtained from the pulp washing stage is a solution with dry solids content varying from 14 % to 18 %, depending on the raw material and the efficiency of the washing plant. The main aim of evaporation stage is to increase the solid content of the black liquor to elevate its heating value before combusting in the chemical recovery boiler. After evaporation, the dissolved solid content of the black liquor should reach the allowed minimum level (65 %) for combusting in the recovery boiler (Ek et al., 2009; Tikka, 2008).

The black liquor evaporation stage comprises three principal unit operations. Through the first unit operation, concentrated black liquor is generated by evaporating a significant amount of its water content. At the second unit, the condensate is processed by separation of clean and fouled condensate fractions. Finally, the formed soap is removed from the black liquor and sent to tall oil production (Tikka, 2008; Tran and Vakkilainen, 2007).

2.2 Chemical recovery boiler

The concentrated (thick) black liquor is combusted in a chemical recovery boiler comprising a furnace which also performs as a heat exchanger and several heat exchanger units. Briefly, the chemical recovery boiler in the kraft mill is responsible for producing high-pressure steam by burning the organic content of the black liquor, recovering the inorganics from the black liquor and reducing the inorganic sulfur compounds of the black liquor to sodium sulfide (Sixta, 2006b). In recent years, serious developments have taken place in chemical recovery boiler design to increase production capacity and enhance energy efficiency (Tikka, 2008).

The most commonly applied design today is the two-drum chemical recovery boiler (Tikka, 2008). In the recovery boiler, the pre-heated black liquor is sprayed through a number of nozzles (typically with a diameter of 2-3 mm), i.e. liquor guns, into the furnace.

In the space between the liquor gun and the bottom of the furnace, after quick drying, the droplets are ignited and burned to form char. The char particles fall down on the char bed which is located on top of the smelt, where the sulfate is reduced to sulfide by carbon combustion, releasing carbon monoxide and dioxide gasses. The resulted smelt which contains mainly sodium carbonate and sodium sulfide is released from the furnace via several smelt spouts. The required oxygen for combustion is provided by pre-heated air injected onto the bottom of the furnace through the primary and secondary levels of the air ports. Various reactions including sulfate reduction in which carbon is the reducing agent happen in recovery boiler (Sixta, 2006b; Tran and Vakkilainen, 2007).

The tertiary level of the air ports is located above the liquor guns to supply the demanded oxygen for completing the oxidation of the gaseous reaction. Most of the inorganic constituents of the black liquor remain in the smelt, while the rest of them leave the furnace as fume with the flue gas products (Sixta, 2006b; Tran and Vakkilainen, 2007). For instance, a significant fraction of sodium and potassium is converted into alkali salt ash particles after releasing into the flue gas (Mikkanen, 2000; Mikkanen et al., 1999).

The temperature of the flue gas is reduced to about 180 °C after passing through the superheaters, boiler bank and economizers. High-pressure steam is generated from the feed water by countercurrent flow of the flue gas. The generated high-pressure steam enters a steam turbine to produce electrical power, low-pressure and medium-pressure process steam. The flue gas carries a considerable dust load, some of which remain as scale on the surface of the heat exchanger and the rest exit the boiler together with flue gas. The dust loads are separated from the flue gas by an electrostatic precipitator (ESP) which is located before the induced draft fans blowing the flue gas into the stack (Sixta, 2006b).

Most of the captured dusts by ESP are mixed with the fed black liquor into the chemical recovery boiler. The flue gas carries also out emissions such as sodium sulfate (Na_2SO_4), sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) (Hupa, 1993). The collected dusts from the flue gas are generally called chemical recovery boiler fly ash, but the specific term of ESP ash is collected dusts from the electrostatic precipitator.

The molar ratio between the total sulfur and sodium of the used black liquor in the recovery boiler is an important factor for the chemistry of the recovery boiler. An ideal recovery boiler converts all the diverse sulfur and sodium compounds into sodium sulfide (Na_2S) and sodium carbonate (Na_2CO_3) in the smelt. However, there is deviation from the ideal recovery boiler in the actual process where the molar ratio (Na_2S/total S) is typically about 90-95 % in the smelt, because sodium sulfate is also formed in the smelt (Hupa, 1993).

2.3 Smelt dissolving tank

The smelt obtained from the chemical recovery boiler is dissolved by mixing with the weak lime mud wash liquor (weak white liquor) at the smelt dissolving tank. Some of the smelt is dissolved to form green liquor, which contains mainly sodium carbonate and sodium sulfide (Sixta, 2006b; Tikka, 2008). According to Lidén (1995), the reason for the green colour of green liquor is probably the presence of an iron ion. The unburned carbon and insoluble inert material which remains in this solution from the smelt are detrimental to the downstream chemical recovery and pulping process. These impurities are so-called dregs, and they are removed from the green liquor in a purification stage before sending it to the causticizing plant (Sixta, 2006b; Tikka, 2008).

2.4 Green liquor purification and dregs handling

Prior to the causticizing plant, the green liquor is purified to remove the green liquor dregs (GLD), and to avoid further contamination in the lime cycle. For this purpose, the solid GLD formed in the smelt dissolving tank is separated from the green liquor in the purification stage by sedimentation or filtration (Ek et al., 2009; Tikka, 2008). Since most of non-process elements (NPEs) in the sludge obtained from the smelt dissolving tank are accumulated in the dregs, green liquor purification is considered as the ’’kidney’’ in the chemical recovery cycle. In other words, the removal of GLD from the chemical recovery cycle is a way to control the level of NPEs in this loop (Kinnarinen et al., 2016; Mäkitalo et al., 2012; Sedin and Theliander, 2004). The accumulation of NPEs in the recovery cycle results in failures, such as scaling of the equipment, i.e. evaporators by the precipitation of sodium aluminosilicate complex caused by Al and Si ions (Park and Englezos, 1998).

GLD handling is necessary before disposal, not only to recover the remaining green liquor, but also to prohibit contamination of the soil and water resources by the release of leachable chemicals. Therefore, the GLD separated from the green liquor is washed and dewatered before landfilling (Sanchez and Tran, 2005; Tikka, 2008).

2.4.1 Green liquor purification

Green liquor purification, which is also called the primary separation process is commonly performed by sedimentation and filtration. During last decades, sedimentation clarification of green liquor has been mostly replaced by filtration due to its higher efficiency (Ek et al., 2009; Tikka, 2008).

As dregs are slow-settling materials, flocculants are required for faster and more efficient separation of dregs in conventional settling clarifiers, especially in a high load condition (Sanchez and Tran, 2005; Taylor, 2013). The accumulation of Mg in the chemical recovery cycle causes problems in green liquor clarification by forming fine dreg particles containing magnesium hydroxide (Tikka, 2008). A research done by Ellis and Empie (2003) showed that dregs settling can be improved by increasing the calcium concentration in the green liquor. Also the formation of poor settling dregs can be prevented by adding aluminum ions to the dissolving tank. For this purpose, aluminum sulfate is added to the weak wash in the smelt dissolving tank (Löwnertz et al., 1996). On the other hand, it is important to reduce the concentration of dissolved aluminum in the green liquor to prevent its accumulation in the chemical recovery cycle. For this purpose, magnesium sulfate is added to the green liquor, to precipitate aluminum (III) ions in the form of double salt hydrotalcite ($Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2}\cdot nH_2O$), which will be removed together with the dregs (Ulmgren, 1987). Hydrotalcite can be formed in the green liquor when the molar ratio of Mg/Al is between 2:1 to 5:1 (Taylor, 2013).

In the conventional green liquor clarifier, sludge is fed through a distribution box located in the middle of the clarifier to make sure that it is distributed evenly in all directions inside the clarifier. In order to stabilize the density, temperature and flow variations of the green liquor sludge, which have an effect on the clarification efficiency, a feed tank is installed for the clarifier. At the bottom of the clarifier, where the dregs are collected due to their density difference with the green liquor, a rake is installed to move them to a hole for sludge removal, which is located at the middle of the tank. The consistency of the removed sludge, which is known as clarifier underflow is 2% to 5%. The overflow of the green liquor containing 60 – 100 mg suspended solids/L is collected from the top of the clarifier (Tikka, 2008).

The sludge blanket clarifier is another type of clarifier used for green liquor purification, with a higher load than a conventional clarifier. In sludge blanket clarifiers, the feed is first brought beneath a flocculated sludge layer. Then the feed flows upward from the bottom of a funnel which is located at the centre of clarifier. At a certain height of the funnel, a balance is reached between the gravitational forces and upward forces on the flocs. Consequently, a layer of remained stationary flocs, i.e. a blanket is formed in this region. This layer acts as a filtration medium which the liquor must pass. As an advantage, the surface area of the blanket clarifier is 5 to 10 times smaller than that of conventional clarifiers, but its need for flocculants is higher (Ives, 1968; Tikka, 2008).

In general, the strengths of green liquor purification by a clarifier are efficient removal of magnesium and iron, as well as low energy demand (Taylor and Bossons, 2006; Taylor and McGuffie, 2007; Tikka, 2008). There are limitations in the use of clarifiers for green liquor purification such as the need for flocculants, low consistency of the withdrawn sludge, a required further deliquoring stage, and large installation space (Campbell and Empie Jr, 1998; Taylor, 2013; Tikka, 2008).

Two major filtration methods for green liquor purification are falling film cross-flow filtration and cake filtration, out of which cake filtration can be performed with or without a precoat layer (Ek et al., 2009; Tikka, 2008). Cake formation is prevented in cross-flow filtration by applying a strong tangential flow, while in cake filtration the filter cake is formed by trapped solids on the surface of the filter cloth (Svarovsky, 2000; Wakeman and Tarleton, 1999).

As an industrial case of a falling film cross-flow filter, an Ahlstrom X-filter was installed in 1994 for green liquor purification at Wisaforest Oy Ab., Jakobstad, Finland. The X-filter has a pressure vessel that includes vertically mounted filter elements (Keskinen et al., 1995). In falling film cross-flow filters, a continuous recirculating falling film of green liquor sludge covers the surface of vertical filtration elements which are installed in a pressure vessel. Then the liquor starts to pass through the filter medium by using compressed air. The increasing concentration of suspended solids in the sludge during filtration reduces the filterability of the sludge. Therefore, the filtration pressure needs to be increased simultaneously to have a constant filtrate flow rate. Filtration will stop when the sludge is thickened enough, and the resulted sludge with high density and solid content is sent to the dregs handling stage for further washing and dewatering (Tikka, 2008).

Direct cake filtration of green liquor without using a precoat of lime mud as a filter aid is performed by a cassette filters as well as horizontal and vertical chamber filter presses (Ek et al., 2009; Sanchez and Tran, 2005; Tikka, 2008). The cassette filter for green liquor purification consists of cartridges, in which tubular filter elements are assembled, and the cartridges are mounted vertically in a pressurized vessel. The green liquor sludge is fed to the vessel until the maximum filtration pressure is reached, and the time required for this stage depends on the filterability of the sludge. Then, pressurized air is introduced into the vessel to empty it. The green liquor is forced to enter the filtration elements with a pressure difference by feeding in pressurized air, while the dregs cake is formed on the surface of the filter cloth. When the vessel is empty, the dregs cake is held on the surface by pressurized air, and the filter cloths are back-washed with simultaneous reslurry and dregs removal. The resulted dregs are prewashed and sent to a dregs filter for further washing and dewatering. Flocculants are added to the green liquor in the cassette filter to speed up the separation (Ek et al., 2009; Tikka, 2008; Wimby et al., 1995).

The filtration of green liquor can be done by a horizontal or a vertical chamber filter press without a need for flocculants and a precoat. This type of filter can be utilized for dregs handling as well. In the vertical type, the filter medium is moveable and the filtration chambers are stacked horizontally, while the horizontal type includes a stationary cloth around a vertically stacked chamber which is closed tightly with a hydraulic cylinder. In both types, the filtration chamber is filled with pressurized green liqour sludge, and the filtrate starts to pass through the filter cloth, while the dregs form a filter cake on the surface of the filter cloth. The feeding of pressurized sludge is stopped when the chambers are filled with the dregs, and then the remained green liquor in the dregs cake is displaced by wash liquor. Finally, the cake is dewatered by squeezing with inflatable diaphragms in the chamber (Sanchez and Tran, 2005; Tikka, 2008).

Previous studies done by Golmaei et al. (2017) and Sedin and Theliander (2004) have revealed that the dregs cake is highly resistant. In the smelt dissolving tank, dregs particles containing a soft, gel-like magnesium silicate compound ($Mg_2(Si_{1-x}Al_x)O_4$) are formed by mixing dissolved magnesium ions with a sodium silicate solution (Taylor, 2013; Taylor and McGuffie, 2007). It was found by Sedin and Theliander (2004) that the ratio of magnesium to aluminum in green liquor dregs has an effect on the average specific cake resistance. The outcome of the study done by Sedin and Theliander (2004) showed that the addition of magnesium increased the cake resistance, whereas the addition of calcium and aluminum ions improved the filterability of the green liquor sludge.

The filterability of green liquor sludge can be improved by using a precoat layer of lime mud in the pressure precoat disc filter. Unlike the cassette filter and chamber filter presses, the pressure precoat disc filter is a continuous filter (Ek et al., 2009; Sedin and Theliander, 2004). The filtration elements in the pressure precoat disc filter are rotating discs covered by a filter cloth that are installed vertically inside a pressurized vessel. When the discs are submerged in the sludge at the bottom of the vessel, the green liquor is forced to pass through the filter cloth and enter the disc due to a pressure difference provided by pressurized air/N_2. At the same time, a dregs cake is formed on the surface of the rotating discs and lifted above the suspension. In the next stages, the rotating discs move the dregs cake to a washing sector, where wash water is sprayed on the cake surface by showers. Finally, the cake is dewatered by forcing air/N_2 to pass through the cake and remove the retained wash effluent (Ek et al., 2009; Tikka, 2008). Prior to the filtration of green liquor sludge, a precoat of lime mud is formed on the surface of the filter cloth by filtering lime milk. After reaching a suitable thickness for the precoat layer, lime milk feeding is replaced by the green liquor sludge (Tikka, 2008). After dewatering, the cake together with a thin slice of blinded precoat is removed from the disc surface by moving scrapers. This means that the thickness of the precoat layer is reduced after each filtration sequence, and it should be renewed after some filtration sequences (Ek et al., 2009; Tikka, 2008).

The strength of the pressure precoat disc filter compared to the equipment described above is that cake washing and dewatering are done with the same equipment and the resulting cake is relatively dry, so there is no need for further dregs handling. The amount of utilized lime mud as precoat is usually equal to the amount of dregs. Therefore, the precoat filter generates a double amount of landfilled dregs residues compared to direct filtration (Golmaei et al., 2017). However, removal of lime from the chemical recovery cycle is necessary to control the dead load and the amounts of NPEs, so the actual increase in the residue production caused by the precoat filter is not that high.

2.4.2 Green liquor dregs washing and dewatering

The collected dregs sludge from the sedimentation clarifier and direct cake filters should be sent to extra stages of washing and dewatering, because they contain a considerable amount of green liquor. When a pressure precoat filter is utilized for green liquor purification, dregs washing and dewatering are performed in the same equipment. In the case of using a clarifier and cross-flow filtration technique for dregs separation, the obtained dregs sludge needs to be washed to recover the remained alkali. Several types of equipment, namely a dregs washing clarifier, vacuum filter and pressure filter are utilized for this purpose. Dregs washing by a clarifier can be performed in one or two stages, depending on the consistency of the removed dregs, and the approximate ratio of water to dregs of 12:1 is required for this washing method. The mixture of water and dregs is prepared in an agitated tank before sending to the washing clarifier. After the washing stage in the clarifier, the removed dregs should be dewatered before landfilling (Sanchez and Tran, 2005; Tikka, 2008). In earlier green liquor dregs handling systems, a rotary vacuum filter was used for dewatering the collected dregs sludge from the washing clarifier, and in new mills a dregs centrifuge is applied for this purpose (Beer et al., 2006; Ek et al., 2009).

A vacuum precoat drum filter is widely applied for dregs handling. In this filter, one or two kilograms of lime mud are utilized as a precoat layer for each kilogram of dregs. The rotating vacuum drum covered by a filter cloth with the precoat of lime is submerged in a basin containing the dregs sludge, and clean liquor is passed through the precoat and the filter cloth and sucked into a drum. The rotating drum lifts the cake from the sludge and cake dewatering starts by air suction into the drum. In an earlier installation of a vacuum drum filter for dregs handling, lime mud was also used through the body feed method by mixing it with the dregs before filtration. The moisture content of dewatered dregs cake in a vacuum precoat drum filter varies from 50 w% to 70 w%, and its soda loss (as Na_2O) is between 2.5% and 5%. The water consumption of a vacuum precoat drum filter is lower than that of a washing clarifier (Beer et al., 2006; Sanchez and Tran, 2005; Tikka, 2008).

The use of lime as a filter aid with the dosages mentioned above increases the amount of solid wastes up to triple size. Thus, the amount of solid wastes can be reduced by using separation equipment, such as a filter press or centrifuge which do not need a filter aid for dregs handling. The filter press is applied widely in mining and mineral industry, but its usage in pulp mills does not have a long history. Horizontal and vertical chamber filter presses have recently become commercially available for dregs washing and dewatering as well. The design features of these filters were explained in the green liquor purification section above (Sanchez and Tran, 2005; Tikka, 2008).

Another equipment applied in dregs dewatering is a decanter-type centrifuge. Like the filter press, the centrifuge has been applied commonly for dregs handling in recent years, and it has been widely used for many decades to dewater industrial and municipal sludge. Different parts of decanter-type centrifuges are a rotating cylinder or bowl and a rotating scroll. Dregs washed with a washing clarifier are fed to the centrifuge through an axial feed pipe which is located at the middle of the centrifuge. Then, the dregs are separated from the liquid phase by their density difference. A liquid ring is formed by clean liquor inside the bowl, and the dregs are separated by centrifugal force, conveyed by a screw to the conical end of the bowl where the dewatered dregs are discharged through installed nozzles (Beer et al., 2006; Tikka, 2008).

2.5 Causticizing plant and lime recovery

A causticizing plant includes the main stages of lime slaking, causticizer train, white liquor separation, and lime mud dewatering. In the causticizing plant, the sodium carbonate content of the purified green liquor is converted to sodium hydroxide by adding reactive lime (CaO). The resulted lime mud, which contains mainly calcium carbonate is sent to the lime recovery cycle. Reactive lime is recovered from the lime mud in a lime kiln by calcination at a high temperature, to be reused in the causticizing plant (Ek et al., 2009; Sixta, 2006b; Tikka, 2008).

2.5.1 Slaker and causticizer train

By adding CaO to the purified green liquor in the slaking stage, favourable circumstances for the causticizing process are created. Slaking is connected to sub-areas such as green liquor cooling, control of the lime dosage to prevent overliming, mixing of lime and green liquor, and separating slaker grits from lime milk. As the slaking reaction is exothermic by itself, the purified green liquor should be cooled down before entering the slaker in order to avoid intense boiling and further safety risks. The temperature of the green liquor is indirectly controlled by cooling the feed weak white liquor, but in a new concept, cooling happens by flashing under vacuum in an expansion cooler (Parthasarathy and Krishnagopalan, 1999; Tikka, 2008).

The first chemical reaction taking place inside the slaker is the exothermic slaking reaction which converts the burned lime (CaO) into calcium hydroxide ($Ca(OH)_2$), as shown by Equation (2.1) (Sixta, 2006b):

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad \Delta H = +65 \text{ kJ kmol}^{-1} \tag{2.1}$$

The slaker is a mixing tank equipped with a classifier to separate unreacted lime from lime milk, which is a mixture of reactive lime and liquor. The major side stream of the slaking stage is the so-called slaker grits which mainly contain unslaked lime. After slaking, a mixture of lime milk and slaker grits is scraped to the classifier part by the bottom rake. The grits settle down in the classifier due to their higher gravity and are removed by a conveyer (Tikka, 2008).

Through the causticizing reaction, the sodium hydroxide is produced from sodium carbonate (Na_2CO_3), as shown by Equation (2.2). It should be mentioned that the causticizing reaction begins in the slaker and continues to 70 % completion before sending to the train of causticizers (Sixta, 2006b).

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3 \tag{2.2}$$

In the causticizer train, the causticizing reaction should proceed to about completion, which means converting lime milk into white liquor (Sixta, 2006b). Calcium carbonate is an insoluble by-product that should be separated from the white liquor. The more purified white liquor means lower alkali contamination in the causticizing plant (Tikka, 2008; Tran and Vakkilainen, 2007).

2.5.2 White liquor purification

Two main applied techniques for the separation of lime mud from white liquor are sedimentation (white liquor clarifier) and filtration. For many years, clarification was the most commonly applied method for white liquor purification, but in modern mills, clarifiers are being replaced by filters. The main advantage of using a clarifier is its low energy demand, while the need for a remarkably large installation space is considered as a disadvantage. It is important to have purified white liquor with high temperature and concentration, so cooling or dilution of white liquor is not allowed during the separation process (Sixta, 2006b; Tikka, 2008).

The conventional white liquor clarifier is equipped with a rake mechanism to collect lime mud from the bottom of the clarifier tank. Then the collected lime mud is sent to the lime mud washing stage. Total solids content of lime mud, i.e. white liquor clarifier underflow is usually between 35% and 40% (between 30% and 35% excluding dissolved solids and salts). The separated white liquor is collected as the overflow of the clarifier (Quesada, 2003; Tikka, 2008). The amount of existing alkali in the lime mud separated by the clarifier can reach 20% of white liquor production. So, the separated lime mud would be diluted and then separated by settling in a similar type of clarifier. The washed lime mud is sent to a storage tank before further dewatering (Theliander and Gren, 1987; Tikka, 2008).

Two commonly applied filters for white liquor purification are a candle filter (pressure tube) and a disc filter using the cake filtration technique (Ek et al., 2009; Sixta, 2006b). A candle filter consists of vertically installed tube-like filtration elements in a pressurized vessel. When the slurry is fed to the pressure vessel, the liquids start to enter the tube-like filtration elements by passing through a filter cloth due to a pressure difference, while the lime mud (solid phase) remains on the outer surface of the filter cloth and forms a filter cake (Tikka, 2008; Wakeman and Tarleton, 1999). The lime mud cake is released from the surface of the filter cloth by back-flushing, and then starts to form a sediment toward the bottom of the pressurized vessel. The settled lime mud at the bottom of the candle filter is withdrawn continuously and sent to the washing stage. Prior to the washing stage, the lime mud slurry is moderately diluted with washing water to reach a certain suspended solid concentration and stored in a tank (Tikka, 2008).

The separation efficiency of a pressurized disc filter for white liquor purification is higher than that of the candle filter and clarifier. Additionally, a pressurized disc filter requires less water than the candle filter and clarifier. In the pressurized disc filter, the slurry is forced to pass through filtration elements (rotating discs covered by filter cloth) with pressure provided by circulating pressurized gas. In this equipment, the filtration sequence consists of cake formation when the rotating discs rise above the slurry level, cake washing with a water shower and deliquoring by passing pressurized air through the cake. Finally, the outer layer of the dried lime mud cake (with dry solids content of about 60 to 70%) is scraped from the rotating discs. The remaining layer of lime mud cake is utilized as a precoat layer on the surface of the disc filter in the next sequence of filtration (Ek et al., 2009; Sixta, 2006b; Tikka, 2008).

2.5.3 Lime mud filtration plant

The lime mud obtained from the white liquor clarifier contains a considerable amount of white liquor which should be recovered by the use of water or a condensate in the washing stage (Ek et al., 2009; Kymäläinen et al., 1999). Two washing stages are required for lime mud with a lower solid content, i.e. separated and dilution-washed by a candle filter or a clarifier. The first washing stage is a simple dilution washing explained above, but the second washing stage could be integrated with dewatering in the lime mud filtration plant (Tikka, 2008).

The lime mud separated by the pressurized disc filter and the stored dilution-washed lime mud should be sent to a lime mud filtration plant for further washing and dewatering. The aim is to increase the solid content of the lime mud even to 80% - 90% by dewatering, which could be achievable at some mills. In addition, the acceptable level of the remaining water-soluble alkali in dewatered lime mud is under 0.15% as NaOH on dry mud. Two commonly applied filters for this stage are the vacuum drum filter and the disc filter, the proximate load of which for lime mud dewatering is 5 – 7 t/m^2 per day (Ek et al., 2009; Sixta, 2006b; Tikka, 2008).

The extra washing together with dewatering of dilution-washed lime mud is mostly carried out by utilizing one vacuum drum filter or in some cases two of that to increase the solid content to about 75 wt-% (Järvensivu et al., 2001; Tikka, 2008). The disc filter has a similar operating principle as the drum filter, and its size is remarkably smaller than that of the drum filter. The level of alkali content in dewatered lime mud could be reduced to a very small amount by using a two-stage disc filter (Sixta, 2006b; Tikka, 2008).

2.5.4 Lime kiln

Before sending the lime mud to a lime kiln, it is dewatered to obtain a high solid content. In the lime kiln, the dried lime mud, which essentially contains calcium carbonate, is calcined at a high temperature. The endothermic chemical reaction of lime calcination which happens at the actual burning zone of the lime kiln is expressed by Equation (2.3) (Sixta, 2006b; Tikka, 2008).

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \Delta H = -178 \text{ kJ kmol}^{-1} \qquad (2.3)$$

The lime kiln is a rotary cylindrical kiln which is sloped slightly toward the firing part. In the lime kiln, the temperature of gas can increase up to 1100 °C. By a direct contact between combustion gas and lime mud in a counter-current operation, the lime mud is calcined to reactive lime. The lime mud is first dried and then calcined in its downward way to the firing end of the kiln (Pöykiö et al., 2006; Sixta, 2006b; Tikka, 2008).

3 Green liquor dregs

Green liquor dregs (GLD) are the major inorganic solid residue of kraft pulp mills, and they account for over 90% of those generated in chemical pulp production and two-thirds of those generated in the world's virgin pulp production. It can be said that GLD is the main inorganic solid residue fraction of the world's virgin pulp production. As explained above, GLD originates from the chemical recovery cycle, where the cooking chemicals are regenerated (Mäkitalo et al., 2012; Pöykiö et al., 2006; Tran and Vakkilainen, 2007). The production of GLD in older overloaded recovery boilers is 6 – 9 kg of dregs/ton of pulp, which may be reduced to 3 – 4 kg of dregs/ton of pulp in newer boilers working at a designed capacity (Beer et al., 2006). This solid residue is landfilled directly or in a mixture with the precoat (lime mud), depending on the utilized separation technique for GLD sludge (Golmaei et al., 2017; Kinnarinen et al., 2016; Tikka, 2008).

Dregs are alkaline (pH>10) solid residues which mainly contain sodium and calcium carbonates, sodium hydroxide, unburned carbon, and sulfides. In addition, non-process elements (NPEs) such as Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Ti, V, and Zn are found in GLD (Jia et al., 2013; Kinnarinen et al., 2016; Martins et al., 2007; Nurmesniemi et al., 2005). The total titratable alkali ($NaOH + Na_2CO_3 + Na_2S$) in green liquor is typically between 140 – 180 g $NaOH$/dm^3, which explains the high neutralization capacity of green liquor in an acidic environment. In addition to high pH, the hydraulic conductivity of dregs is low, and it can be changed by the water/solid ratio of the dregs and probably by freezing (Jia et al., 2013; Mäkitalo et al., 2012; Tikka, 2008; Zambrano et al., 2010).

Concentrations of different elements in 20 GLD samples collected in this study from 10 different Finnish kraft pulp mills have been analyzed, and summary of the results is presented in Table 3.1. The concentrations of the elements in the samples were measured with a Thermo Fisher Scientific ICAP6500 Duo (Thermo Fisher Scientific Inc., Cambridge, UK) inductively coupled plasma optical emission spectrometer (ICP-OES). Prior to the ICP-OES analysis, the GLD samples were digested thoroughly by using the method 3051 introduced by the US Environmental Protection Agency (1995).

Table 3.1. Measured concentrations of elements in the total suspended solids (TSS) of 20 washed GLD samples collected from 10 Finnish kraft pulp mills.

Elements	Total concentration in green liquor dregs (mg/kg $_{TSS}$)
Al	1010 - 20200
As	< 3
Ba	230 - 920
Be	< 1
Ca	99000 - 346000
Cd	3,8 - 30
Co	3,1 - 29
Cr	33 - 240
Cu	78 - 420
Fe	970 - 20700
K	260 - 7590
Mg	8970 - 97600
Mn	4760 - 31600
Mo	< 1,0 - 6,2
Na	6360 - 107000
Ni	16 - 340
P	600 - 4920
Pb	3,8 - 47
S	4160 - 58100
Sb	< 3
Se	< 3
Sn	< 3
Ti	< 50 - 450
V	< 2 - 54
Zn	620 - 5790

According to the concentrations of elements in Table 3.1, Ca. Mg, Mn, Na and S could be generally considered as major elements in GLD. Also, considerable variations can be seen in the concentration of Al , Fe, K, Mg, Mn, Na, Ni, P, S, Ti, V and Zn, which have probably happened due to differences in the process type and the minerals associated with wood and make-up chemicals. The table also shows that traces of NPEs such as Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Ti and V can be found in GLD. According to the study published in Paper IV, rare earth elements (REE) such as Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb, and Y, and even Th and U could be found in a parts per billion (ppb) level in GLD.

The most abundant form of sodium in the dregs is sodium carbonate (Na_2CO_3), the other two major compounds in the dregs being sodium sulfide (Na_2S) and sodium hydroxide (NaOH). In addition, a smaller amount of sodium can be found in the dregs in form of sodium sulfate (Na_2SO_4), sodium sulfite (Na_2SO_3), and sodium thiosulfate ($Na_2S_2O_3$) (Tikka, 2008). The recognized chemical compounds of calcium in GLD are calcite ($CaCO_3$), calcite containing a small amount of magnesium ($Ca_{(1-x)}Mg_xCO_3$), calcium oxide (CaO), dihydrate ($CaSO_4.2H_2O$), anhydrite ($CaSO_4$), and portlandite ($Ca(OH)_2$) (Jia et al., 2013; Martins et al., 2007; Taylor and McGuffie, 2007).

In GLD, some NPEs such as As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Ti, V, and Zn are found in low water soluble compounds, e.g. hydroxides and carbonates. Cd is not water soluble and traces or very small amounts of Zn, Pb and Ni are soluble in water. Also, As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, and Zn are found in the form of oxidizable minerals, e.g. metal sulfides in GLD (Nurmesniemi et al., 2005). It is supposed that Fe and Mn are most commonly found as oxides in GLD, presented in an easily reduced fraction, according to a sequential leaching study done by Nurmesniemi et al. (2005). The oxides of Fe and Mn are able to cover other elements, especially Ba, Co, Ni, V and Zn (Nurmesniemi et al., 2005). Aluminosilicates pargasite ($NaCa_2Mg_3Fe^{2+}Si_6Al_3O_{22}(OH)_2$) and vermiculite ($Mg_{1.8}Fe^{2+}{}_{0.9}Al_{4.3}SiO_{10}(OH)_2{\cdot}4(H_2O)$) are recognized compounds of Al and Fe in dregs (Taylor and McGuffie, 2007).

4 Circular economy in kraft pulp mills – New products from GLD

Over the last decade, circular economy has attracted growing attention due to the scarcity of resources and environmental pollution. Circular economy is considered as a suitable alternative for the traditional linear economy model which is so-called take-make-use-dispose practice. Various definitions are available for circular economy (Ghisellini et al., 2016; Lieder and Rashid, 2016). It can be realized as a closed loop for material flow in a whole economic system (Geng and Doberstein, 2008). Also, in association with the 3R principle (reduction, reuse and recycling), the core of circular economy can be defined as ’’circular (closed) flow of materials and the use of raw materials and energy through multiple phases’’ (Lieder and Rashid, 2016; Yuan et al., 2006).

Alongside various definitions, a Circular Economy System Diagram has been developed by the organization of Ellen MacArthur Foundation (EMF) to describe the idea of circular economy (MacArthur, 2013). In the European Union, a related initiative policy on supplying raw materials from industrial residues is a step towards enhancing circular economy activities. The recovery of valuable materials or producing new products from residues is also considered as a component of circular economy (EC-European Commission, 2015, 2014).

Making new sustainable products from the residues of pulp mills is not only a way to create circular economy, but also a method to make pulp mills cleaner and more environment friendly. According to the increases in disposal fees, tougher legislation and limitation of landfill lifespan, the reuse of the residues is also economically important for the pulp and paper industry (Gagnon and Ziadi, 2012). Finding technical solutions to reduce the level of hazardous metals and materials in the inorganic residues of the kraft pulp mills, it is necessary to convert them into safe raw materials for other industries. Next, the production of new sustainable materials from green liquor dregs (GLD), which is the main inorganic solid residue of kraft pulp mills is discussed.

4.1 Forest fertilizer and soil amendment products from GLD

Tree harvesting results in the removal of nutrients from the ecosystem, as well as soil acidification. Therefore, returning the residues of pulp mills, especially those containing base cations (K, Ca and Mg which are the major nutrients in the soil taken up by trees) to forest sites as a fertilizer is an ecological way to limit the environmental threats of tree harvesting. In addition, returning the alkaline residues of pulp mills, such as green liquor dregs (GLD) would facilitate soil de-acidification (Mahmoudkhani et al., 2004; Mäkelä et al., 2012; Rothpfeffer, 2007). Compared to wood ash, GLD contains less nutrients (K, Ca and Mg). Thus, a mixture of these two residues could be utilized for efficient recycling of nutrients to forest sites (Rothpfeffer, 2007).

The spreading of alkaline residues would become easier, if they were prepared in the form of granules. It is also necessary to optimize the leaching property of the granules and control their release of alkaline metals. In order to convert GLD to a liming product with the mentioned properties, it should be processed in a series of drying, pelletization or granulation steps, followed by heat treatment. During the heat treatment stage, heavy metals such as Cd, As and Pb which are able to damage the soil would be separated, while most of the nutrients would remain in the materials. Heat treatment is also a method to control the leaching properties of aggregates, and recirculation of GLD to the forest needs the knowledge about its leaching properties (Mahmoudkhani et al., 2004). A study done by Cabral et al. (2008) proved that GLD together with other inorganic residues of a pulp mill such as fly ash from wood incineration and slaker grits are suitable enough to replace commercial agricultural limestone as liming material (Mäkelä et al., 2012).

In order to have uniform standards for fertilizing and liming products all around the European Union, various product function categories (PFC) of CE-marked fertilizing products have been defined by the EC-European Commission (2016). GLD can be categorized as some of the CE-marked fertilizing products explained in the following. CE-marked organic fertilizers (PFC 1(A)) are defined as a ’’*product aimed at providing nutrients to plants*’’ which basically means that they should contain carbon and nutrients. CE-marked liming material (PFC 2) is defined as a ’’*product aimed at correcting soil acidit*y’’ which contains oxides, hydroxides, carbonates or silicates of calcium or magnesium. A CE-marked organic soil improver (PFC 3(A)) should contain material of solely biological origin. CE-marked inorganic soil improvers (PFC 3(B)) are materials other than organic soil improvers. A CE-marked growing medium (PFC 4) is a ’’*material other than soil intended for use as a substrate for root development*’’ (EC-European Commission, 2016).

In the European Union, it is necessary to investigate the composition and extractability of industrial residues for landfill approval or their utilization. As an example, the values for As, Cd, Cr, Cu, Ni, Pb, Zn and Hg were set by Finnish statutory limits and came into force in March 2007 for using residues such as GLD as fertilizers in forestry (Dahl et al., 2009; Manskinen et al., 2011). Also, the maximum allowed concentration for As, Cd, Hg, Ni, and Pb for the above mentioned CE-marked fertilizing products were determined by the EC-European Commission (2016). The limitations for CE-marked fertilizing products are listed in Table 4 in Paper IV.

In a study conducted by Österås et al. (2005), the influence of wood ash pellets and GLD utilized as soil fertilizers on the accumulation of Ca, Cd, Cu and Zn in the wood and bark of Norway spruce were examined from a long-term perspective. According to their study, the spreading of these residues to forest sites should not increase the content of Cd, Cu and Zn in the stem of Norway spruce. Even a possible decrease of Cd accumulation in those trees was observed by Österås et al. (2005) in the forest site where GLD was spread.

4.2 Potential applications of GLD in other industries

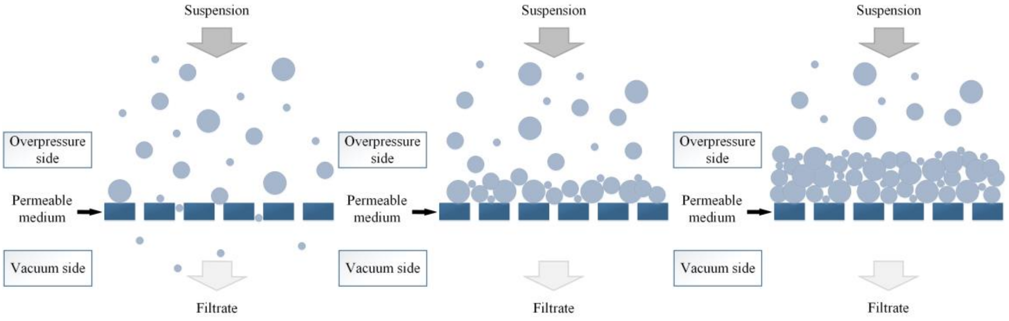
Conventional aggregates in bituminous mixtures could be replaced by a mixture of GLD and slaker grits. According to a study by Modolo et al. (2010), grits can be used directly as an aggregate in the production of bituminous materials, while the direct use of GLD for this purpose is not possible due to its high soluble salts content. Slaker grits are compatible with conventional aggregates such as crushed stones, but the GLD received from mills should be washed in extra stages to be suitable for using in bituminous mixtures. The soluble salts content in aggregates is an important factor that causes a problem in terms of ’’conserved strength’’ properties influencing the quality of the final product.

GLD can also be considered as a potential construction material due to its mineral contents, but unfortunately, this application of GLD has not been studied enough yet. Depending on the applied filtration technique in the process, GLD could be used in a mixture with lime mud which contains $CaCO_3$, CaO and $Ca(OH)_2$. According to a study conducted by Mymrin et al. (2016), a mixture of GLD with other wastes such as grits, lime mud and lime production waste can be utilized as the main components for producing construction material with a high standard of mechanical properties. On the other hand, previous studies done by Watkins et al. (2010), and Siqueira and Holanda (2013) confirm that slaker grits can be used as earth construction material, especially because they have a low concentration of heavy metals. It is even possible to replace Portland cement in soil-cement bricks partially with slaker grits (Siqueira and Holanda, 2013).

The properties of GLD, such as high buffering capacity (high pH value), low hydraulic conductivity and high water retention capacity make it suitable material to be used as an alkaline barrier (Jia et al., 2014; Mäkitalo et al., 2014). In sulfide mine processes, great amounts of tailings are generated and commonly landfilled in the vicinity of the mines. The oxidation of tailings results in the formation of acid rock drainage (ARD), which is known as a long-term environmental threat. Typically, a soil sealing cover is utilized as a barrier against oxygen which causes sulfide oxidation and consequently ARD formation (Jia et al., 2013; Mäkitalo et al., 2014, 2012). ARD formation facilitates the mobilization of metals from the tailings and probably the pollution of water resources. Using GLD as an alkaline low hydraulic conductive barrier for covering sulfide mine tailings prevents water percolation and oxygen transport to mine waste, and consequently inhibits ARD formation. In addition, the alkalinity of GLD helps the buffering of mining residues (Jia et al., 2014; Mäkitalo et al., 2014, 2012). In fact, using the alkaline waste of kraft pulp mills for covering an acidic waste of sulfide mines would solve two environmental problems simultaneously.

5 Cake filtration

Cake filtration is a separation method in which a liquid is forced to pass through a relatively thin permeable medium, while the solids start to form a filter cake on the surface of the medium. In cake filtration, the driving force for suspension is a pressure difference through the permeable medium provided by overpressure or a vacuum. A schematic view of filter cake formation is presented in Figure 5.1.



(I) **(II)** **(III)**

Figure 5.1. A schematic view of filter cake formation. I) Feeding suspension, II) Filter cake formation, III) Filter cake growth. Depending on the design of the filter, either overpressure or vacuum can be used.

As depicted in Figure 5.1, at the very beginning when filter cake is not formed, particles that are smaller than the pores of the medium are able to pass the permeable medium together with the filtrate (liquid phase). In a short period, filter cake starts to be formed by deposited solids on the surface of the medium, and these solids bridge over the pores of the medium to collect even very fine particles and prevent them from passing through the medium. As the process continues, the filter cake will grow by retaining other solid particles on its surface, and this step will continue as long as suspension feeding continues.

Any filtration process comes with complicated phenomena that make it hard to predict the filtration characteristics of a specific suspension. A theory of conventional cake filtration was developed first by Ruth (1946, 1935, 1933) and Ruth et al. (1933) to simplify the understanding of the filtration process by assuming that total filtration resistance is caused by medium and cake resistances. Further development on the conventional theory for the compressible behaviour of filter cakes has been done by Tiller (1953), Tiller and Cooper (1960), and Tiller and Shirato (1964), and others (Lee and Wang, 2000).

Prior to the formation of the cake, the filter medium causes an initial pressure drop, which increases due to the resistance of the formed cake. Accordingly, the filtration operation modes can be divided into two main categories, which are known as constant flow rate (constant rate) filtration and constant pressure filtration. In order to keep the filtrate flow rate constant, the pressure during the filtration needs to be elevated to overcome the increasing resistance of the filter cake. In constant pressure filtration, the pressure difference over the cake and medium is kept constant throughout the filtration stage (Tarleton and Wakeman, 2007; Wakeman and Tarleton, 2005). In the present study, filtration experiments were done with the constant pressure difference mode to allow the determination of cake properties by a straightforward method for data processing, where the driving force is constant over time.

5.1 Theory of conventional cake filtration

The basis for the development of cake filtration theory is the equation originally formed by Darcy (1856), when he had done a study on the permeability of limestone beds. On the basis of Darcy’s study, the volumetric flow rate of liquid flowing through a porous bed could be determined by Equation (5.1) (Svarovsky, 2000; Wakeman and Tarleton, 2005).

$$\frac{q}{A} = K\,\frac{\mathit{\Delta} p}{\mu L} \tag{5.1}$$

where q is the volumetric flow rate of the liquid, A is the bed surface area (later simply referred to as filtration area), $\mathit{\Delta} p$ is the pressure drop across the bed, μ is the constant dynamic viscosity of the liquid, L is the depth of the bed (later referred to as cake thickness), and K is the permeability of the porous structure or the filter cake.

Later on, the well-known Kozeny-Carman equation was formed according to a model describing a laminar condition of flow through capillaries with a total specific surface area which is equal to that of the solids comprising the bed. The Kozeny-Carman equation is determined by Equation (5.2) (Svarovsky, 2000).

$$\frac{q}{A} = \frac{\Delta p}{\mu L} \frac{\varepsilon^3}{K_0(1-\varepsilon)^2 S_0^2} \tag{5.2}$$

where K_0 is the Kozeny constant, ε is the voidage, i.e. porosity of the bed, and S_0 is the volume-specific surface area of the bed. The Kozeny constant is frequently taken as 5.0 for uniform particles with lower ranges of porosity of particles and with almost spherical shapes, but it varies according to the size, shape and porosity of the particles (Svarovsky, 2000; Wyllie and Gregory, 1955). In a study done by Wyllie and Gregory (1955), it was found that the Kozeny constant was around 5.0±10% for a packed bed with porosity of about 40% consisting of irregular particles.

Darcy’s law (Eq. 5.1) was further modified by Ruth (1935) to the form where the ratio between L and K is expressed by the total filtration resistance R. Equation (5.3) represents the Ruth form of Darcy’s law (Svarovsky, 2000):

$$\frac{q}{A} = \frac{\Delta p}{\mu R} \tag{5.3}$$

In cake filtration, the total pressure drop (Δp) is a sum of the pressure drop caused by the filter cake (Δp_c) and the pressure drop caused by the filter medium (Δp_m) (Tarleton and Willmer, 1997) as is shown by Eq. (5.4):

$$\Delta p = \Delta p_c + \Delta p_m \tag{5.4}$$

The total filtration resistance R is a sum of the separate resistances of the filter cake (R_c) and filter medium (R_m). Therefore, Equation (5.3) can be expressed as Equation (5.5):

$$q = \frac{A\Delta p}{\mu\,(R_c + R_m)} \tag{5.5}$$

The dynamic viscosity of the filtrate μ is typically constant during the filtration process, and it depends on the temperature and concentration of dissolved components in the filtrate. The filter medium resistance is also assumed to remain constant during the filtration, but the pores of the medium may be clogged by penetrating fine particles inside the pores. This fouling effect, together with the compression of the filter medium under the influence of pressure, can increase its resistance. The filter cake grows continuously during the filtration, and consequently its resistance increases. The resistance of the growing cake is proportional to the amount of deposited solids on the filtration area, as expressed by Equation (5.6).

$$R_C = \alpha w \tag{5.6}$$

where α is the specific cake resistance and w is the mass of the solids per unit of the filtration area. Equation (5.7) is derived from Equation (5.5) after replacing the resistance of the cake by the specific resistance:

$$q = \frac{A\Delta p}{\alpha\mu w + \mu R_m} \tag{5.7}$$

In a batch filtration process, the mass of the cake per unit of filtration area w is increased by time t, and is also related to the cumulative volume of filtrate V as expressed by Equation (5.8):

$$wA = cV \tag{5.8}$$

where c is determined as the mass of solids per unit volume of the filtrate, which is mostly referred to as filtration concentration. Equation (Equation (5.7)) is modified to Equation (5.9) after the substitution of the mass of the solids per unit of filtration area according to Equation 5.8):

$$q = \frac{A\Delta p}{\alpha\mu c(\frac{V}{A}) + \mu R_m} \tag{5.9}$$

The filtrate flow rate q in Equation (5.9) can be replaced by its integral function of filtrate volume and time (Equation (5.10)) to give the so-called general filtration equation (5.11):

$$q = \frac{\mathrm{d}V}{\mathrm{d}t} \tag{5.10}$$

$$\frac{\mathrm{d}t}{\mathrm{d}V} = \alpha\mu c\,\frac{V}{A^2\Delta p} + \frac{\mu R_m}{A\Delta p} \tag{5.11}$$

As the pressure difference Δp is assumed not to change in constant pressure filtration, Equation (5.11) can be integrated:

$$\int_0^t \mathrm{d}t = \frac{\alpha\mu c}{A^2\Delta p}\int_0^V V\mathrm{d}V + \frac{\mu R_m}{A\Delta p}\int_0^V \mathrm{d}V \tag{5.12}$$

giving:

$$t = \alpha\mu c\frac{V^2}{2A^2\Delta p} + \mu R_m\frac{V}{A\Delta p} \tag{5.13}$$

which could be represented in another form:

$$\frac{t}{V} = \frac{\alpha\mu c}{2A^2\Delta p}V + \frac{\mu R_m}{A\Delta p} \tag{5.14}$$

The obtained Equation (5.14) is a common form of the general filtration equation used for the determination of specific cake resistance and medium resistance in constant pressure filtration applications. The determination of cake characteristics is discussed in the next section.

5.2 Determination of cake characteristics

In practice, it takes time to have stabilized pressure in the filtration chamber. This stable condition is assumed to happen at time t_s, when the obtained volume of filtrate is V_s. Therefore, these variables can be inserted into the general filtration equation (Equation (5.11) to form Equation (5.15) (Svarovsky, 2000):

$$\frac{t - t_s}{V - V_s} = \frac{\alpha\mu c}{2A^2\Delta p}\left(V + V_s\right) + \frac{\mu R_m}{A\Delta p} \tag{5.15}$$

Specific cake resistance is constant for incompressible cakes, while it depends on the pressure difference for compressible cakes (Svarovsky, 2000). In practice, all cakes are known to be compressible, but to different degrees (Wakeman and Tarleton, 2005), and the specific resistance of a compressible cake is influenced by local changes of pressure drop across the cake. Thus, the specific cake resistance in Equation (5.15) is typically replaced by the average specific cake resistance α_{av} for compressible cakes.

The average specific cake resistance and medium resistance can be determined by using experimental data in Equation (5.15), which is considered as a linear equation where slope a is determined by equation (5.16):

$$a = \frac{\alpha_{av}\mu c}{2A^2 \Delta p} \tag{5.16}$$

and interception point b is determined by Equation (5.17):

$$b = \frac{\mu R_m}{A \Delta p} \tag{5.17}$$

First, a linear graph of $(t\text{-}t_s)/(V\text{-}V_s)$ against $V + V_s$ is plotted by using the recorded volume or mass of the filtrate versus time during the filtration test with constant pressure. In Figure 5.2, examples of linear graphs for filter cakes at different filtration temperatures (20, 40, 60, 80 °C) are given (Paper I).

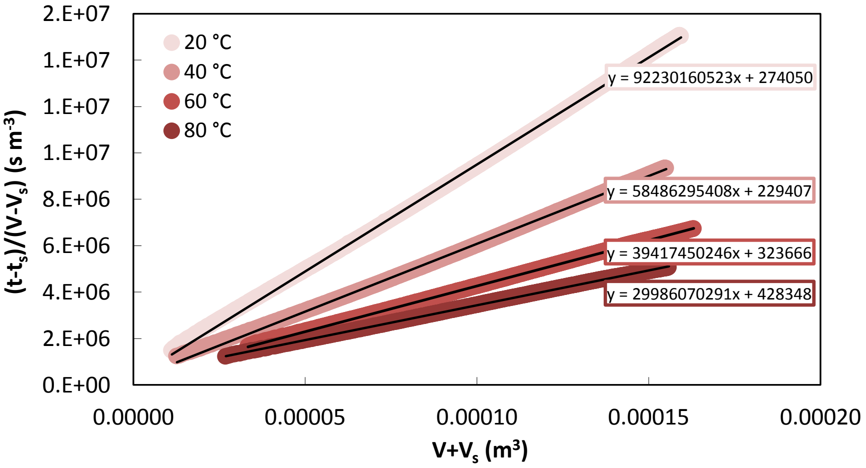


Figure 5.2. Examples of plotted linear graphs by recorded volume of the filtrate versus time during filtration tests with constant pressure and filtration temperatures of 20, 40, 60, 80 °C (Paper I).

The average specific cake resistance and the resistance of the filter medium (including some pores blocking in initial layers) can be calculated by using the slope of the linear graph in Equation (5.16), and its interception point in Equation (5.17), respectively.

The above is a common method for the determination of average specific cake resistance when experiments are carried out at laboratory scale. As discussed above, filter cakes are mostly compressible, and the specific resistance of such cakes is affected by pressure drop across the cake, Δp_c. In such cases, the relation between average specific cake resistance and pressure drop can be determined by Equation (5.18) (Svarovsky, 2000):

$$\frac{1}{\alpha_{av}} \equiv \frac{1}{\Delta p_c} \int_0^{\Delta p_c} \frac{\mathrm{d}(\Delta p_c)}{\alpha} \tag{5.18}$$

The relationship between average specific cake resistance and pressure drop across the cake can be determined by experiment-based empirical Equation (5.19):

$$\alpha_{av} \equiv \alpha_0 (\Delta p_c)^n \tag{5.19}$$

In Equation (5.19), α_0 is the specific cake resistance at a unit applied pressure drop and n is the compressibility index which can be determined by using experimental data. The compressibility index is zero for incompressible filter cakes.

The compressibility index n can be determined by the use of obtained data from repeated filtration tests with the same parameters at different pressures, and constructing a graph in which the horizontal axis and vertical axis represent total pressure drop Δp and α_{av}, respectively. In this graph, the exponent of the power-type trendline represents the compressibility index, as shown in Figure 5.3.

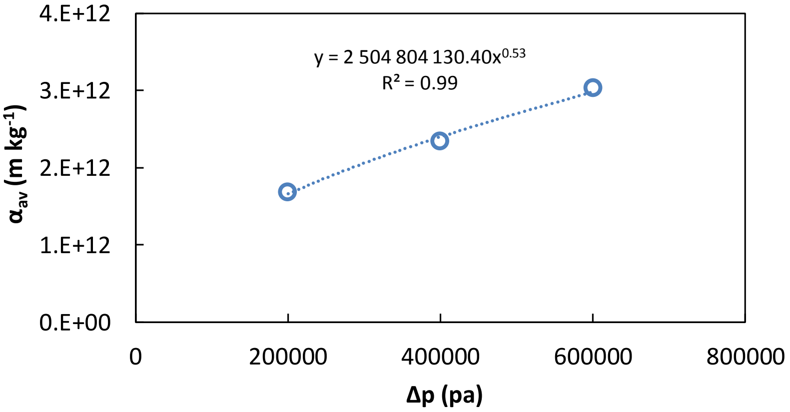


Figure 5.3. Example of plotted power-type trendline by the use of obtained data from repeated filtration tests with the same parameters at pressures of 200000 Pa, 400000 Pa and 600000 Pa.

In the plotted power-type trendline in Figure 5.3, the compressibility index of the filter cake is 0.53. It can be clearly seen in this figure that the average specific resistance of the studied cake increases with pressure, i.e. the cake is compressible.

5.3 Scale-up of the filtration area

The filtration area can be calculated for a larger scale filtration equipment by the use of experimental data obtained in laboratory scale. For this purpose, quadratic Equation (5.20) is derived from the general filtration equation (Equation (5.11)).

$$A^2 - \frac{\mu R_m V}{\Delta pt} A - \frac{\alpha \mu c V^2}{2 \Delta pt} = 0 \tag{5.20}$$

The variables, such as the dynamic viscosity of the filtrate μ and filtration concentration c are the same for the large scale and laboratory scale. In order to have the same specific cake resistance α (which is replaced by its average α_{av} for compressible cakes) for laboratory scale and large scale, the pressure difference should be the same for both scales. The filtration area for the large scale can be calculated by solving quadratic Equation (5.20) and inserting all required variables together with the recorded volume of the filtrate.

6 Chelating agents as extractants for toxic metals

Chelating (complexing) agents have a wide usage in industries like photographic, textile and metal finishing industries, as well as pulp and paper industry. Chelating agents are utilized in total chlorine free (TCF) pulp bleaching process (Nowack and Sigg, 1996; Suess, 2010). Chelating agents have a wide usage also in the treatment of contaminated soils and sediments by mobilizing the heavy metals from the solids (Di Palma and Mecozzi, 2007; Kim et al., 2003; Kocialkowski et al., 1999; Reddy and Chinthamreddy, 2000; Sun et al., 2001).

In soil washing techniques and enhanced phytoextraction, chelating agents are utilized for toxic metal desorption from contaminated soil by the formation of strong water-soluble complexes. Soil washing is a technique in which an aqueous solution of surfactants and mineral acids is utilized for the separation of particles according to their size and chemical extraction. In the phytoextraction technique, the easily soluble toxic metals are removed from the polluted soil by accumulation in plant species. Chelating agents can be used to enhance phytoextraction by elevating the desorption of toxic metals from solids and their mobility with water solution (Leštan et al., 2008). Chelating agents can also be utilized in the treatment of some industrial residues, such as municipal solid waste incinerator fly ash (K. Hong et al., 2000; K.-J. Hong et al., 2000).

Chelating agents were successfully utilized for the first time in the treatment of GLD by extraction of hazardous metals in this study, and the outcome of the study was published in Paper III.

Chelating agents are able to extract metals from coordination sites by complexation, while other extractants such as redox agents and strong acids need to decompose the solid matrix to release the metals (Das et al., 1995). Generally, two mechanisms are known for enhancing the mobilization of metals from the solid phase by chelating agents. Through a fast thermodynamically favorable complexation mechanism, the weak bonds between some cationic metals and solids are broken down directly by the chelating agent (Margerum, 1978; Zhang et al., 2010). Chelating agents participate in metal complexation by forming two or more coordinate bonds with a metal atom (Dwyer, 2012). In the other mechanism, the metals bound to the oxides and organic matters are indirectly mobilized through a slow chelating agent -promoted dissolution which disrupts the solid structure partially (Garrabrants and Kosson, 2000; Margerum, 1978; Zhang et al., 2010).

Various chelating agents, e.g. ethylenediaminetetraacetic acid (EDTA), ethyleneglycol tetraacetic acid (EGTA), nitrilotriacetic acid (NTA), ethylene diamine tetraacetate (EDDS), anionic polyacrylamide (APAM), iminodisuccinic acid (IDSA), methylglycine diacetic acid (MGDA), diaminocyclohexanetetraacetic acid (DCyTA), and diethylenetriamine pentaacetic acid (DTPA) are commercially available (Giannis et al., 2009, 2010; Lan et al., 2013; Peters, 1999; Tandy et al., 2004). The synthetic chelating agent EDTA is the most commonly used chelating agent due to its strong complexation ability for various heavy metals, but its low biodegradability brings some environmental limitations for field applications (Di Palma and Mecozzi, 2007; Garrabrants and Kosson, 2000; Giannis et al., 2010; Nörtemann, 1992). On the other hand, its relatively low price makes it an economically feasible chelating agent for large scales (Leštan et al., 2008). According to previous studies, EDTA can remove Pb, Zn, Cu and Cd effectively from polluted soils (Sun et al., 2001).

When a chelating agent is utilized in the extraction solution to desorb metals from a solid sample, the chelating agent tries to make complexes with all present metals, which leads to a competition between the metals for complexation. This competition and the influence of other present metals on the extraction of a specific metal is not fully understood yet. Hence, the order of metal mobility by using a specific chelating agent should be studied case by case (Kim et al., 2003; Peters, 1999). However, the efficiency of metal complexation with chelating agents can be studied by their stability constants and the metal speciation in a given solid matrix (A. E. Martell and R. M. Smith, 1974; Leštan et al., 2008). Choosing a suitable chelating agent for the extraction of specific metals is quite challenging due to many incomparable conditions (Kocialkowski et al., 1999). The chemical properties of the solid phase, such as pH and the chemical compound of competing metals have an effect on the extractability of metals (Kim et al., 2003; Peters, 1999; Sun et al., 2001). Furthermore, physical factors related to the solid phase, such as porosity, specific surface area and particle size, as well as the liquid-to-solid ratio influence the extractability of constituents from the solids. These physical factors influence the percolation patterns, such as diffusion and advection, and consequently the contact modes between the solids and the extractant solution (Sabbas et al., 2003).

As mentioned above, metal-EDTA complexes are low-biodegradable, which results in their accumulation in the aquatic environment like ground water, rivers and lakes. Ca-EDTA, Zn-EDTA, and Fe(III)-EDTA are the most commonly recognized complexed species of EDTA in natural waters (Nowack and Sigg, 1996). The removal of stable heavy metal-EDTA complexes from the extractant solution can prohibit its environmental hazards in field applications. Several methods have been studied for the treatment of this solution, e.g. decomposition of the metal-EDTA complex by an H_2O_2/UV process and the removal of released metals by adsorption (Finžgar and Leštan, 2006; Jiraroj et al., 2006), photocatalytic oxidation of Cd-EDTA with titanium dioxide (Davis and Green, 1999), precipitation of metals by the use of Na_2S enhanced with $Ca(OH)_2$ and EDTA recycling (Zeng et al., 2005), using an electrochemical membrane cell to release the binary metals from the complex and EDTA recycling (Juang and Wang, 2000a, 2000b), and adsorption of metal-EDTA complexes onto Goethite (α-FeOOH) and anion exchange resin (Nowack and Sigg, 1996; Tejowulan and Hendershot, 1998). In addition to environmental benefits, EDTA consumption in the treatment process could be reduced by its recovery (Sun et al., 2001).

There are naturally-formed organic chelating agents in sediments and soils that influence heavy metal cycling and their environmental distribution. These organic chelating agents elevate the metal mobilization from organic and mineral substances and translocate them through specific environmental compartments (Fischer, 2002). In a study done by Fischer and Bipp (2002), two organic chelating agents of D-gluconic acid and D-glucaric acid (D[+]-saccharic acid) were utilized for heavy metal removal from polluted soil.

7 Mechanical classification by a hydrocyclone

A hydrocyclone is a static device that can be utilized for continuous phase separations such as solid-liquid, liquid-liquid and liquid-gas separations. For about a century, this separation equipment has been applied widely in the industry due to its high capacity, simple operation, low capital and operating cost, as well as simple maintenance operations (Bai et al., 2009a; Cilliers, 2000). Hydrocyclones are applied in various industries, such as chemical, mineral, pulp and paper, and pharmaceutical industries (Bradley, 2013; Delgadillo and Rajamani, 2005). In a solid-liquid mixture (suspension), the solid particles are classified by the hydrocyclone into finer overflow and coarser underflow fractions according to their size, density, shape, and even their magnetic field (Bai et al., 2009b; Ghadirian et al., 2015).

The main parts of the hydrocyclone body are a cylindrical head and a conical part. The suspension is injected through a tangential inlet to the cylindrical head of the hydrocyclone to generate a centrifugal field accelerating the particles towards the wall by a downward helical vortex. This rotational downward flow moving close to the wall is called the primary or outer vortex. When the primary vortex approaches the underflow outlet, coarser particles exit the underflow outlet with a fraction of the liquid, while the finer particles are moved towards the vortex finder by a reverse helical upward flow, the so-called secondary or inner vortex. Through the vortex finder, the finer and lighter particles are directed to the overflow outlet with a fraction of the liquid. In the center of the cylindrical head, a tube, the so-called vortex finder is installed axially from the top of the hydrocyclone body towards the lower edge of the feed entry (Cilliers, 2000; Cullivan et al., 2004; Ghadirian et al., 2015; Svarovsky, 2000). A schematic view of a hydrocyclone is illustrated in Figure 7.1.

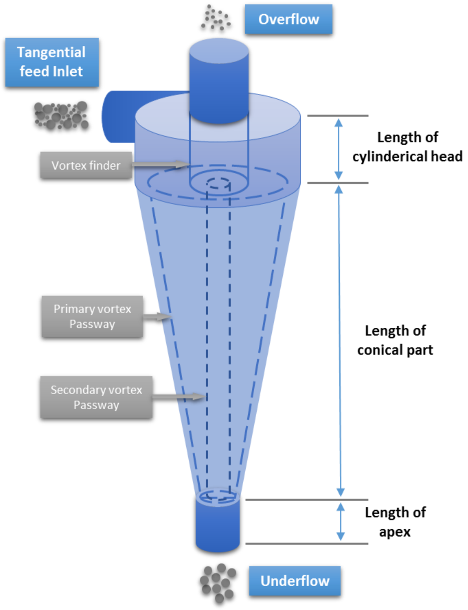


Figure 7.1. Schematic view of a hydrocyclone.

The actual separation of solids by their size and density takes place at the interface between the primary and secondary vortex, which is located close to the underflow outlet. In the hydrocyclone, the primary vortex generates high pressure areas near the walls, while the secondary vortex causes low pressure zones in the center of the hydrocyclone (air core). There are forces in radial and axial directions acting on the particles and influencing the migration of fine particles in the pressure zones (Ghadirian et al., 2015). The three main governing forces in hydrocyclone separation are the centrifugal buoyancy force (F_B), centrifugal force (F_C) and centrifugal drag force (F_D). The coarser particles move close to the wall of the hydrocyclone and migrate downward to the underflow outlet, when $F_C > F_B + F_D$. The finer particles migrate to the vortex finder through the upward helical flow towards the central axis, when $F_C < F_B + F_D$ (Ghadirian et al., 2015; Kawatra et al., 1996; Nowakowski et al., 2004).

The total separation efficiency of a hydrocyclone (E_t) is determined by Equation (7.1):

$$E_t = \frac{m_u}{m_i} \cdot 100\% \tag{7.1}$$

where m_i is the mass of the solids in the feed flow and m_u is the mass of the collected solids in the underflow. A higher separation efficiency means that more solids are collected in the underflow and higher efficiency of light particle recovery. The total separation efficiency depends strongly on the size distribution of the solids in the feed flow. Therefore, total separation efficiency is not suitable enough to be a generic criterion for separation efficiency (Svarovsky, 2000).

The particle size separation performance of a hydrocyclone can be quantified by plotting the partition curve, also called the performance curve or grade efficiency curve (Cilliers, 2000). In order to plot the partition curve, the partition number $P(d)$ should be determined by Equation (7.2).

$$P(d) = \frac{m_u u(d)}{m_i f(d)} \tag{7.2}$$

where $u(d)$ and $f(d)$ are weight fractions of particle size d in the underflow and feed flow, respectively. Then, the partition curve of the partition number (vertical axis) against the particle size (horizontal axis) can be plotted. Thus, it is necessary to measure the particle size distribution (PSD) in the underflow and feed flow for plotting the partition curve. By the use of the partition curve, the two factors of cut size and sharpness of classification can be determined. The cut size is defined as the particle size which corresponds to 50 wt-% of the suspended solid partition to the underflow (Cilliers, 2000). The sharpness of classification is a measure of the partition curve steepness (Frachon and Cilliers, 1999; Svarovsky, 2000). Sometimes a fish-hook phenomenon can be observed in the partition curve, when the partition values are lower than the bypass for a range of particle sizes (Finch, 1983).

In hydrocyclones, the partition number of small particle sizes is not zero, because that fraction of particles in the feed bypasses the hydrocyclone classification. The partition number of those particles is a particular value that is referred to as the bypass B_P. This value can be assumed to be equal to zero for a monotonic experimentally measured partition curve. Generally, a corrected partition number $C_P(d)$ is calculated to consider the effect of the weight fraction of the particles bypassing the hydrocyclone $r(d)$ on the classification performance, as expressed by Equation (7.3) (Cilliers, 2000; Frachon and Cilliers, 1999):

$$C_P(d) = \frac{P(d) - r(d)}{1 - r(d)} \tag{7.3}$$

By measuring the volumetric particle size distribution, the Sauter mean diameter $D[3,2]$ of solids can be obtained. The Sauter mean diameter of solid particles is an average of particle size achieved by comparing the volumetric distribution to the surface area distribution, as defined by Equation (7.4) (Allen, 2003).

$$D[3,2] = \frac{\sum_{i=1}^{n} d_i^3\, v_i}{\sum_{i=1}^{n} d_i^2\, v_i} \tag{7.4}$$

where d is the diameter of a solid particle and v_i is the proportion of particles in the size fraction. The Sauter mean diameter of solids collected in the finer overflow fraction is smaller than that of those collected in the coarser underflow fraction and solid particles in the feed flow (Golmaei et al., 2018b).

Another widely used equation in particle size measurement is proposed by the Rosin-Rammler-Bennett (RRB) model, expressed by Equation (7.5) (Rosin and Rammler, 1933):

$$F(x) = 1 - \exp[-\left(\frac{d}{X_\mathrm{R}}\right)]^{n_\mathrm{R}} \tag{7.5}$$

where $F(x)$ is the distribution function for the particle size d, X_R is the size parameter and n_R is a dimensionless uniformity index. This model can be fitted to the measured volumetric particle size distribution in the overflow and underflow fractions to calculate the size parameters and uniformity index. The calculated size parameters for coarser fractions are larger than those of the finer fractions (Golmaei et al., 2018b).

Two major factors affecting the performance of a hydrocyclone are operating and design variables. The operating variables are the solid concentration and viscosity of the feed, as well as the pressure drop and feed flow rate (Braun and Bohnet, 1990; Cilliers, 2000; Kawatra et al., 1996). On the other hand, design variables, such as the overflow port to the underflow port diameter ratio, the cone angle, the diameter of the cylindrical part, the length of the conical part, and the length of the vortex finder affect the separation performance of a hydrocyclone (Cilliers, 2000; Ghadirian et al., 2015; Hwang et al., 2008; Wang and Yu, 2006).

The performance of the hydrocyclone can be enhanced by using higher feed pressure or flow rate, which forces the coarser particles to move faster towards the walls of the hydrocyclone (Frachon and Cilliers, 1999; Ghadirian et al., 2015). The increase of pressure drop causes a reduction in cut size, while the sharpness of classification can increase or decrease (Cilliers, 2000). However, energy consumption is an important issue that should be taken into account. The characteristic Euler number Eu of the hydrocyclone is a value which determines the relationship between the pressure drop across the hydrocyclone and the kinetic energy per volume. This dimensionless number for a hydrocyclone with the diameter of D_C is defined by Equation (7.6) (Vieira and Barrozo, 2014):

$$Eu = \frac{\pi^2 D_C^4 (\Delta P)}{8\rho Q^2} \tag{7.6}$$

where ΔP is the pressure drop, ρ is the density of the liquid and Q is the feed volumetric flow rate. A higher Euler number means higher energy demand for operating a hydrocyclone (Vieira and Barrozo, 2014).

The efficiency of finer particles recovery is enhanced by reducing the diameter ratio of the overflow to underflow ports (Ghadirian et al., 2015). According to the literature (Cilliers, 2000; Hwang et al., 2008), the use of a smaller underflow port diameter increases the cut size and sharpness of classification in the hydrocyclone. By increasing the cut size, coarser particles will be collected into the underflow according to the grade efficiency curve (Svarovsky, 2000). The efficiency of light particle recovery is enhanced by increasing the length of the vortex finder (Ghadirian et al., 2015). In addition, increasing the length of the conical part improves the separation efficiency of the hydrocyclone, especially in small hydrocyclones (Wang and Yu, 2006). The cut size and sharpness of classification are increased in a hydrocyclone with a larger diameter (Cilliers, 2000). According to a study done by Chu et al. (2004), the separation performance of a hydrocyclone could be improved by installing a solid core inside the hydrocyclone to eliminate the air core.

8 Study on the filtration characteristics of green liquor dregs

At the first series of the experimental study, the effect of filtration variables on the filterability of green liquor sludge without using filter aids was investigated. The outcomes of this study are useful for optimizing the operation parameters to enhance the filterability of green liquor sludge. Furthermore, the distribution of elements between the dregs cake and green liquor (filtrate) was investigated. The outcome of this study was published in Paper II.

8.1 Methodology of cake filtration

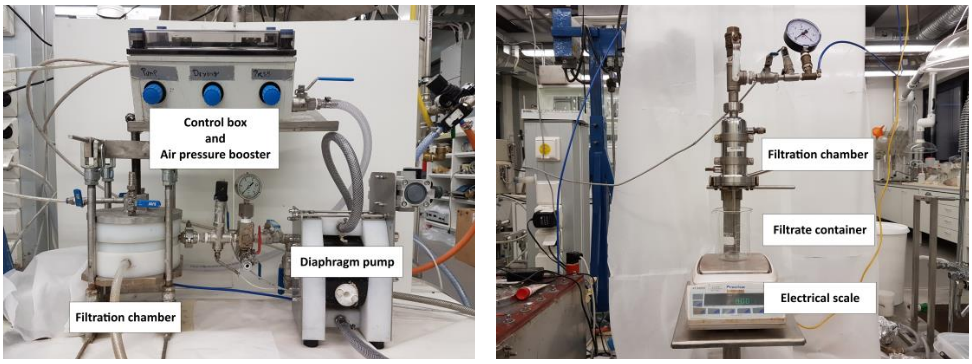
A series of filtration experiments was designed to investigate the influence of filtration variables such as pressure, temperature and sludge storage period on the characteristics of the dregs cake. The effects of these variables and filter cloth permeability on the filterability of GLD sludge were also investigated. In addition, the distribution of elements between the cake and filtrate was studied by elemental analysis.

8.1.1 Materials

The required GLD sludge samples for cake filtration were acquired from two different kraft pulp mills located in Finland. The selected mills used different techniques for green liquor purification. At the first mill, where a clarifier was installed to separate purified green liquor to the overflow, the unwashed thick GLD sludge was collected from the underflow. At the other mill, green liquor clarification was carried out by a falling film cross-flow filter consisting of a series of vertically installed filter elements in a pressure vessel, and the unwashed thick GLD sludge was collected from the reject side of the filter. The utilized GLD sludges for the filtration did not contain precoat material, and their total suspended solids contents (TSS) ranged from 4.97 to 7.14 wt-%. The total dissolved solids contents (TDS) of the GLD sludge samples were between 15.55 and 16.11 wt-%.

8.1.2 Filtration experiments

The cake filtration experiments (Paper II) were carried out by using two different laboratory-scale pressure filtration test units, a Labox-100 (manufactured by Outotec Oy, Finland) and a Nutsche filter. The filtration area of Labox-100 is 100 cm^2 which is considerably larger than the 20 cm^2 filtration area in the applied Nutsche filter. The Labox-100 test unit consisted of an air pressure booster, a control box, a diaphragm pump, and a filtration chamber with adjustable height. The filtration chamber of the Nutsche filter was equipped with a heating jacket to regulate the filtration temperature. Photos of the Labox-100 test unit and the Nutsche filter are shown in Figure 8.1.



(a) **(b)**

Figure 8.1. **a)** Labox-100 test unit, **b)** Nutsche filter set-up.

A cellulosic filter sheet of grade T 1000 (produced by Pall Filtersystems GmbH, Germany) was utilized in the Nutsche filter, and woven propylene filter cloths with different specific air permeabilities (varied from 0.08 to 3.00 $m^3m^{-2}min^{-1}$) in Labox-100.

A Nutsche filter equipped with a heating jacket for the filtration chamber was utilized to investigate the effect of filtration temperature on the filterability of GLD sludge and the characteristics of the dregs cake. The filtration temperature was varied from 20 to 80 °C at filtration pressures of 2, 4 and 6 bar. Another series of filtration experiments was carried with the Labox-100 test unit to study the effect of the permeability of the filter cloth on the filterability of GLD sludge, and the effect of storage of GLD sludge on the filtration properties.

8.1.3 **Analysis and measurements techniques**

The moisture contents of the filter cakes were measured by drying the cake samples at a temperature of 105 °C in an electrical oven for 24 h. The total dissolved solid contents (TDS) of the filtrate samples were measured by drying them at a temperature of 180 °C in an electrical oven for a specific duration, after which no more liquid was evaporated. In addition, the density of the liquid samples at their filtration temperature were measured by weighing a certain volume of those samples, taken by a pipette.

Elemental analysis of the filtrate samples was performed with a Thermo Fisher Scientific ICAP6500 Duo (Thermo Fisher Scientific Inc., Cambridge, UK) inductively coupled plasma optical emission spectrometer (ICP-OES) to measure the concentration of elements in the samples. Elemental analysis of the filter cakes was done with the same equipment after their wet digestion by using the US EPA method 305 (US Environmental Protection Agency, 1995). Prior to the wet digestion of the filter cake samples, they were dried at 105 °C in an electrical oven for 24 h, and then crushed by using a ceramic mortar and a pestle.

8.2 Filtration characteristics of GLD

According to the results published in Paper II, the filtration characteristics of GLD sludge were enhanced when using a more permeable filter cloth and higher filtration temperature. The same study revealed a negative effect of longer storage time on the filtration characteristics of GLD sludge. In addition to the filtration characteristics of the sludge, the average specific resistance and compressibility of the dregs cake at different temperatures were studied. The effects of the filtration temperature on the average specific resistance and compressibility index of the dregs cake were discussed in Paper II, and the results are summarized in Figure 8.2.

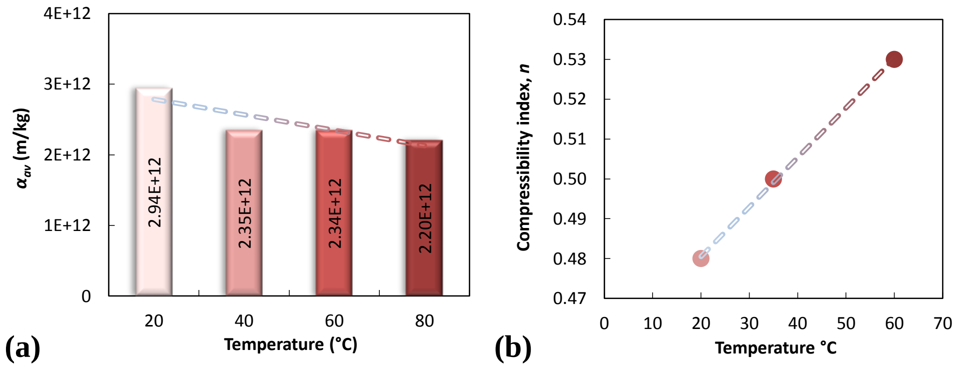


Figure 8.2. **a)** Average specific resistance of formed cake at different filtration temperatures (20, 40, 60 and 80 °C) and at filtration pressure of 4 bar in a Nutsche filter. **b)** Compressibility index of the dregs cake at different temperatures (20, 35 and 60 °C).

In Figure 8.2 the specific resistance at 20C is tangibly higher than at the higher temperatures. This may be due to that salts (most likely Na2CO3) has precipitated. At the higher temperatures there are relatively small differences regarding the specific filtration resistance and at the pressure applied. Also, less compressible cakes are formed at lower temperature. However, filtration of GLD sludge at a higher temperature could be less challenging. This result is supported by the results of filtrate flowrates presented in Paper II (Figure 5), in which the filtrate flowrate increased at a higher filtration temperature. On the other hand, the slight increase in the compressibility index of the filter cake with temperature indicates that the resistance of filter cakes is more sensitive to pressure changes at a higher filtration temperature.

As discussed in the theory part, the separated dregs cake still contains sodium, which is a valuable process element, and its recovery and conversion to cooking chemicals is of high importance to kraft pulp mills. Therefore, the dregs cake is mostly washed with water to recover its sodium content.

8.3 Distribution of elements in the dregs cake and the filtrate

The distribution of elements between the filtrate (green liquor) and the dregs cake obtained by the filtration of two samples of GLD sludge collected from different kraft pulp mills was discussed in Paper II, and the main results were presented in Table 5. The weight percentages of some elements (of interest) separated as dregs cake by the filtration of Sludge A and B are summarized in Figure 8.3.

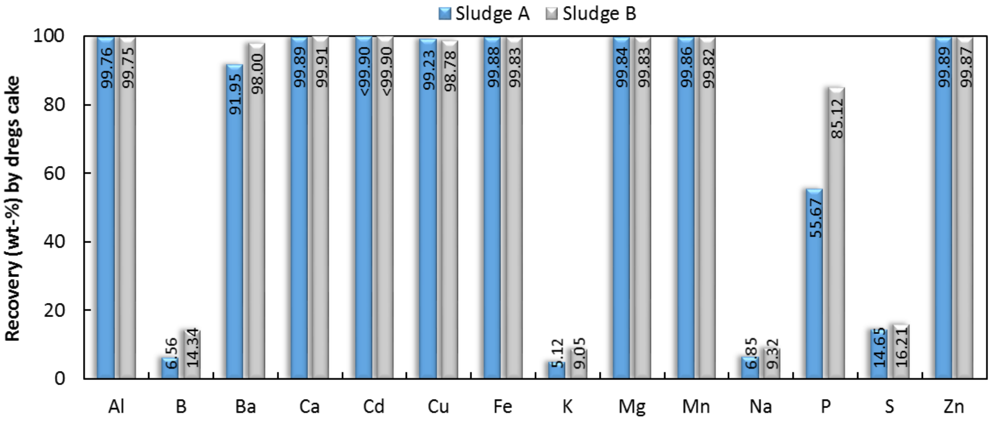


Figure 8.3. Weight percentages (wt-%) of elements present in GLD sludge located in the dregs cake. Sludge A and B were collected from two different kraft pulp mills.

According to the data presented in Figure 8.3, elements such as B, K, Na, and S are mostly and P is partially dissolved in the filtrate, as a low weight percentage of these elements remains in dregs cake after filtration. However, other elements such as Al, Ba, Ca, Cd, Cu, Fe, Mg, Mn, and Zn are mostly accumulated in the dregs.

9 Separation of hazardous metals from green liquor dregs

In the second part of this study, efficient separation of target hazardous metals including Cd, Ni, Pb and Zn from GLD was investigated. The aim of this part of the study was to find practical methods for the treatment of GLD to produce less hazardous residues or even its utilization as fertilizing products. A novel method, extraction of Cd, Ni, Pb and Zn from GLD by a chelating agent (ethylenediaminetetraacetic acid) was discussed in Paper III. In addition, the present study is the first one in which the efficient separation of hazardous trace metals from GLD by a hydrocyclone has been investigated, and promising results were published in Paper IV.

9.1 Extraction of hazardous metals from GLD by chelating agents

In the preliminary study on the extraction of trace hazardous metals from green liquor dregs (GLD), two different chelating agents, ethylenediaminetetraacetic acid (EDTA) and ethyleneglycol tetraacetic acid (EGTA), were utilized as extractants. According to the results of this preliminary study, EDTA was a more appropriate extractant for the extraction of hazardous metals from GLD. Therefore, EDTA was utilized in further experiments to investigate the effect of extractant dosage, liquid-to-solid (L/S) ratio ($ml_{Extractant\ solution}/g_{dregs}$) and contact time on the removal rate of hazardous metals from GLD, and the outcome of this study was published in Paper III.

9.1.1 Batch extraction experiments and analysis techniques

The dregs required for the extraction experiments were prepared by GLD sludge filtration, dregs drying and crushing. The sample of GLD sludge was collected from the reject side of an X-Filter (a falling film cross-flow filter) at a Finnish kraft pulp mill. The total concentrations of the elements in the dregs were measured with an inductively coupled plasma optical emission spectrometer (ICP-OES). The extractant solutions were prepared by dissolving the chelating agents in Millipore water. After complete dissolution of the chelating agents, the pH values of the extractant solutions were adjusted to the desired level by adding an acidic solution (HCl 0.1 M) or an alkaline solution (NaOH 0.1 M).

Then the pH-adjusted extraction solution was added on 4 g of dregs in plastic bottles, and the suspension was shaken in an orbital shaker for 24 h at ambient temperature (20 ± 0.5 °C). After completing the batch extraction, the suspension was centrifuged at 4000 rpm (3082 g) and 20 °C for 30 min. Then the supernatant phase, which was mostly separated from the remaining dregs by centrifugation, was filtered through a syringe filter (Phenex RC 0.45 mm) and sent for elemental analysis. The concentrations of elements in the supernatant samples were measured by inductively coupled plasma mass spectrometry (ICP-MS). The flow diagram in Figure 9.1 illustrates the procedure of a batch extraction test.

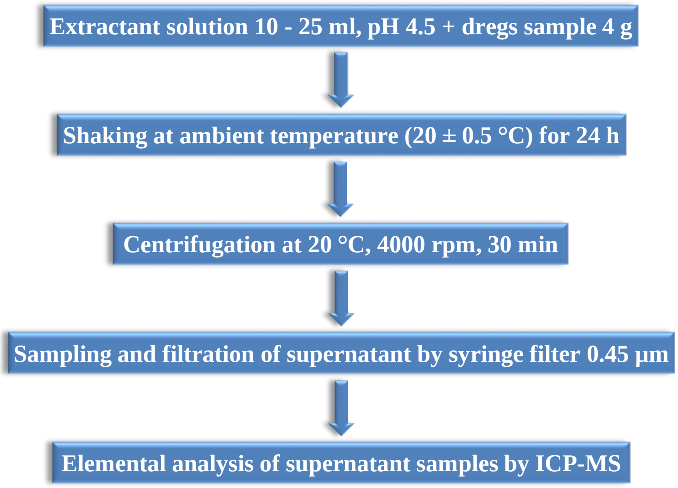


Figure 9.1. The procedure of a batch extraction test.

Various dosages of EDTA, from 0.00025 to 0.035 $\text{g}_{\text{EDTAsalt}}/\text{g}_{\text{dregs}}$, which equals 0.003 to 2.4 EDTA/sum of metals (Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) molar ratio (-) were utilized in the extraction experiments. The L/S ratio was varied from 2.5 to 6.25 $\text{ml}_{\text{extractant solution}}/\text{g}_{\text{dregs}}$, and the batch extraction experiments were performed with different durations (contact time) of 30, 60, 120, 300, 720, 1440 and 2160 min.

9.1.2 Results and discussion

In the first step of the extraction experiments, the extractability of elements such as Ca, Cd, Co, Cu, Mn, Pb and Zn by two different chelating agents, EDTA and EGTA was investigated. Figure 9.2 shows the results of the preliminary experiments in which the concentration of the chelating agents in the extractant solutions was 0.01 M, and the adjusted pH of the extractant solution was 9. The preliminary extraction experiments were done with an L/S ratio of 6.25 $\text{ml}_{\text{extractant solution}}/\text{g}_{\text{dregs}}$ and contact time of 24 h.

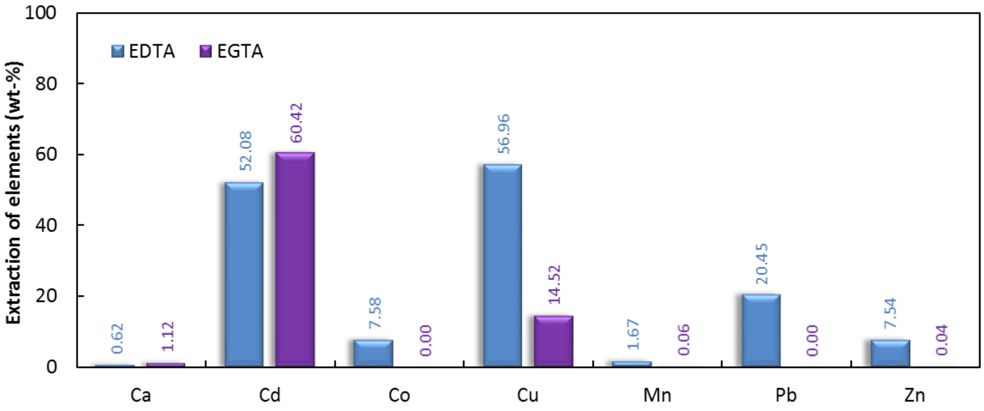


Figure 9.2. Extraction of elements by the use 0.01 M of EDTA and EGTA extractant solutions with pH-adjusted to 9. The batch extraction experiments were done with the L/S ratio of 6.25 $ml_{extractant\ solution}/g_{dregs}$ and at contact time of 24 h.

According to the data presented in Figure 9.2, EGTA was more efficient than EDTA in the extraction of Cd, while much higher amounts of the other two hazardous trace metals Pb and Zn, together with Co, Cu and Mn were extracted by EDTA. So, EDTA was generally more efficient than EGTA in the extraction of hazardous trace metals, and it was selected for the continuation of the extraction experiments.

In addition, the effect of the pH of the extractant solution on the removal of metals from the dregs was investigated in preliminary experiments. The pH of the prepared dregs suspensions for the extraction experiments was 10.3 at 1:5 mass ratio of dregs to Millipore water. The measured pH of the suspensions after the batch extraction experiments were high enough to prove that the pH of the extractant solution had no tangible influence on the final pH of the suspension. In addition, the results of the preliminary tests did not show a considerable effect of the pH of extractant solution on the extractability of elements. Therefore, the variable of pH was no more considered in further experiments, but as a standard method, the pH of all prepared extraction solutions were adjusted to 4.5.

The further study on the extraction of Ca and hazardous metals together with NPEs such as Co, Cr, Cu, Mn from GLD by the use of EDTA was published in Paper III. According to this study, the increasing dosage of EDTA from 0.00025 to 0.035 $g_{EDTA\ salt}/g_{dregs}$ at an L/S ratio of 6.25 $ml_{extractant\ solution}/g_{dregs}$ improved the extraction of all discussed elements considerably, except for Cr. In addition, EDTA was not able to extract a considerable amount (less than 1 wt-%) of Ca at EDTA dosage of 0.035 $g_{EDTA\ salt}/g_{dregs}$. A redundant increase of the dosage of EDTA from 0.035 to 0.23 $g_{EDTA\ salt}/g_{dregs}$ did not show considerable improvement in the removal of Cd, Ni, Pb and Zn. Figure 9.3 shows the extraction of elements Ca, Cd, Co, Cr, Cu, Mg, Mn, Ni, Pb, and Zn from GLD at the

EDTA dosage of 0.23 $g_{\text{EDTA salt}}/g_{\text{dregs}}$ and L/S ratio of 6.25 $ml_{\text{extractant solution}}/g_{\text{dregs}}$ with contact time of 24 h.

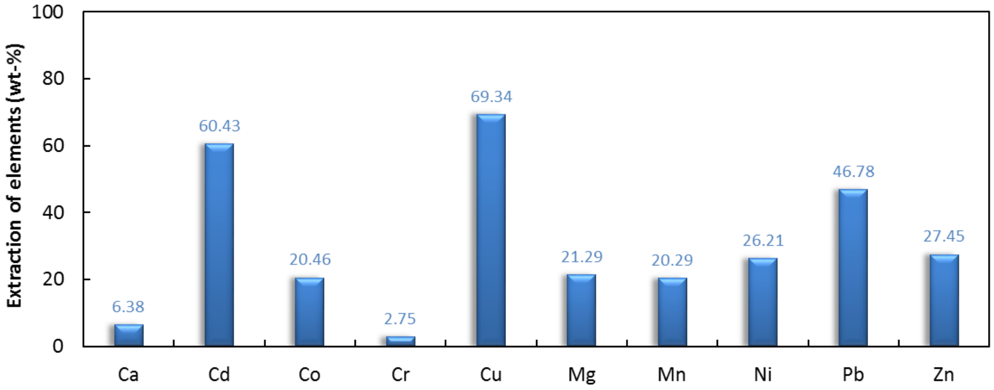


Figure 9.3. Extraction of elements Ca, Cd, Co, Cr, Cu, Mg, Mn, Ni, Pb, and Zn from GLD at an EDTA dosage of 0.23 $g_{\text{EDTA salt}}/g_{\text{dregs}}$ and L/S ratio of 6.25 $ml_{\text{extractant solution}}/g_{\text{dregs}}$ with contact time of 24 h.

As shown in Figure 9.3, EDTA was able to extract a high amount of Cd (60 wt-%) and a considerable amount of other hazardous metals, such as Ni, Pb, and Zn, while keeping most of Ca. On the basis of Table 3.1, Ca is the main mineral nutrient present in the GLD. Thus, EDTA is able to extract hazardous metals from GLD, while keeping the main mineral content of GLD. In other words, EDTA can be utilized as an efficient extractant for the treatment of GLD and make this residue an appropriate raw material for producing fertilizers.

According to the results published in Paper III, the effect of increasing the L/S ratio was on average positive for the extraction of all elements, except for Mn and Ni. Furthermore, most of the studied elements were extracted from the dregs for the most part during the first 30 min of extraction.

9.2 Separation of hazardous metals from GLD by a hydrocyclone

In the study published in Paper IV, a hydrocyclone was utilized for mechanical separation of hazardous trace metals (Cd, Ni, Pb and Zn), rare earth elements, and other trace metals into the overflow and underflow fractions. The experiments in this study were designed to investigate the effect of parameters such as the overflow to the underflow outlet diameter ratio and inlet pressure on the efficiency of elemental classification into finer overflow fractions and coarser underflow fractions. In addition, the effect of mechanical classification by the hydrocyclone on the filtration properties of GLD sludge was discussed in detail in Paper IV. The required GLD sludge for the experiments was collected from the reject side of a GLD X-Filter operating at a Finnish kraft pulp mill. The utilized GLD sludge did not contain precoat material, and its total suspended solids content (TSS) was 5 wt-% and the total dissolved solids content (TDS) of the sludge was 21 wt-%.

9.2.1 Classification and filtration experiments

Classification experiments were carried out by using a standard narrow-angle hydrocyclone with a relatively long and narrow cylindrical part. The hydrocyclone classification was performed as a single-pass process. The dimensions of the applied hydrocyclone are presented in Figure 9.4.

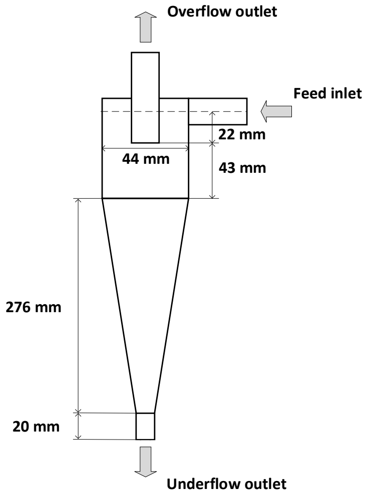


Figure 9.4. The dimensions of the hydrocyclone applied for the classification of GLD.

The hydrocyclone was connected to a screw-type positive displacement pump which fed GLD sludge into the hydrocyclone from a feed tank located under the underflow outlet. The overflow to underflow outlet diameter ratios (*Do*/*Du*) were varied by changing the underflow diameter from 3 to 8 mm, while the overflow diameter was 11.1 mm in all tests. Feed pressures of 1 and 1.5 bar were used in the hydrocyclone classification. After the hydrocyclone tests, a series of constant pressure filtration tests were carried out to investigate the effect of mechanical classification on the filtration properties of GLD. These experiments were carried out at room temperature with a laboratory-scale Nutsche pressure filter with the filtration area of approximately 20 cm^2 and using a cellulosic filter sheets (grade T 120, produced by Pall Filtersystems GmbH (Germany)).

The moisture content of filter cakes was measured by drying them in an electric oven at 105 °C. The fractionation of the elements between the overflows and underflows were calculated by using the results of elemental analysis on the dried dregs cakes. After crushing the dried dregs cakes with a ceramic mortar and pestle, the solid samples were digested according to the US EPA method 305 (US Environmental Protection Agency, 1995). Then, the concentration of elements in the resulted liquid samples were measured with an inductively coupled plasma optical emission spectrometer (ICP-OES).

9.2.2 Classification of elements into overflow and underflow

As described above, the concentrations of elements in the dregs collected by the overflows and underflows were measured with ICP technique. The analysis results were used in calculations to find out the classification of each element by the hydrocyclone. The classified fractions (wt-%) of the dregs and elements such as Al, Ba, Ca, Cd, Cr, K, Mg, Mn, P, and Zn into overflows are summarized in Figure 9.5.

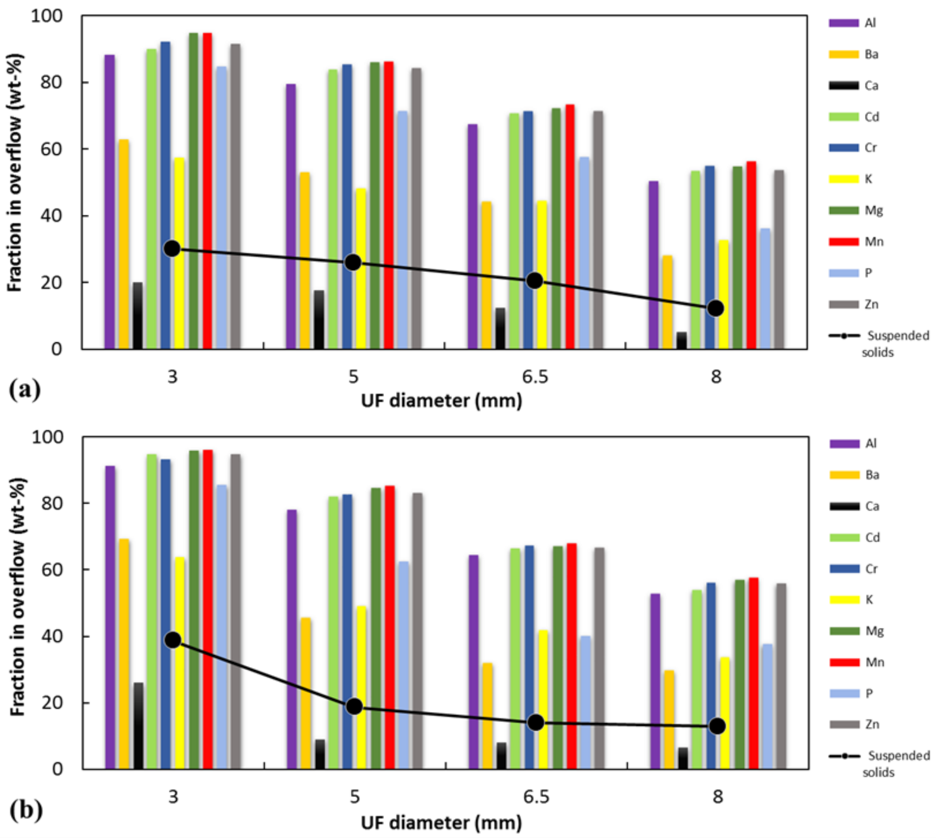


Figure 9.5. The fraction (wt-%) of Ca, Al, Cd, Cr, Cu, Fe, Mg, Mn, Ni, and Zn with suspended solids collected by overflows at underflow diameters of 3, 5, 6.5 and 8 mm with a fixed overflow diameter of 11.1 mm and hydrocyclone pressure of 1 bar (a) and 1.5 bar (b).

As can be seen in Figure 9.5, a relatively small fraction of dregs (suspended solids) and a majority of hazardous metals, such as Cd, Ni, and Zn were separated into the overflow, while Ca was mostly separated into the underflow. Also, the separation efficiency of finer dregs and elements into the overflow was reduced when increasing the diameter of underflow. It was observed that the metals present in GLD were mostly concentrated in the finer overflow fractions. In other words, the classification of the dregs by the hydrocyclone resulted in two fractions: overflow rich in hazardous metals and underflow rich in Ca. According to the results published in Paper IV, REEs such as Er, Eu, Gd, Ho, La, Nd, Pr, Sm, Tb, Tm, Yb, and Y together with trace metals such as Ag, Th, U, Co, Li, Rb, Ti, and Zr were mostly accumulated in the finer overflow fraction.

Assessment of utilizing the underflow fraction as different product function categories (PFC) of CE-marked fertilizing products was included in Paper IV. According to the study, the levels of hazardous metals in some underflow fractions were lower than their maximum allowed levels in some of the CE-marked fertilizing products determined by the European Commission in March 2016 (EC-European Commission, 2016). This means that purified dregs can be used as raw material for producing certain fertilizing products.

9.2.3 Effect of mechanical classification on the filtration characteristics of GLD

The effect of hydrocyclone classification on the filtration properties of the underflow and overflow fractions was studied in Paper IV. The coarser dregs were separated into the underflow, while the finer dregs migrated rather to the overflow. The filterability of the underflow fractions containing coarser particles was better than that of the original GLD sludge and the overflows. In addition, the underflow cakes had lower moisture contents and lower average specific resistances, compared to the original sludge and overflow cakes. Calculation of the required filtration area for overflows, underflows and original sludge gives a reasonable comparison of filterability. In Figure 9.6, the filtration areas required for the original GLD sludge are compared with the filtration areas required for the overflows and underflows of a hydrocyclone with a 10.8 t/h feed rate of GLD sludge at inlet pressures of 1 and 1.5 bar.

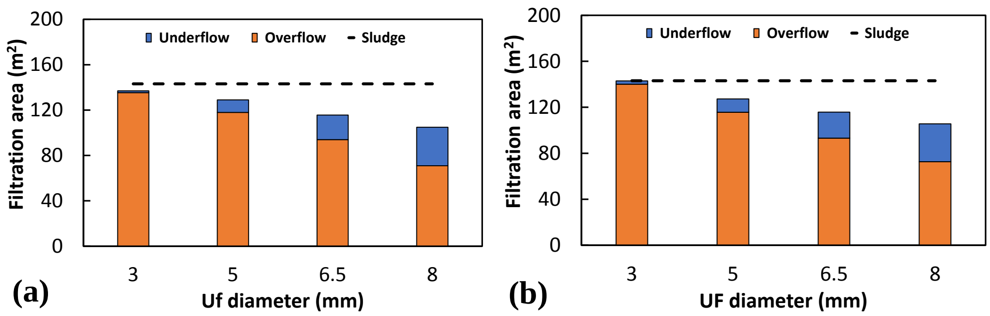


Figure 9.6. Required filtration areas for overflows and underflows, compared with the initial GLD sludge at the filtration pressure of 6 bar, when 10.8 t/h of sludge is fed to the hydrocyclone at pressure differences of 1 bar (a) and 1.5 bar (b) by using different diameters of the underflow (UF).

Figure 9.6 shows how the filterability of GLD sludge can be improved by utilizing a hydrocyclone at the pre-treatment stage. As can be seen in this figure, the total required filtration area for the overflows and underflows is generally lower than that required for the original sludge. Also, the total required filtration area for the overflows and underflows can be reduced when a larger underflow diameter is used in the hydrocyclone.

10 **Conclusions**

In this thesis, novel methods for the treatment of green liquor dregs (GLD) were studied to find new applications for GLD instead of landfilling. In the first part of the study, the filtration characteristics of GLD were investigated to find the effect of filtration variables on the filterability of GLD sludge. In the second part, separation of target hazardous metals, including Cd, Ni, Pb and Zn, from GLD by chemical and mechanical separation methods were investigated. In a batch process, chelating agents were utilized for the extraction of hazardous metals from GLD. Separation of hazardous metals from GLD by hydrocyclone classification was investigated in the second part as well.

Filtration variables like temperature and storage time have considerable effects on the filterability of GLD sludge, due to the great amounts of dissolved solids present in the liquid phase of the GLD sludge. At an elevated filtration temperature, the filterability of GLD sludge was improved. Moreover, the compressibility of the dregs cake increased slightly by heating, which means that the effect of pressure difference on cake resistance is considerable at a higher temperature. In other words, the filterability of GLD sludge can be improved by optimized filtration parameters, and consequently, the required amount of precoat lime mud which is applied to ease the filtration of GLD sludge can be reduced. This means a considerable reduction potential of solid residues in kraft pulp mills as well. The solubility of elements such as Na, K and B in green liquor is slightly influenced by filtration temperature, so the removal of these elements from the dregs cake can be enhanced by optimizing the filtration temperature. Elemental analyses of the dregs cakes proved that metals like Al, Cd, Fe, Mn and Zn are mostly insoluble in green liquor and they are accumulated in the GLD.

According to the outcome of the first part of the study, the poor filterability of GLD sludge, which is known to be a challenge, could result partly from non-optimized filtration parameters. In addition, it was found that the target hazardous metals are not soluble in green liquor, so they mostly remain in dregs cake after filtration. On the other hand, based on the literature, Cd is not water soluble and traces or very small amounts of other target hazardous metals are soluble in water. Hence, novel methods rather than currently applied filtration and dregs washing with water for removal of target hazardous metals from GLD were looked for. In the second part of the study, removal of target hazardous metals from GLD by chemical extraction and mechanical classification were investigated.

Through a chemical separation method, extraction of target hazardous metals from GLD by using chelating agents was studied. Of the target hazardous metals, Cd was efficiently extracted (up to 60 wt-%) from GLD dregs by using both chelating agents EDTA and EGTA, while only EDTA was able to extract other hazardous metals, such as Pb and Zn. At the EDTA dosage of 0.23 $g_{\text{EDTA salt}}/g_{\text{dregs}}$ and L/S ratio of 6.25 $ml_{\text{extractant solution}}/g_{\text{dregs}}$, 60 wt-% of Cd, 26 wt-% of Ni, 47 wt-% of Pb and 27 wt-% of Zn were extracted after 24 h of contact time. Considerable amounts of hazardous metals were extracted from the dregs during the first 30 min of contact time. The removal of target hazardous metals was not improved considerably by further increase of the dosage of EDTA from 0.035 to 0.23

$g_{EDTA\ salt}/g_{dregs}$. In addition, less than 1 wt-% of Ca was extracted from GLD at the EDTA dosage of 0.035 $g_{EDTA\ salt}/g_{dregs}$.

In a wider view, the results show that the chelating agents are capable to extract a considerable weight ratio of target hazardous metals from GLD in a relatively short period of batch extraction and low concentration of a chelating agent. However, the effect of particle size on the extractability of target hazardous metals was not discussed in this study. In finer dregs particles, the target hazardous metals are likely to be more available for complexation with chelating agents due to their high specific surface area. In other words, the extraction of target hazardous metals from GLD with the same studied variables of batch extraction might be enhanced by having an extended grinding stage for GLD. Prior to developing this treatment method in a large scale, extraction and immobilization of metal-EDTA/EGTA complexes from the supernatant phase should be considered in order to prevent an environment-polluting effect by their release into water resources. Therefore, the open question remaining after this part of the study is to find practical solutions for treatment of the supernatant phase.

By hydrocyclone classification, GLD was divided into a finer overflow and a coarser underflow fraction. According to the results, all target hazardous metals were accumulated in the finer overflow fractions. The results showed that 90 wt-% of Cd, 70 wt-% of Ni and 91 wt-% of Zn were accumulated in 30 wt-% of the dregs separated into the finer overflow fraction. Also, 81 wt-% of Ca present in the dregs was separated into the underflow fraction containing r 70 wt-% of dregs and a smaller share of hazardous metals. This means that the target hazardous metals were mostly separated into the overflow fraction, and the underflows containing a larger share of dregs and Ca could be used as raw material for fertilizing products. However, finding practical methods for the treatment of overflow fractions still remains an open question for this part of the study. Furthermore, the filterability of GLD sludge was improved by hydrocyclone classification, as the total filtration area required for the overflows and underflows was lower than that required for the original sludge. In other words, the fixed and maintenance costs of filtration systems currently utilized for green liquor dregs could be reduced when hydrocyclone classification is used as the pre-treatment method.

The present study is the first one where chemical and mechanical separation methods have been used successfully to separate hazardous metals like Cd, Cr, Ni and Pb from GLD. Compared to the studied chemical method, hydrocyclone classification was more efficient in the separation of the target hazardous metals, and could be applied as a pre-treatment process to improve the filterability of GLD as well. Moreover, a further treatment process is necessary for the chemical method to remove metal-chelating agent complexes from the supernatant phase, to prevent serious environmental pollution. On the other hand, hydrocyclone classification has challenges of its own. The most significant challenge is changes in the properties of the generated GLD, which affects the separation efficiency of hydrocyclone classification.

According to the study published in Paper IV, the concentration of hazardous metals in the underflow fractions of hydrocyclone classification is lower than their maximum allowed level in some of CE-marked fertilizers. This means that the dregs separated into underflow fractions can possibly be utilized as a raw material for the production of fertilizers in the future. GLD has the biggest share among the inorganic residues of the kraft pulping process, and its usage as sustainable products is not only a significant success as regards material usage in the circular economy, but also a step towards more environment-friendly pulp mills. As a continuation for this study, the extraction of target hazardous metals from overflow fractions of hydrocyclone by the use of chelating agents, as well as treatment of supernatant phase could be investigated to reduce the landfill disposal of GLD further.

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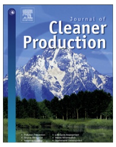

Review

Separation, treatment and utilization of inorganic residues of chemical pulp mills

Teemu Kinnarinen*, Mohammad Golmaei, Eeva Jernström, Antti Häkkinen

LUT School of Engineering Science, Lappeenranta University of Technology, P.O. Box 20, FI-53851 Lappeenranta, Finland

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A B S T R A C T

The major inorganic solid residues of chemical pulp mills include green liquor dregs, various lime residues, recovery boiler fly ash, and salt cake produced at the chlorine dioxide generator. Only a small proportion of these residues is currently utilized outside the mill area: landfill disposal and reuse at the mill are the most typically applied methods. The situation should be improved in the future for environmental and economical reasons. The focus of this review is on the separation of inorganic pulp mill residues to enhance the possibilities of their utilization. Solid-liquid separation operations, such as filtration and sedimentation, and the associated treatment processes, are described in close detail. The review aims at recognizing the most promising residues for utilization, as well as enhancing the understanding of the material balance of chemical pulp mills. The review also covers the most potential industrial applications for the utilization of residues, as well as the possibilities of using them as raw material in value-added products.

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* Corresponding author.
E-mail address: teemu.kinnarinen@lut.fi (T. Kinnarinen).

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1. Introduction

Chemical pulp mills produce a number of different waste streams, which can be roughly divided into organic and inorganic residues. The focus of this review article is on the main inorganic side streams, including green liquor dregs (GLD), various lime residues, fly ash of the recovery boiler, and the sodium sesquisulfate produced in the ClO_2 generator. Out of these residues, all except sesquisulfate are more or less alkaline. The motivation for this study has arisen from the increasing need to utilize these residues as valuable materials and products instead of the currently applied landfill disposal and recirculation in the chemical recovery cycle of the mill. The general trend in the pulp and paper industry has been towards the minimization of landfill disposal (Monte et al., 2009). Some of the most important drivers towards the utilization of inorganic residues are probably the increasing cost of landfill disposal (Eroglu et al., 2006), the decreasing availability of high-grade mineral resources (Tilton, 2001), the high price of fertilizers (Brunelle et al., 2015), and the increasing demand of soil amendments due to intensified agriculture (Edmondson et al., 2014). GLD and lime mud are produced and stacked in landfill sites in relatively large quantities, whereas the other inorganic residues are available at much smaller amounts.

Appropriate separation technology is of high importance in the chemical recovery cycle of Kraft mills. Solid-liquid separation is performed for green liquor to get rid of the dregs, and for the lime slurry to remove grits from the slaker and to separate white liquor from the solids after recausticizing. Washing of the separated solids is typically carried out in a sedimentation system or a filter unit, sometimes sequentially in both. The separation technology does not only enable efficient operation of the mill, but may also enhance the possibilities of utilizing the inorganic residues. Purification may be necessary to reduce the pH and to remove harmful components, such as heavy metals (Nurmesniemi et al., 2005; Cabral et al., 2008; Sanchez and Tran, 2005). Soil contamination is one possible environmental side effect of landfilling the inorganic wastes generated in pulp mills which contain heavy metals. The leachability of heavy metals from GLD has been extensively studied by Manskinen et al. (2011) and Pöykiö et al. (2014). The study of Cabral et al. (2008) supports the idea of possible release of metals into the soil from inorganic wastes of pulp mills. Furthermore, the water resources near the landfill area are in threat of pollution by the liberated heavy metals. In the best case, the purification and dewatering steps which are sometimes required for utilization outside the mill area could be performed in the existing separation equipment of the mill (Tikka, 2008). For this reason, the currently applied separation techniques and their challenges are paid special attention to in this review. The separation aspects are discussed with respect to the overall chemical balance of the mill, because proper removal of non-process elements (NPE) from the recovery cycle is of crucial importance. The most potential applications of the residues found in the literature are also discussed.

2. Chemical recovery in Kraft pulping

2.1. Chemical recovery cycle

The recovery boiler is the heart of a Kraft pulp mill: it is essential for the recovery of the cooking chemicals, and it utilizes the heating value of the extracted wood components. Good runnability of the chemical recovery cycle of the process is the key to economical and material-efficient operation of a pulp mill. The efficiency of the recovery of pulping chemicals can be as high as 97% (Sretenovec, 2012). The sodium-sulfur balance in black liquor after cooking is affected by the quality of the raw material of the mill, and by several process-related factors. The sulfur in black liquor takes many forms, for instance sulfide, thiosulfate, sulfite, sulfate, and organic sulfur (Hupa, 1993). Sodium is present e.g. as NaOH, Na_2O, and with sulfur e.g. as sodium sulfide Na_2S, thiosulfate $Na_2S_2O_3$, sulfate Na_2SO_4, sodium sulfite Na_2SO_3, and sodium bound in organic material. Sodium and sulfur account for approximately 20% and 3–6% of the dry solids in black liquor, respectively (Mikkanen, 2000).

The aim of the recovery cycle is to be able to reuse the sodium- and sulfur-containing pulping chemicals. The cooking liquor is effective only if the chemicals are in a reactive form as NaOH and Na_2S. Therefore, it is important to be able to obtain a high degree of sulfur reduction in the recovery boiler (Tran and Vakkilainen, 2007). However, after the burning of the concentrated black liquor in the recovery boiler, a great proportion of the cooking chemicals in the smelt are in an ineffective form as sodium carbonate Na_2CO_3 and sodium sulfate Na_2SO_4. Among the smelt compounds, only Na_2S is effective without further conversion. The sodium carbonate content is converted back to the effective hydroxide form by recausticizing (Tikka, 2008). A simplified sketch showing the four major operations in the chemical recovery cycle

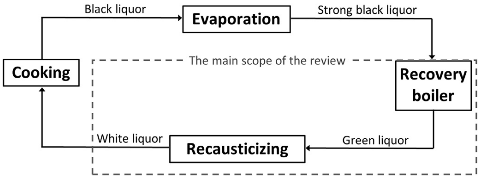


Fig. 1. The main operations of the chemical recovery cycle at Kraft pulp mills.

and the most important process liquors is presented in Fig. 1, which also shows the scope of this review.

2.2. Chemistry of recausticizing

The dissolution of the smelt from the recovery boiler can be regarded as the starting point of the recausticizing process. In order to avoid loss of chemicals, sodium in particular, weak wash liquor obtained from lime mud and green liquor dregs washings is fed into the dissolver. At this stage sodium is soluble Na_2CO_3 and most of the sulfur is in the reduced form as soluble sodium sulfide Na_2S, which is an effective cooking chemical and should not therefore be affected by the recausticizing process (Sixta, 2006).

The main reaction in the recausticizing process is conversion of the Na_2CO_3 content of the green liquor to NaOH (Pöykiö et al., 2006a). All the important reactions taking place at the recausticizing plant are well-known and have been presented in a countless number of literature sources, for instance by Tikka (2008), Theliander (2008) and Sanchez (2008). The main reaction, conversion of sodium carbonate to hydroxide, requires large quantities of soluble hydroxide, which is obtained by the calcination of lime mud ($CaCO_3$) in the lime kiln to produce CaO, which is subsequently converted according to Eq. (1) to $Ca(OH)_2$ with green liquor in the slaker, where the recausticizing reaction is initialized:

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq) \tag{1}$$

The produced calcium hydroxide is slightly soluble in the liquid. Its solubility in water is 1.9 g L^{-1} at 0 °C and 1.3 g L^{-1} at 50 °C (National Lime Association, 2007). It is, however, reactive enough with the sodium carbonate content of the green liquor to be slowly converted to sodium hydroxide in a series of causticizing reactors:

$$Ca(OH)_2(aq) + Na_2CO_3(aq) \rightarrow 2NaOH(aq) + CaCO_3(s) \tag{2}$$

The recausticizing reaction is exothermic and is typically performed in a series of 5–9 stirred tank reactors, where the impeller is usually either of the pitched-blade or the Rushton turbine type and rotates at a speed of 60–80 rpm (Theliander, 2008). The reaction is reversible, which means that it is impossible to obtain a complete conversion. The equilibrium is influenced by the concentration of the total titratable alkali at the applied level of sulfidity (Mehtonen, 2013).

The solid byproduct of recausticization, calcium carbonate, present in lime mud is converted to the reactive calcium oxide form in the lime kiln according to

$$CaCO_3(s) \xrightarrow{Heat} CaO(s) + CO_2(g) \tag{3}$$

The lime kiln is typically a long (50–120 m) cylindrical rotary kiln with a diameter of about 2–4 m (Järvensivu et al., 2001a; Hagemoen, 1993). The specific energy consumption of the lime kiln is considerable, varying usually from 5.5 to 6.5 GJ per ton of CaO (Järvensivu et al., 2001a). The purity of the obtained CaO is over 80%, and the main impurities are unburnt calcium carbonate, silica and magnesium oxide (Bharathi et al., 2006).

In practice, various inorganic impurities consisting e.g. of inert material and non-process elements must be removed from the recovery cycle to enable trouble-free operation of the mill. These impurities originate mainly from limestone containing inert $CaCO_3$, oxides of iron, aluminum, and silicon (Lewis and Crocker, 1969; Andreola et al., 2011), as well as from insoluble compounds removed from the green liquor. The most essential factors affecting the recausticization system include the quality of lime and its relative dosage, green liquor concentration, temperature, and the stirring conditions in the reactors (Andreola et al., 2011).

3. Inorganic pulp mill residues

3.1. Origin of the residues

The major inorganic side streams in the recovery cycle are formed (Fig. 2) due to various reasons:

- Green liquor dregs consist of insoluble residue of the smelt dissolver, where the suspended solids content is 600–2000 mg L^{-1} (Tikka, 2008). The reported pH of GLD from the output of a precoat filter is typically within the range of 10–12.8 (Manskinen et al., 2011). The dregs are of high importance regarding the disposal of the non-process elements (Ulmgren, 1997; Ellis and Johnson, 2011).
- Lime mud is the solid byproduct of causticizing, regenerated in the lime kiln. Part of it is removed from the process as a precoat in the GLD filter (Tikka, 2008). The pH of lime mud varies, and is often at the same level with that of GLD (He et al., 2009; Sthiannopkao and Sreesai, 2009).
- Slaker grits are formed as a coarse residue on the bottom of the lime slaker, from where they are removed with a rake or an inclined screw. The dwell time of the suspension in the slaker is typically about 15–25 min, and the solids contents of slaker grits is typically about 75% (Sanchez and Tran, 2005). The pH of slaker grits is usually higher than 12.5 (Li et al., 2012a).
- Other lime residues are either dusts formed in the lime dryer or the lime kiln, from where they are collected by electrostatic precipitation, or miscellaneous solids collected sporadically by mechanical cleaning of the kiln. These minor residues do not have much practical importance, so they are not discussed in closer detail in this review.
- Fly ash formation in a recovery boiler is initialized in the gas phase. The temperature in the recovery boiler (max. 1300–1400 °C) is high enough to volatilize alkali metals, such as Na and K, as well as other elements (S, Cl, and C), which are necessary for alkali salt formation (Mikkanen et al., 1999). Most volatilized Na is converted in the gas phase to NaOH, which is subsequently converted with SO_2 to Na_2SO_4 (Saturnino, 2012). The pH of recovery boiler fly ash is typically lower than that of lime residues, as reported e.g. by Sthiannopkao and Sreesai (2009). The fly ash from the recovery boiler is precipitated by electrostatic precipitators (ESP). The fly ash differs from various power boiler fly ashes so significantly that it is often called ESP salt instead of fly ash.
- Sesqui salt is generated at mills producing ClO_2 for bleaching. The reaction incorporates reduction of sodium chlorate by methanol in strongly acidic conditions (Chen et al., 2004). The solid byproduct, sodium sesquisulfate $Na_3H(SO_4)_2$, is produced as a salt cake and separated with a filter, and the second byproduct, formic acid, results from the oxidation of methanol (Thompson et al., 1995; Burke et al., 1993):

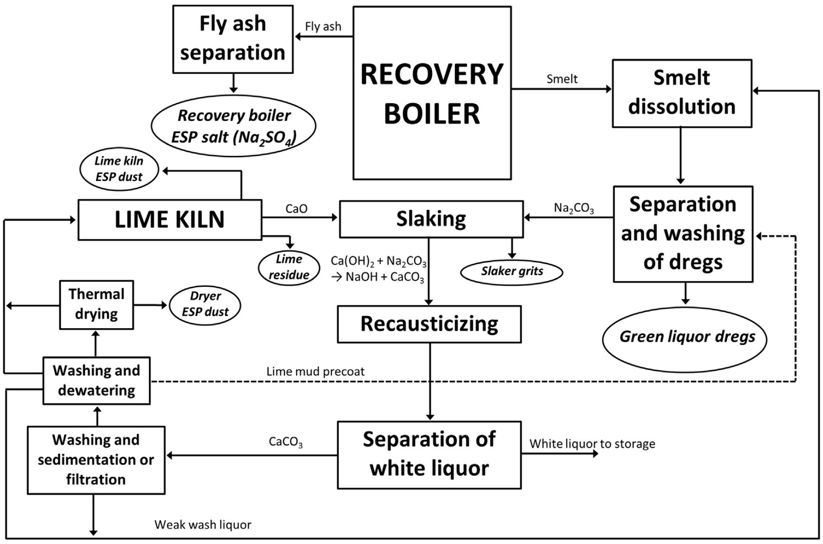


Fig. 2. The origin of inorganic residues in Kraft pulping.

$$2CH_3OH + 9NaClO_3 + 6H_2SO_4 \rightarrow 9ClO_2 + 3Na_3H(SO_4)_2 + 0.5CO_2 + 1.5CHOOH + 7H_2O \qquad (4)$$

It is common to use excess sulfuric acid in order to ensure a high reaction rate, so the sesquisulfate product contains approximately 20 w-% of sulfuric acid (Bucher et al., 2009; Burke et al., 1993). Sodium sesquisulfate formation takes place outside the chemical recovery cycle, but as the salt cake is often mixed with black liquor to recover sodium and sulfur, it contributes to the chemical balance of the mill.

3.2. Quantities of residues

The annual quantity of *landfilled* GLD solids in Finland was 64,200 metric tons in 2012 (Finnish Forest Industries, 2013). The figure includes also the lime mud used as a precoat. Manskinen (2013) mentions that 90,000 metric tons of GLD were *generated*, according to an earlier report of Finnish Forest Industries from the year 2012. Assuming an annual Kraft pulp production of 7 million tons in Finland, and the fact that GLD from semi-chemical pulping was not included in the number, the specific production rate in chemical pulping was 12.8 $kg_{dregs}\ t_{pulp}^{-1}$. This is in accordance with the typical range of 4–20 kg per ton of pulp, reported by Nurmesniemi et al. (2005).

Statistics about global GLD production are not available. Rough approximation of the quantities can be performed on the basis of available sources. Sanchez and Tran (2005) report GLD production of four North American mills to vary from less than 3000 to over 13,000 kg per day, corresponding to 4–11 $kg_{dregs}\ t_{pulp}^{-1}$, and report a typical value for a Kraft mill to be 5–6 kg t_{pulp}^{-1}. This specific production rate is in good agreement with that of the Finnish mills discussed above. If the same amount of GLD is approximated with relation to the global production of Kraft pulp, 117 million tons per year (Sixta, 2006), the annual quantity of GLD generated globally ranges from 0.5 to 1.3 million tons. Most of globally generated GLD is currently landfilled (Manskinen, 2013; Pöykiö et al., 2006a).

Table 1 lists the two major lime fractions, their production amounts, and the currently used methods of disposal and reuse.

Out of the lime residues, only lime mud is available in considerable quantities. The amount of slaker grits typically increases when the quality of the burned lime is poor (Sanchez, 2008).

The amount of recovery boiler ESP salt generated at pulp mills is relatively small, and statistics are not available. The ESP salt produced in recovery boilers represents only a very small proportion of all ashes generated in the industry: earlier studies have reported the share of ESP salt to be about 1% of the total ash production (Elliott and Mahmood, 2006).

The production of one ton of ClO_2 (Eq. (4)) generates 1.35 tons of sodium sesquisulfate $Na_3H(SO_4)_2$, which is often neutralized with NaOH to obtain 1.46 tons of Na_2SO_4 (Thompson et al., 1995). Alternative processes for chlorine dioxide production, for instance a H_2O_2 based process have been developed to reduce the environmental impacts (Burke et al., 1993; Chen et al., 2004; Crump et al., 1998; Qian et al., 2007).

3.3. Composition of residues

The composition of the inorganic residues varies between mills and by time. The elemental and mineralogical compositions of the residues are discussed below.

3.3.1. Green liquor dregs

Green liquor dregs are separated from green liquor as a thick slurry or cake: the moisture content varies from less than 60 to about 70 w-% (Matilainen et al., 2014). The main solid compounds in GLD are calcium carbonate $CaCO_3$, magnesium hydroxide $Mg(OH)_2$, carbon, and metal sulfides, especially FeS (Sanchez and

Table 1
The main lime fractions, their quantities and current disposal, and reuse at the pulp mill.

Lime fraction	Quantity	Reuse(s)	Reference(s)
Lime mud	About 0.5 ton per 1 ton of pulp	Burning to CaO in lime kiln, disposal with GLD	Sun et al. (2013); Tikka (2008); Wirojanagud et al. (2004)
Slaker grits	Small[a], varies a lot	Direct disposal, treatment and disposal with GLD	Sanchez (2008); Sanchez and Tran (2005)

[a] Loss of alkali with slaker grits may correspond to about 0.02% of the total alkali in the recovery cycle (Sanchez, 2008).

Tran, 2005; Jia et al., 2014). The liquid phase contains alkaline compounds, such as Na_2CO_3 and NaOH, which are responsible for the high pH. From the economical point of view it is important that these alkaline compounds are recovered by GLD washing (Tikka, 2008).

Martins et al. (2007) have characterized dried GLD with different methods. The main elements in the oven-dried solids in decreasing order were Ca, O, Mg, Na, Fe, S, Mn, Si, Al, K, and P. The most abundantly present mineral phase was calcite, typically present with some associated Mg content, i.e. $Ca_{1-x}Mg_xCO_3$. In calcined samples, the most abundant phases were, correspondingly, $Ca_{1-x}Mg_xO$ and MgO. Thermogravimetric analysis revealed the presence of gipsite $CaSO_4 \cdot 2H_2O$, which started to degrade at low temperatures, and calcite, which was calcined at 700–1000 °C. Rothpfeffer (2007) reports average concentrations of different metals and phosphorus in the GLD of a large number of samples collected from three mills, determined with inductively coupled plasma mass spectrometry (Table 2).

3.3.2. *Lime residues*

The two major lime kiln residues exist in the slurry form as lime mud and slaker grits. Both these residues consist of $CaCO_3$, CaO and various impurities. Previous research has typically focused only on lime mud, and to some extent on slaker grits (Tikka, 2008).

According to the mineralogical characterizations performed by Martins et al. (2007), $CaCO_3$ accounts for approximately 90% of the mineral phases in lime mud. Gypsum (<4 w-%) in the dihydrate form $CaSO_4 \cdot 2H_2O$ is also present. However, the calcium carbonate content in lime mud seems to be higher than 90% at most mills. Bharathi et al. (2006) report $CaCO_3$ contents of 92–95 w-%, and Tran (2008) extends the upper limit to 97 w-%, listing also other elements, such as Mg, Si, Al, Fe, P, Na, K, and S, which are present in various forms in small amounts. Martins et al. (2007) report that, unlike lime mud, slaker grits contain considerable quantities of Ca_2SiO_4 (almost 30 w-%), $CaNa_2(CO_3)_2 \cdot 2H_2O$ (about 20–30 w-%), $Ca(OH)_2$ (12%), and also 2–4% of $Mg(OH)_2$. As above in the case of GLD, the high percentage of Si- and Na-containing mineral phases does not mean that Si and Na are actually present in proportionally high quantities.

Table 2
Mean concentrations of different metals and phosphorus in the GLD of three sulfate pulp mills (Rothpfeffer, 2007), classified into major (g kg^{-1}) and minor (mg kg^{-1}) elements.

Major elements (≥1 g kg^{-1})			Minor (trace) elements (<1000 mg kg^{-1})		
Element	Mean concentration (g kg^{-1})	Confidence interval (g kg^{-1})	Element	Mean concentration (mg kg^{-1})	Confidence interval (mg kg^{-1})
Al	5.3	1.6	As	0.3	0.06
Ca	253	28	B	634	8
K	3.1	0.9	Ba	523	96
Mg	30	5.7	Cd	9.4	2.1
Mn	12	2.3	Co	74	13
Na	35	10	Cr	118	20
P	3.8	0.9	Cu	102	20
Zn	1.0	0.16	Mo	1.7	0.6
			Ni	84	12
			Pb	13	2.5
			V	1.9	0.4

The moisture content of slaker grits is typically about 24 w-%, the Ca and Na contents are slightly below 400 g kg^{-1} and 30 g kg^{-1}, respectively, and the concentrations of other elements are below 10 g kg^{-1} each (Li et al., 2012a).

3.3.3. *Recovery boiler ESP salt*

The composition of recovery boiler fly ash, i.e. recovery boiler ESP salt, differs significantly from that of other boilers. While conventional biomass boilers generate mainly metal oxides, the recovery boiler generates sodium sulfate Na_2SO_4 and sodium carbonate Na_2CO_3 as the main components, accounting for approximately 80–85 w-% and 8–15 w-%, respectively (Monte et al., 2009; Sretenovec, 2012). Other salts, e.g. K_2SO_4, NaCl, and K_2CO_3 may be present at lower quantities (Sthiannopkao and Sreesai, 2009; Sretenovec, 2012). The concentration of K is typically 2–7 w-% (Mikkanen et al., 1999; Johansson, 2005).

3.3.4. *Salt cake from chlorine dioxide production*

The salt cake produced in the chlorine dioxide generator consists mainly of sodium sesquisulfate and sulfuric acid. The wet cake may also contain low concentrations of other reaction chemicals and products (Eq. (4)), and probably traces of intermediate products (Burke et al., 1993).

4. Current separation practices

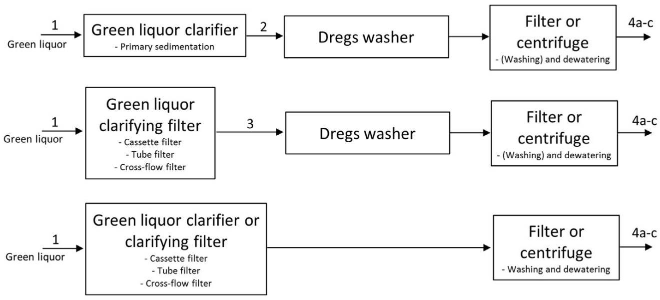
4.1. *Washing and filtration of green liquor dregs*

There are three main goals in green liquor treatment: the separation of dregs from green liquor, the treatment of dregs to an appropriate quality for disposal, and decreasing the temperature of green liquor for recausticizing (Tikka, 2008). Previous studies (Mattsson and Richards, 2009; Sedin and Theliander, 2004) have shown that the separation of dregs from green liquor is difficult in practice. Fig. 3 shows the conventional process sequences for the separation of GLD.

4.1.1. *Separation of dregs from green liquor*

Dregs are separated from green liquor by sedimentation or filtration, which is often followed by a washing and dewatering stage, to minimize the impact of the disposed dregs on the environment and to recover valuable alkaline compounds (Empie et al., 1999; Mattsson and Richards, 2009; Theliander, 2008). Dregs are removed as the underflow at the consistency of 2–5 w-%, while the green liquor overflow contains 60–100 mg L^{-1} of suspended solids. Flocculants can be used in order to obtain faster and more efficient separation (Sanchez and Tran, 2005; Taylor, 2013). Sometimes a specially designed sludge blanket clarifier, where the slurry is fed beneath a flocculated sludge layer, is used to operate at a high capacity, which, however, requires plenty of flocculants (Ives, 1968; Tikka, 2008).

Gelatinous magnesium silicate $Mg_2(Si_{1-x}Al_x)O_4$ is known to reduce the settling rate. A high level of magnesium in black liquor, originating from oxygen delignification, may cause slow settling



Stream	TSS content ($g\ kg^{-1}$)	Description	Reference
1	0.6-2	Green liquor	Tikka (2008)
2	20-50	Clarifier underflow	Tikka (2008)
3	≈ 50	Filter reject	Keskinen et al. (1995)
4a	300-500	Cake from vacuum precoat filter	Tikka (2008)
4b	450-500	Cake from decanter centrifuge	Beer et al. (2006)
4c	350-650	Cake from chamber filter press	Beer et al. (2006)

Fig. 3. Alternative processes for the treatment of green liquor dregs (Keskinen et al. 1995).

(Taylor, 2013; Taylor and McGuffie, 2007; Ulmgren, 1987). However, the addition of magnesium salt helps to precipitate aluminum with hydrotalcite (Ulmgren, 1987), but causes formation of adverse magnesium silicate (Taylor, 2013). Additionally, low temperature and high concentration of total titratable alkali in green liquor leads to the crystallization of pirssonite ($Na_2Ca(CO_3)_2 \cdot 2H_2O$), which causes a higher loss of sodium with the dregs (Zakir et al., 2013).

Filtration systems have become more popular in primary clarification, because they have a better separation efficiency and are more tolerant to process variations. Tube, cassette and cross-flow filters are applied commonly in the primary removal of GLD, while (hyperbaric) precoat disc filters and chamber filter presses excel in the separation and washing of dregs (Sanchez and Tran, 2005; Theliander, 2008; Tikka, 2008). The filter medium is in all cases cleaned with water, but it can be also washed by acid, or replaced with a new one at certain intervals (Theliander, 2008; Tikka, 2008). Lime mud is used as the precoat material when dregs are separated with rotary disc filters (Tikka, 2008), due to the very poor filterability of the dregs sludge. The average specific cake resistance without a precoat is typically about 10^{13} m kg^{-1}, and increases with pressure (Theliander, 2008), which indicates a compressible cake (Svarovsky, 1981). In disc filters, the formed cake is washed if needed and dewatered by displacement of liquid by gas, and finally removed by a scraper mechanism (Theliander, 2008; Wakeman and Tarleton, 1999). Aluminum sulfate or lime mud can be added into the smelt dissolving tank to improve the separation (Taylor, 2013; Sedin and Theliander, 2004).

4.1.2. Washing and dewatering of dregs sludge

When clarification and cross-flow filtration techniques are used for the clarification of green liquor, the resulted dregs sludge has to be washed to recover the soluble alkali by using secondary clarifiers, vacuum filters or pressure filters. The approximate ratio of water to dregs in washing clarifiers is 12:1. The removed dregs from washing clarifiers should be dewatered by filtration or centrifugation before landfilling (Sanchez and Tran, 2005; Tikka, 2008). In earlier dregs handling systems, a clarifier followed by a rotary vacuum filter was applied (Theliander, 2008).

According to the literature (Sanchez and Tran, 2005; Tikka, 2008), the vacuum precoat filter uses less water, but has a higher loss of alkali in comparison with the washing clarifier. The lime mud requirement is 1–2 times the mass of separated dregs, so the precoat is a surplus to the amount of cake to be landfilled. The use of filter presses to squeeze the dregs at a high pressure helps to minimize the quantity of cake. Decanter centrifuges can also be effectively utilized for the separation of dregs.

4.2. Separation of lime residues

After the causticizing reaction, the formed lime mud has to be separated from white liquor, to recover alkali, to separate potential impurities, and to enable energy-efficient operation of the lime kiln (Parthasarathy and Krishnagopalan, 1999; Tikka, 2008; Tran and Vakkilainen, 2007). Removal of NPE from the recovery cycle is important in order to maintain the quality of the lime mud, which is necessary for trouble-free operation of the lime mud separation units and the lime kiln (Tikka, 2008; McGuffie and Taylor, 2007). Additionally, the sulfur (TRS) emissions of the lime kiln can be reduced by lime mud washing (Das and Jain, 2001). Sedimentation and filtration are most typically applied at this stage. The dewatered lime mud can be dried by using e.g. a flash mud dryer before sending to the lime kiln (Järvensivu et al., 1999; Lee et al., 2006; Tran and Vakkilainen, 2007).

4.2.1. Separation of lime mud

The conditions in the slaking and causticizing process have an effect on the separation of lime mud. Factors such as temperature, lime dosage, speed of the stirrer and residence time affect the sedimentation rate of lime (Theliander and Gren, 1987). The results of the study of Theliander and Gren showed that a longer residence time and an increased lime dosage resulted in a slower settling rate. The quality of lime has an important role as well. The clarification process has been described in close detail in the literature (Quesada, 2003; Theliander and Gren, 1987; Tikka, 2008). The solids content of lime mud, i.e. the clarifier underflow, is usually between 35 and 40 w-%. The concentration of alkali in separated lime mud can reach 20% of white liquor production, so washing in another clarifier is often performed prior to final dewatering with a filter.

The most typically used filters, i.e. candle and disc filters, are relatively similar to those used in green liquor handling (Sixta, 2006; Theliander, 2008). In a candle filter, the lime mud solids remain on the outer surface of the filter cloth and build up a cake of sufficient thickness. The filtration elements are back-flushed to remove the cake and to keep the pores of the filter medium open. Dilution washing in a separate tank is applied for the recovery of remaining alkali from the cake, and the suspension is filtered again with either a candle filter or a belt-type filter (Tikka, 2008; Wakeman and Tarleton, 1999). As in the case of clarifiers, the suspended solids content of washed lime mud slurry is 30–35 w-%, and has to be reduced prior to calcining (Tikka, 2008). Pressurized disc filters are more complex, with higher power consumption than clarifiers, but their separation efficiency and water requirement are better (Tikka, 2008; Theliander, 2008; Sixta, 2006). As a summary, the solid content of lime mud varies from 35 to 70 w-%, depending on the equipment used.

According to Tikka (2008), a final solid content of up to 80–90 w-% is expected for dewatered lime mud, and the concentration of water-soluble alkali as NaOH, on a dry basis, should be under 0.15 w-%. The approximate solid load is 5–7 t m^{-2} d^{-1} when a lime mud precoat layer of 10–15 mm is applied (Sixta, 2006; Theliander, 2008; Tikka, 2008). The average specific cake resistance is relatively low, typically $< 10^{10}$ m kg^{-1}, and the cake is slightly compressible (Ek et al., 2009). Based on the wash curve presented by Eriksson et al. (1996), the wash ratio has to be quite high, probably higher than 2, to obtain the target level of NaOH content. The filtrate of the lime mud washing step is called weak white wash (liquor) and is reused in the smelt dissolver, while only the surface layer of the cake is scraped off. After dewatering, lime mud can be dried further by flue gas in a lime mud drier and sent to the lime kiln (Järvensivu et al., 2001a).

Problems in lime mud filtration can occur due to a high silica content and formation of aluminosilicate (Tran and Vakkilainen, 2007; McGuffie and Taylor, 2007; Taylor and Bossons, 2006). It has also been observed that the level of the TRS emissions of the lime kiln correlates with the residual alkali, and can be reduced by efficient lime mud filtration (Järvensivu et al., 1999, 2001a,b).

4.2.2. *Separation of slaker grits*

In the slaker, the heavy and relatively coarse insoluble grits settle on the bottom and are removed e.g. with an inclined screw conveyer, which may be equipped with a washing mechanism (Sixta, 2006; Tikka, 2008). The slaked lime is collected as the overflow and pumped to the causticizer train. The pH of washed grits may increase by time, due to slow slaking of residual lime (Sanchez and Tran, 2005). Slaker grits can also be ground with a ball mill or a hammer mill and reused in the lime slaker or on the GLD filter as a precoat (Sanchez and Tran, 2005).

4.3. *Electrostatic precipitation and treatment of recovery boiler salt*

4.3.1. *Electrostatic precipitation*

The ESP is a conventional particulate control system, where an electrical field is applied to collect electrically charged particles. The typical concentration range of collected fine (0.2–1 μm) dust is 5–15 g m^{-3} of flue gas (Hupa, 1993), and the separation efficiency is often over 99% (Lind et al., 2006). Electrostatically separated fly ash is typically mixed with black liquor and re-burned in a recovery boiler. Typically about 10% of the sodium in black liquor remains in this fly ash circulation, and only a small proportion of sodium and sulfur leaves the process (Hupa, 1993).

4.3.2. *Treatment processes*

The ESP ash can be treated either periodically or continuously in order to lower the levels of NPE in the recovery cycle to prevent operational problems, such as plugging of the recovery boiler due to the reduced melting point of the solid deposits (Hart et al., 2010; Brown et al., 1998; Jaretun and Aly, 2000) and accelerated corrosion of the recovery boiler (Rapp and Pfromm, 1998a; Jaretun and Aly, 2000; Minday et al., 1997). The most potential ESP ash treatment techniques are introduced below.

- Ion exchange

Ion exchange has become an attractive technique for ESP ash treatment. The commercial Recoflo system, described e.g. by Brown et al. (1999), is often used. This technology utilizes amphoteric fine resins, short columns, high flow rates, and very short cycle times for the selective separation of chloride. The ash is dissolved in water to form a concentrated solution. The mixture is filtered in a pressure pulse filter to separate the insoluble solids, and the filtrate is treated in a salt separation unit, where NaCl is adsorbed by the resins. The purified solution of Na_2SO_4/Na_2CO_3 is pumped back to the recovery cycle. Ion exchange is efficient at chloride removal, has relatively low costs and a small footprint. However, the process is not efficient in potassium removal and may suffer from bed plugging in the mill environment (Johansson, 2005).

- Leaching

The target of ESP ash leaching is to dissolve chloride and potassium and prevent the dissolution of sodium. In an industrial case, reductions of over 50% in the recovery cycle have been reported for Cl and K (Hart et al., 2010), and the loss of soda inevitably increases with the reduction of NPE (Saturnino, 2012). The weight ratio of ESP ash to warm water is varied from 1.2 to 1.6. After leaching, the resulted slurry is centrifuged to separate solids enriched by Na_2SO_4. The moisture content of the centrifuged ash is less than 10 w-%. In comparison to the ion exchange process, leaching is more simple and less expensive (GonCalves et al., 2008; Hart et al., 2010; Johansson, 2005). The addition of spent sulfuric acid can be used for the conversion of Na_2CO_3 to Na_2SO_4, but it causes corrosion and plugging of pipelines in the installation (Jaretun and Aly, 2000). The ash leaching process has been commercialized by a few equipment manufacturers, e.g. Metso and Andritz.

- Crystallization

In the evaporation/crystallization process, the ESP ash is dissolved in excess of water or condensate, using a low ash/water ratio. Crystals of Na_2SO_4 are formed by subsequent vacuum evaporation, followed by separation in a filter or centrifuge, to produce solids with a moisture content of 15–25 w-%. The method is relatively expensive and complicated (Johansson, 2005; Minday et al., 1997). The second alternative, freeze crystallization, is a fairly efficient technique, but also expensive (Johansson, 2005).

- Electrodialysis

The electrodialysis process may be a combination of a pre-concentration step, electrodialysis, and crystallization via vacuum evaporation (Rapp and Pfromm, 1998a). The ash is first dissolved in water or a condensate before feeding to the electrodialysis unit, which consists of dilute and concentrate cells, separated by anion- and cation-exchange membranes (Pfromm, 1997a,b). The separation takes place in the electric field as described by Rapp and Pfromm (1998b). Electrodialysis is a relatively uneconomical technique, in particular when pretreatment is required to prevent fouling (Rapp and Pfromm, 1998a; Boudihel and Benslimane, 1997).

4.4. Separation of sodium sesquisulfate

Sodium sesquisulfate cake is typically separated in the chloride dioxide generator by filtration. The existing scientific literature does not provide details about solid–liquid separation at this stage.

5. Methods and requirements for utilization

Landfill disposal is the prevailing method for the disposal of dregs, lime mud and slaker grits. The most potential alternatives for landfill disposal, as well as the treatments required to enable the utilization, are discussed in this section and summarized in Fig. 4.

5.1. Reuse at the pulp mill

The reuse of inorganic residues at a pulp mill has been a good option for decades. The high degree of loop closure has made reuse at the mill more challenging.

5.1.1. Criticality of non-process elements

Loop closure results in the concentration of non-process elements (NPE) in the recovery cycle (Patrick et al., 1994). Elements forming insoluble compounds with either green liquor or white liquor (Table 3) are removed from the cycle with various inorganic residues, such as GLD, lime mud and slaker grits, while elements with high solubility in the process liquors are removed with recovery boiler fly ash, and to some extent with lime kiln ESP dust. According to the literature (Ulmgren, 1997; Manskinen et al., 2011; Lundqvist, 2009; Taylor, 2013; Taylor and McGuffie, 2007; Taylor and Bossons, 2006; Park and Englezos, 1998; Ellis and Johnson, 2011), the problems caused by NPE include scaling (Al, Si, Ca, Ba), corrosion (K, Cl, Mg), plugging of the recovery boiler (K, Cl), increase of lime kiln dead load (Mg, P, Al, Si), poor lime and lime mud quality, plugging of filters (Si, Al, Ca), effects on bleaching (e.g. Mn, Fe, Cu), and environmental impacts due to nutrients and hazardous trace elements.

Table 3
Alkali solubility and removal of different non-process elements from the recovery cycle, according to Törmälä and Markusson (2013), Ulmgren (1997), and Doldán et al. (2011).

Non-process element	Solubility in green liquor	Solubility in white liquor	Primary sink(s), excl. waste water
Cl, K	High	High	Recovery boiler fly ash
Ca, Mg, Mn, Fe, Ba, etc.	Low	Low	GLD, lime residues
Al	Medium	Medium	GLD, lime residues
Si	High	Medium	Lime mud, lime kiln ESP dust
P	High	Low	Lime mud, lime kiln ESP dust

5.1.2. Green liquor dregs: waste treatment applications

Pöykiö et al. (2006a) used GLD for the liming of the acidic wastewater of a chemical pulp mill. In comparison with the liming capacity of a commercial lime product, the results were excellent: 0.96 tons of GLD corresponded to one ton of the commercial ground limestone typically used for the neutralizing purpose. According to Pöykiö et al. (2006a), Stora Enso Veitsiluoto mill in Kemi, Finland, started to test the use of GLD for wastewater neutralization in 1990, and proceeded to continuous use in 2004, when about half of GLD was utilized. The utilization of GLD has enabled cost savings, but has increased the (heavy)metal concentrations in the mill effluents and in the biosludge. Therefore, the system is not economically applicable at inland mills located by fresh water. The neutralization of wastewater by GLD may also cause operational problems by increased recirculation of NPE as a result of burning the wastewater sludge in the recovery boiler.

Zambrano et al. (2010) performed composting experiments with Kraft mill secondary sludge, by using GLD as a pH-stabilizing additive. Their results show that the sufficient dosage of dregs is 5–8 w-%, and that this amount does not hinder the microbial degradation of organic matter.

UPM Kymmene Oyj, Finland, has patented (pat. numbers FI 117125 and SE 528884) a process for sulfur removal from flue gases by contacting the flue gas with the green liquor sludge. However, the process is not apparently used in production scale currently.

5.1.3. Lime residues: various applications

The most typical on-site application of lime mud and slaker grits is the use as precoat material in the GLD filter. The details of this option were discussed above in Section 4. Lime and limestone are, however, multipurpose materials with many potential applications at the mill.

A recent review article written by Zhang et al. (2014a) summarizes the current methods of lime mud utilization. The three most interesting applications mentioned by Zhang et al. (2014a) regarding on-site applications of lime mud are 1) neutralization of acidic wastewaters, 2) production of precipitated calcium carbonate (PCC), described by Huege (1998), and 3) desulfurization of

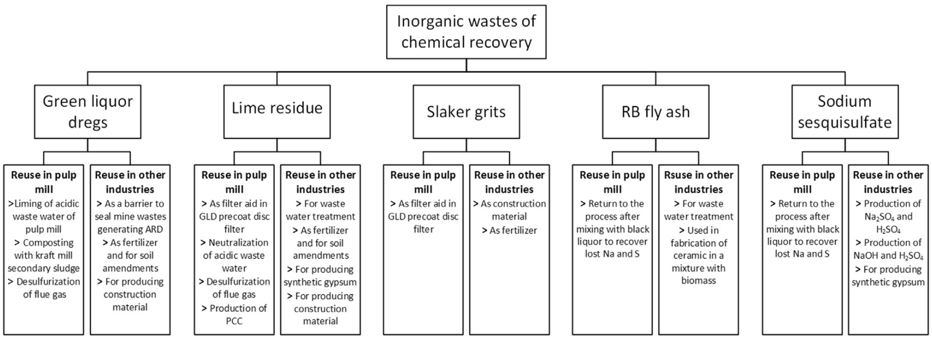


Fig. 4. An overview of reuse options of inorganic residues produced at chemical pulp mills.

flue gas, discussed in closer detail by Li et al. (2012b). Leaching of hazardous trace elements from lime residues should be taken into account when planning the method of utilization.

Li et al. (2012b) investigated the use of lime mud for neutralizing the acidic wastewater of the main sewer sump of the AP Maryvale pulp mill in Australia. The dissolution of grits was slow: the pH was increased only by 0.2 units during the normal residence time of 40 min, and it was therefore concluded that the use of grits is not reasonable in practice, because a significant lime addition was still necessary to obtain the target level of pH 6.

The production of PCC, which can be used as a coating pigment in an integrated paper mill, is possible by using lime kiln dust as the raw material. The CaO in lime kiln dust is first hydrated to form $Ca(OH)_2$, which is subsequently precipitated as $CaCO_3$ by using carbon dioxide (Huege, 1998). Quite similarly, all lime residues containing CaO can be regarded as potential carbon capture chemicals which can be used to remove CO_2 from the flue gases of the recovery boiler and lime kiln by simple carbonation (Bobicki et al., 2012; Sun et al., 2013). However, it should be considered carefully whether it makes sense to use great quantities of energy to calcine $CaCO_3$ to CaO in the lime kiln, and to carbonate the costly lime back to the less valuable $CaCO_3$.

Li et al. (2012b) compared calcined lime mud with commercial calcined limestone in flue gas desulfurization. The results obtained with lime mud were better than those obtained with commercial limestone in the same conditions, which can for the most part be explained by the higher specific surface area and near-optimal pore size of the calcined lime mud. Additionally, the good desulfurization capacity of lime mud may also be explained by its impurities, such as Na_2CO_3 (Laursen et al., 2003).

When the pulp mill operates as a biorefinery, lime mud can be used as an adsorbent to remove impurities from various liquids, such as biomass hydrolysates. Shen et al. (2011) investigated a process where lime mud was mixed with wood chip prehydrolysate, separated by filtration, and calcined then in the lime kiln as usual.

5.1.4. Recovery boiler ESP salt: source of Na and S

The primary value of recovery boiler ESP salt lies in its high sodium sulfate content, which makes it a good source of Na and S. The washed ESP salt is returned to the process by mixing it with black liquor. Recovery efficiencies of 63 and 68% were obtained for Na and S, respectively, when 90% of Cl and 82% of K were removed by the leaching of ESP salt at the Aracruz mill in Brazil (GonCalves et al., 2008). Hart et al. (2010) report that over 50% removal of Cl and K, and a soda recovery of over 80% has been obtained at MWV's Evadale mill in TX, USA.

5.1.5. Sodium sesquisulfate: source of Na, S, NaOH and H_2SO_4

The salt cake obtained from the ClO_2 generator is often mixed with black liquor to recover sodium and sulfur, but the current trend seems to be towards disposal after neutralizing with NaOH (Bucher et al., 2009; Burke et al., 1993). Alternatives to disposal have been developed, for instance production of Na_2SO_4 and H_2SO_4 by metathesis (Thompson et al., 1995), and production of NaOH and H_2SO_4 by bipolar membrane electrodialysis, as discussed in detail by Paleologou et al. (1997). Another potential option of H_2SO_4 separation is the short-bed ion exchange process introduced by Bucher et al. (2009), which enables the Na_2SO_4 to be utilized in the pulping process and the sulfuric acid to be reused e.g. for pH adjustment at the bleaching plant.

5.2. Utilization as bulk chemicals in other industrial applications

The high buffering capacity of green liquor dregs makes them suitable for using as an alkaline barrier in the sealing of mine wastes generating acidic waters (Jia et al., 2013, 2014; Mäkitalo et al., 2014; Ragnvaldsson et al., 2014). The oxidation of sulfidic mine waste generates acid rock drainage (ARD), which causes serious hazards for the environment by the mobilization of great amounts of metals and semi-metals. A cover of soil is typically used on mining wastes in order to prevent oxidation and the resulting ARD formation. Mäkitalo (2012) reports that GLD has good potential as a cover for mining residues, due to its high water retention capacity and low hydraulic conductivity, which helps to prevent the water percolation and oxygen transport to the depth of the mine waste. In addition to GLD, other alkaline wastes like fly ash and lime mud from pulp mills have the potential to be utilized for this purpose (Mäkitalo et al., 2014). In fact, inhibition of ARD by the use of alkaline residues could solve two waste disposal problems at the same time (Mäkitalo, 2012).

Lime mud and recovery boiler ash can be used for removing heavy metals from the acidic wastewaters of the metal industry by sorption and precipitation (Sthiannopkao and Sreesai, 2009; Wirojanagud et al., 2004). The good efficiency of calcite for this purpose is well documented in the literature (Garcıa-Sánchez and Alvarez-Ayuso, 2002). In the case of recovery boiler ash, which contains significant amounts of highly soluble salts, heavy metals are most likely removed primarily by precipitation, and the removal efficiency is lower than that of lime mud (Sthiannopkao and Sreesai, 2009).

Lime has been successfully used for microbial and physical stabilization of domestic sewage sludge (Valderrama et al., 2013). Among pulp mill residues, only lime kiln dust and possibly also the mechanically removed lime kiln residue provide CaO with some reactivity, which reduces the possibilities to stabilize sludges with pulp mill residues in a large scale.

The only potential heavy industrial application of the major pulp mill residues, not dealing with the treatment of other industrial wastes, seems to be the improvement of anaerobic bioprocesses by lime mud addition, to provide nutrients and pH buffering capacity. The topic has been investigated by Zhang et al. (2014b), who conclude that the lime mud addition of 10 g L^{-1} is optimal for increasing biogas production from wood waste. Zhang et al. (2013) report that hydrogen production by bacteria is also facilitated by lime mud, the optimum dosage being 15 g kg^{-1}.

5.3. Production of value-added products and materials

5.3.1. Fertilizers and soil amendments

Harvesting trees results in a loss of nutrients from the forest ecosystem. These lost nutrients, in particular base cations, can be found in alkaline inorganic solid residues of Kraft mills. Returning these residues to the ecosystem is beneficial both ecologically and economically, regarding the decreased need for landfilling (Mahmoudkhani et al., 2004). Due to the increases in disposal fees, tougher legislation and limitations of landfill lifespan, the use of pulp mill residues to maintain the fertility of agricultural soils has been evaluated regarding the utilization of lime mud, green liquor dregs, slaker grits, and lime kiln waste (Mahmoudkhani et al., 2004; He et al., 2009; Cabral et al., 2008; Gagnon and Ziadi, 2012; Pöykiö et al., 2006b). Alkaline industrial residues may prevent the acidification of soils and can be an alternative for chemical fertilizers in the future (Mäkelä et al., 2012). The recirculation of inorganic pulp mill residues to the forest requires knowledge of their leaching properties. The Na and K salts in pulp mill residues are easily soluble, while Ca and Mg salts have limited solubility (Mahmoudkhani et al., 2004). GLD and lime mud also contain heavy metal constituents such as Cd, Cu and Zn, which are hazardous to the environment (Österås et al., 2005). In Finland, an environmental permit is required for the use of the residues from Kraft mills as forest fertilizers. The Finnish limits, which came into force in March 2007, determine the maximum allowed concentrations of hazardous trace elements, such as As, Cd, Cr, Cu, Ni, Pb, Zn and Hg in forest fertilizers (Dahl et al., 2009; Manskinen et al., 2011). The concentrations of hazardous trace elements in GLD and slaker grits, reported by Manskinen et al. (2011) and Nurmesniemi et al. (2010), respectively, were lower than the Finnish statutory limit values for forest fertilizers.

Inorganic residues containing calcite can be utilized for the production of synthetic gypsum (mainly dihydrate). In addition to other extensive industrial use of gypsum, it is utilized as a fertilizer (Strydom et al., 1995). Gypsum could possibly be precipitated for fertilizing applications by reacting sulfuric acid obtained (or separated) from the sesqui salt with calcite, such as lime mud, as demonstrated with pure calcite and H_2SO_4 by Bard and Bilal (2011).

5.3.2. Construction materials, ceramics and catalysts

According to the amended frame introduced by the European Council Waste Framework Directive in 2010, resource usage should be reduced by the waste policy. Besides this frame, the Finnish environmental legislation sets limitations for the hazardous components of waste materials used for earth construction. The low concentration of hazardous trace elements in slaker grits makes them potentially suitable as earth construction materials instead of landfilling (Watkins et al., 2010). As an example, slaker grits can partially replace Portland cement in soil-cement bricks (Siqueira and Holanda, 2013). It has been shown that GLD and slaker grits can be used instead of conventional aggregates in bituminous mixtures: slaker grits can be used directly, while GLD requires a washing process to remove its soluble salts (Modolo et al., 2010). Besides grits and GLD, lime mud residues can also be potentially utilized in construction materials. The chemical compatibility of lime mud with the traditionally used materials enables it to be utilized as secondary raw material in the production of clinker/cement (Buruberri et al., 2015). Furthermore, lime mud is an appropriate alternative material for the stabilization of forest roads (Habip et al., 2006). As a mixture with biomass fly ash, lime mud can also be used in the fabrication of ceramics (Qin et al., 2015). The main drawback of utilizing these residues for the production of construction materials is that variations in the composition of the residues may cause serious variation in the quality of the products.

Lime mud waste can also be applied as a heterogeneous catalyst in the transesterification reaction in biodiesel production (Li et al., 2014b). However, the raw lime mud has to be activated by a series of processes, such as drying, grinding, sieving, and calcination (Li et al., 2014a). In another method, lime mud is doped with potassium fluoride to prepare the heterogeneous catalyst. In this method, lime mud is first ground and activated at a high temperature. A certain proportion of activated lime mud is then mixed with the aqueous solution of potassium fluoride. This process is followed by drying and calcination of the resulted mixture (Li et al., 2014b). The economy of both processes is, however, questionable, so reuse at the pulp mill is most likely more feasible.

6. Discussion

The utilization potential of inorganic pulp mill residues as industrial chemicals and as raw materials for the manufacture of various products has been recognized. However, challenges still remain related to feasible industrial utilization. The globally generated amount of these wastes is most likely over one million metric tonnes per year. Green liquor dregs with the lime mud precoat provide the best possibilities for industrial utilization, due to their good availability. However, there are two important aspects which have to be taken into account when the possibilities for utilization are evaluated:

1) The overall chemical balance of the mill, including the removal of non-process elements from the process, should not be negatively affected, and
2) The variation in the chemical composition of the residues may cause occasional challenges regarding the allowable composition, such as concentration of hazardous trace elements and residual alkalinity.

The removal of unwanted components from the materials before utilization increases the costs, but should be investigated in closer detail in the future from both technological and economical points of view in order to increase the feasibility of utilization. The removal of hazardous trace elements, in particular cadmium, is crucial for enabling utilization for fertilizing purposes. It is clear that the existing process equipment at the mills should be utilized to enable economical treatment, taking into consideration the overall water balance of the mill as well. The equipment applied for the separation and treatment of green liquor dregs, lime mud and recovery boiler fly ash are summarized in Table S1 (Supplemental material).

It is apparent that the reuse of these waste materials will sooner or later be a more sustainable option than extensive landfill disposal. When it comes to large-scale applications, it seems that soil improvement and further refining of the residues to various fertilizers may be the most interesting options. The nutrient-rich composition of green liquor dregs with lime mud precoat is favorable for fertilizing applications. The carbonate content of this combined residue is also high, which is a benefit regarding slow enough liberation of the nutrients into the soil.

The basicity of treated inorganic pulp mill residues is a positive feature when the product is used in areas where the natural pH of the soil is relatively low, as it is typically in Finland. Local use of residues as construction materials could also have some potential in the large scale. The current situation, however, is that there are hardly any applications where the residues are used outside the mill area.

7. Conclusions

The separation, treatment and utilization of inorganic residues of chemical pulp mills have been discussed in this review. The main challenges in the utilization of the residues are related to the economical viability of the required treatment processes, as well as to maintaining the overall material balance of the mill. A few inorganic residues of chemical pulp mills have been identified as potential for value-added utilization. Only green liquor dregs and lime mud are available in significant quantities, which does not mean that the minor residues should be totally omitted when utilization opportunities are considered. The use of suitable separation techniques facilitates the purification of all these residues and helps increase the recovery of process chemicals. Hazardous trace elements and residual alkali are regarded as the main reasons why the abundantly available mixtures of green liquor dregs and lime mud precoat have not been widely utilized in the past. In spite of the current challenges of residue handling, previous academic studies have concluded that several applications for the residues can be found. Most of those applications are related to novel environmentally friendly technology, such as prevention of various discharges, improvement of bioprocesses, and replacement of traditional fertilizers and soil improvement chemicals in the agriculture. The inorganic pulp mill residues may be used as sustainable bulk chemicals outside the mill, provided that the transportation distance is relatively short. The production of value-added products, which requires the use of appropriate mechanical and chemical treatment techniques, seems to be more challenging to realize in the near future. It is apparent that the most promising large-scale applications for utilization, i.e. fertilizing and soil improvement, should be investigated more rigorously in the future. The related legislation should also be developed to maximize the obtainable environmental benefits.

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Appendix A. Supplementary data

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Appendix A. Supplementary data related to Publication I

Table S1. Comparison of equipment applied for the separation and treatment of green liquor dregs (GLD), lime mud (LM), and recovery boiler fly ash (RBFA).

	Aim of treatment	**Applied equipment**	**Advantages**	**Disadvantages**	**Reference(s)**
GLD	Separation of dregs from green liquor	Clarifier	Stability; reliability; low energy consumption; efficient in iron removal from green liquor	Low efficiency in alkali recovery; need for a further washing stage; need to use a precipitating agent	Taylor (2013); McGuffie and Taylor (2007); Tikka (2008)
		Cassette filter	No precoat required; high alkali removal	Low consistency of separated dregs; an extra thickener is often required	Sixta (2006); Tikka (2008)
		Cross-flow filter	No precoat required; efficient removal of suspended solids	Need for higher pressure to achieve sufficient capacity	Keskinen et al (1995); Tikka (2008)
		Pressurized vessel disc filter w/ precoat	Higher filtration capacity; simultaneous separation and washing	Increase in the amount of discharged solids due to the precoat	Sedin and Theliander (2004); Tikka (2008)
	Handling of GLD: washing and dewatering	Vacuum precoat filter	Improved soda recovery, low wash water consumption	Increase in the amount of discharged solids due to the precoat	Beer et al (2006); Sanchez and Tran (2005)
		Filter press	Low moisture content of dregs; no precoat required	Not practical for the handling of dregs with poor filtration characteristics	Beer et al (2006); Sanchez and Tran (2005)
		Centrifugation	No precoat used; good flexibility	A two-stage process may be required	Beer et al (2006); Tikka (2008)
LM	Separation of lime mud from white liquor	Clarifier	Stability; reliability; low energy consumption	Large footprint; low efficiency in alkali recovery; need for a further washing stage	Theliander and Gren (1987); Tikka (2008)
		Candle filter	No need for cooling or dilution of white liquor for separation; efficient separation of suspended solids	Low efficiency in alkali recovery; need for a further washing stage	Sixta (2006); Tikka (2008)
		Pressurized vessel disc filter	Good efficiency of operation; moderate wash water requirement; simultaneous separation and washing	Relatively high maintenance requirement	Sixta (2006); Tikka (2008); Tran and Vakkilainen (2007)
	Handling of LM: washing and dewatering	Vacuum drum filter	Good soda recovery; high solid content of cake	Large size of equipment; need for spray washing of the blinded precoat	Sanchez and Tran (2005); Tikka (2008)

		Vacuum disc filter	Compact size compared with drum filters; improved washing and dewatering capacity; enable to incorporate countercurrent washing	Need for spray washing of the blinded precoat	Tikka (2008)
RBFA	Separation of fly ash from flue gas	Electrostatic precipitator (ESP)	Excellent separation efficiency		Lind et al (2006)
	Treatment of RBFA to remove NPE	Ion exchange	Efficient in chloride removal; low capital and maintenance cost; small space required for installation	Not efficient in potassium removal; may cause resin plugging in the pulp mill environment	Johansson (2005); Brown et al (1998)
		Leaching	Simple and inexpensive process, efficient in the removal of *K* and *Cl*	Poor recovery of sodium	Johansson (2005); GonCalves et al (2008)
		Crystallization	Fairly efficient in chloride removal	Expensive process according to its high requirement for electricity	Johansson (2005)
		Electrodialysis	Continuous process without a need for chemicals; viable for operation without any kind of pre-filtration	Membrane fouling; poor economy for RBFA treatment	Rapp and Pfromm (1998a); Rapp and Pfromm (1998b)

ARD	Acid Rock Drainage
ESP	ElectroStatic Precipitator
GLD	Green Liquor Dregs
LM	Lime Mud
NPE	Non-Process Elements
PCC	Precipitated Calcium Carbonate
RB	Recovery Boiler
RBFA	Recovery Boiler Fly Ash
TRS	Total Reduced Sulphur
TSS	Total Suspended Solids

Publication II

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Study on the filtration characteristics of green liquor dregs

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Study on the filtration characteristics of green liquor dregs

Mohammad Golmaei *, Teemu Kinnarinen, Eeva Jernström, Antti Häkkinen

LUT School of Engineering Science, Lappeenranta University of Technology, P.O. Box 20, FI-53851 Lappeenranta, Finland

HIGHLIGHTS

- The higher filtration temperature results in less resistant filter cake.
- The formed cake in higher temperature is more compressible.
- Storage period has negative effect on filtration properties of studied sludge.
- Effect of temperature on removal of Na, S, K and B from cake is not tangible.
- NPE elements such as Al, Ba, Ca, Fe, Mg, Mn and Zn mostly remain in filter cake.

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ABSTRACT

Separation of dregs from green liquor is a major challenge in kraft pulp mills, and it results in compressible filter cakes with high specific cake resistance. In industrial applications, the use of lime mud as a filter aid is a practical approach to reduce the resistance of the dregs cake. However, the amount of solid waste then increases considerably, because the lime mud has to be disposed with the dregs. In this study, green liquor sludges from two different pulp mills were filtered without filter aids by using laboratory-scale pressure filters. The effect of some variables, such as the permeability of the filter cloth, the temperature of filtration, the filtration pressure, and the storage period on the filterability of the green liquor sludges was investigated. The results provide information for optimizing the process parameters to improve the filterability of the sludge. The lowest cake resistance ($2.20 \cdot 10^{12}$ m/kg) was obtained at filtration the temperature of 80 °C. However, the higher operating temperature did not necessarily have a positive effect on the recovery of sodium (valuable element for the process) from the cake. The results showed that higher amounts of certain elements, such as Na, K and B were recovered from the dregs cake at the filtration temperature of 60 °C. It was also observed that the storage period had a negative effect on the filtration properties. In addition, elemental analysis of the filtrate and dregs cake samples showed that harmful metals, such as Al, Cd, Fe, Mn and Zn were mostly insoluble and remained in the dregs.

1. Introduction

Series of improvements have been seen during the recent years in the chemical recovery cycle of kraft pulp mills. The forces driving this evolution have been demands for improved material and energy efficiency, as well as environmental concerns. More efficient handling of green liquor dregs (GLD) is a part of this development [1]. In kraft pulping, a cooking liquor (white liquor), which is an aqueous solution of sodium hydroxide and sodium sulfide [2–4], is utilized to remove lignin from the wood chips. After lignin removal, the cooking liquor is then regenerated from the resulting solution (black liquor) in the digester and brown stock sections in a chemical recovery cycle. The solid content of the watery black liquor is first increased by evaporation, after which, the concentrated black liquor is combusted in a chemical recovery boiler. In the recovery boiler, the organic content of the black liquor is combusted to produce energy in the form of high pressure steam. The main task of the chemical recovery boiler is to generate a molten flow of sodium-enriched inorganics (smelt). The smelt obtained from the recovery boiler is then mixed with weak white liquor in a smelt dissolving tank to generate green liquor. Finally, white liquor is prepared through conversion of the existing sodium carbonate in the green liquor to sodium hydroxide in a causticizing plant [5–7]. The chemical recovery cycle can play a pivotal role in ensuring the economic feasibility of kraft pulping by reducing the need of make-up cooking chemicals. In addition to the economy of the process, the chemical recovery brings environmental benefits as well [3,8].

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* Corresponding author.
E-mail address: mohammad.golmaei@lut.fi (M. Golmaei).

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Green liquor contains suspended solids which are so-called dregs and partially soluble alkali contents such as sodium carbonate, hydroxide and sulfide. The concentration of dregs in green liquor varies from 0.6 g/L to 2 g/L, depending on the raw material used and the process operations [1]. The capacity of dregs production in newer recovery boilers is 3–4 kg/ton pulp [9]. Typically, the dregs contain carbonates, for instance, sodium carbonate and calcium carbonate, sodium hydroxide, sulfides, unburned carbon, and traces of heavy metals [10]. The dissolved sodium hydrosulphide is the reason for the green color of the sludge [11]. In addition to the listed compounds in dregs, the crystals of calcium phosphate can be precipitated from green liquor [12]. Generally, calcium is the most abundant element in the dregs [8,13]. The presence of such dregs in the green liquor makes it an inappropriate feed for a causticizing plant. Hence, the green liquor sludge must first be treated through a series of separation operations. This treatment process comprises three main stages, separation of dregs from the green liquor in a purification stage, dregs handling by washing and dewatering to an appropriate moisture level for disposal, and cooling of the green liquor in preparation for causticizing [1,14]. The high pH of treated GLD can open new possibilities of using it as a liming agent or alkaline barrier instead of landfilling [8,15]. It could be a suitable alternative liming material for the soil and improve the chemical availability of nutrients, specially in acidic soils [16,17]. It is also possible to use the composted mixture of organic and inorganic residues from pulp mills for soil improvement in agricultural plants [18]. On the other hand, the alkaline content (pH 11–13) and low hydraulic conductivity (10^{-7}–10^{-9} m/s) of GLD make it suitable for constructing a sealing layer [19,20]. The oxidation of sulfidic mine waste generates an acidic leachate, so-called Acid Mine Drainage (AMD), which causes serious hazards to the environment [21,22]. By the use of GLD as a barrier against atmospheric oxygen, the formation of AMD and the mobilization of toxic metals to the soil will be inhibited [15,23,24].

Purification of green liquor is mostly done by sedimentation and filtration. In new mills, green liquor filtration systems have widely replaced sedimentation clarification due to their higher separation efficiency [1,25]. Filtration systems currently utilized for green liquor dregs can be divided into falling film cross-flow filtration and cake filtration approaches [25–27]. Unlike in cake filtration where the solids build up as a filter cake on the surface of the filter cloth, the formation of cake is prevented in cross-flow filtration by applying a strong tangential flow [28]. Cake filtration can be employed for green liquor purification with or without a precoat layer of a filter aid. Cassette filters and tube filters in pressurized vessels are used in direct cake filtration of green liquor dregs. When precoat disc filters are used for cake filtration of green liquor dregs, a precoat layer of lime mud is applied on the surface of the filter medium. When precoat disc filters and chamber filter presses are utilized, the purification of green liquor as well as dregs washing and dewatering occur in the same equipment [1,6,25,26,29]. When using cassette filters, tube filters and cross-flow filters, on the other hand, the low consistency of the separated dregs makes it necessary to employ further washing and deliquoring stages. These extra stages are typically done in a vacuum precoat drum filter (with lime mud used as the precoat layer), filter press or a decanter-type centrifuge [1,9,30]. The limitations and strengths of the applied separation methods for GLD are listed in Table 1.

Green liquor purification faces a number of challenges at the industrial scale. For example, low temperatures and a high concentration of total titratable alkali (TTA) in green liquor can lead to crystallization of pirssonite ($Na_2CO_3.CaCO_3{\cdot}2H_2O$) [39]. Pirssonite scale can cause higher sodium removal with the dregs. Consequently, insulated systems are required for green liquor handling to keep the temperatures sufficiently high and to reduce variation in the concentration of TTA [9]. Effective green liquor purification is important because of the need to control the level of non-process elements (NPE) in the causticizing stage. Despite effective dregs removal, dissolved impurities generally remain in the green liquor [1,32]. The presence of NPEs, such as aluminum (Al), calcium (Ca) and silicon (Si) in the recovery cycle is a major concern. The precipitation of complex components formed from these NPEs causes scales on the process equipment that are hard to remove [40]. For this reason, the green liquor purification stage is considered as the "kidney" in the process where NPEs are expelled [27,37].

Previous studies by Sedin et al. [37] and Mattsson et al. [38] show that the filter cake in the filtration of green liquor sludge has a high specific cake resistance. Poorly settling dregs particles contain a soft, gel-like magnesium silicate compound with a higher molar amount of silicon than aluminum (e.g. $Mg_2(Si_{0,3}Al_{0,7})O_4$ and $Mg_2(Si_{0,65}Al_{0,35})O_4$). The bulk density of these gelatinous inorganic compounds is slightly higher than the density of the green liquor. The gel-like compounds are originally formed in the dissolving tank, where dissolved magnesium ions are mixed with sodium silicate solution [32]. It was further found by Sedin et al. [37] that the resistance of the cake was affected by the ratio of aluminum to magnesium in the green liquor sludge. In their study, it was noted that the addition of aluminum and calcium ions improved the filterability of the sludge, whereas added magnesium increased the cake resistance. Also the research done by Murray et al. [41] proves that a higher concentration of calcium in the green liquor improves the settling of the dregs. The accumulation of these ions in the recovery cycle is, however, detrimental to the pulping process. For example, an excess of aluminum has been found to result in the formation of harsh scales of sodium aluminosilicates in black liquor evaporators [33,42,43]. On the other hand, aluminum concentrations have been shown to reduce significantly during dregs separation. The aluminum loss during the separation of dregs is

Table 1
Limitations and strengths of methods utilized for filtration of GLD.

Separation method	Equipment	Limitations	Strengths	References
Sedimentation	Conventional and blanket clarifier	Use of flocculants as settling aids, low consistency of the withdrawn sludge, further dregs deliquoring is required, large space requirement	Efficient removal of magnesium and iron from green liquor, low energy demand	[1,31,32,33,34,35,36]
Cake filtration	Cassette filter, pressure precoat disc filter, horizontal and vertical filter press	High cake-specific resistance, use of lime mud as filter aid	Cake washing and dewatering are done in the same equipment, relatively dry dregs cake	[1,9,25,27,30,35,37,38]
Cross-flow filtration	X-Filter (a pressure vessel with vertical filter elements)	Extra washing and deliquoring stages for separated dregs are required	No need for lime mud as filter aid	[1,9,25,26]
Centrifugation	Horizontal decanter-type centrifuge	A two-stage process is required to reduce alkali loss	No filter aid is required, dregs washing is done in the same equipment	[1,9]

probably caused by cooling of the filtrate and a consequent reduction in the solubility of the aluminum [44].

The use of lime mud as a filter aid in the filtration of green liquor sludge decreases the resistance of filter cakes significantly. Therefore, lime mud is commonly used in industrial scale operations. The lime mud is also a byproduct of chemical recovery cycle in kraft pulp mills. An amount of lime mud equal to the solid content of dregs is frequently used in the filtration of green liquor. However, the use of such a large amount of lime mud means that the volume of solids to be landfilled doubles. In addition, the phosphorous components in lime mud are soluble in green liquor and will be liberated to the process with the recovered alkali [1,37]. In the present study, a series of filtration tests were done on three green liquor sludges obtained from GLD clarifier underflow in two Finnish kraft pulp mills. Laboratory scale pressure filters were employed in the experimental work to perform wide-ranging study on the filtration properties of the green liquor sludge. The experiments were designed according to the principles of statistical factorial designs to ascertain that it would be possible to determine the effects of filtration variables on the filterability of the sludges and the characteristics of the filter cakes.

2. Experimental

2.1. Green liquor sludge samples and their properties

The green liquor sludge for the experiments was obtained from two different kraft pulp mills (A and B) in Finland. In these kraft pulp plants, the dregs are first settled in a clarifier and then the underflow is sent for further treatment performed by a pre-coat disc filter. In both mills, the samples for this study were collected from the underflow stream of the green liquor clarifier. The first two samples of green liquor sludge from plant A and B were collected in the summer, but the sludge from plant B was collected again in the winter. Prior to the filtration tests, the properties of the samples were measured, and the results are presented in Table 2. In order to dissolve the precipitated salts, the sludge was heated up to a temperature of 40 °C before measuring the dissolved and suspended solid content. The green liquor sludges were dried in an oven at a temperature of 180 °C for 24 h to measure the total solid content (suspended and dissolved). The reason for the high temperature of the drying was the existence of dissolved solids in the sludge. The suspended solid content was measured through a series of separation and washing stages in a laboratory-scale sedimenting centrifuge, followed by drying of the suspended solids at 105 °C for 24 h in the oven.

In addition, approximate volumetric particle size distributions (PSD) of the samples were measured with a Mastersizer 3000 particle size analyzer (manufactured by Malvern Co, UK). The Fraunhofer model was applied for calculating the PSD from the in measurement data. Table 3 gives the statistical particle sizes of measured PSDs for all three samples of green liquor sludge.

As is clear from the tables, the properties of green liquor sludge vary from one pulp mill to another. The measured properties of sludges depend on the type of the process, the chemicals used and the feed of the pulp mill. The properties of green liquor sludge are not exactly the same for one pulp mill at different dates. This variation in key properties of the sludge, like the PSD of solids, pH, and suspended and dissolved solid contents has effects on the filtration properties.

2.2. Filtration experiments

Two different pressure filtration apparatus were used in the experiments: a Labox 100 filter and a Nutsche filter. The filtration area of Labox 100 is 100 cm^2 and it is 20.3 cm^2 in Nutsche filter. Labox 100 is a laboratory-scale pressure filter manufactured by Outotec Oy, Finland, and its woven filter cloths are made of propylene filaments with various permeabilities in this apparatus. Different commercial models of filter cloths with specific air permeabilities, such as AINO K11 (0.08 $m^3\,m^{-2}\,min^{-1}$), AINO K10 (0.20 $m^3\,m^{-2}\,min^{-1}$), AINO K13 (1.00 $m^3\,m^{-2}\,min^{-1}$), AINO T30 (2.50 $m^3\,m^{-2}\,min^{-1}$), and AINO T32 (3.00 $m^3\,m^{-2}\,min^{-1}$) were utilized in the experiments. The main parts of Labox 100 test unit are a diaphragm pump, an air pressure booster, a filtration chamber, and a control box. A photo of Labox 100 test unit is shown in Fig. 1 (a). The pressure booster provides the required pressurized air for pressing, cake drying and the feed pump. The height of the filtration chamber was constant (33 mm) in all tests, and it was selected on the basis of preliminary filtration tests. The sludge was pumped into the filtration chamber by a diaphragm pump, and the formed wet cake was pressed by introducing compressed air into the space above the elastic diaphragm located at the top of the chamber. During the filtration, the sludge was kept well mixed by means of a mixing tank ($V = 20\ dm^3$) equipped with baffles to ensure that the easily settling solids were evenly dispersed in the whole slurry. The sludge was heated up to the desired temperature (35 °C) in the same tank before starting the filtration test. For this purpose, the heating jacket of the mixing tank was connected to a compact low-temperature thermostat (LAUDA RC6-CP manufactured by LAUDA Dr. R. Wobser GmbH & Co. KG, Germany). The other pressure filter used in the experiments was a laboratory-scale Nutsche filter. This filter was equipped with a heating jacket to regulate the filtration temperature, and a cellulosic depth filter sheet of grade T 1000 (produced by Pall Filtersystems GmbH, Germany) was used as the filter medium. A photo of the utilized Nutsche filter is shown in Fig. 1 (b).

Table 2
Measured properties of sampled green liquor sludge.

	pH	Total solid content (wt%)	Dissolved solid content (wt%)	Suspended solid content (wt%)
Sample A	13.1	23.21	16.07	7.14
Sample B1[1]	13.2	21.08	16.11	4.97
Sample B2[2]	13.3	21.23	15.55	5.68

[1] Sampled in summer.
[2] Sampled in winter.

Table 3
Particle size distribution in each green liquor sludge.

	Dx (10) µm	Dx (50) µm	Dx (90) µm	D [4,3] µm	D [3,2] µm
Sample A	3.5	18.4	242.0	72.1	6.8
Sample B1	3.3	30.6	176.0	68.6	7.6
Sample B2	5.7	42.1	283.0	115.0	13.4

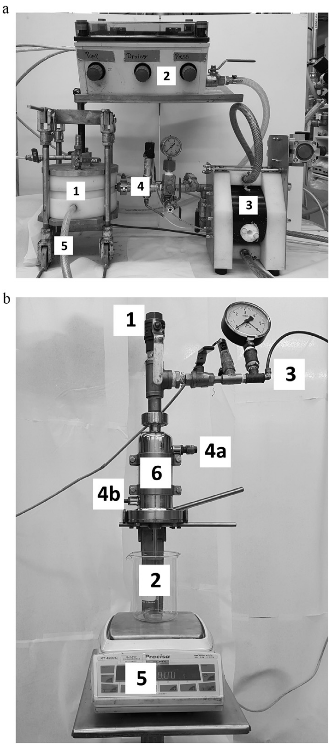

Fig. 1. a) Labox-100 filter press. Filtration chamber (1), control box including air pressure booster (2), feed pump (3), slurry inlet (4), filtrate and wash filtrate outlet (5). b) Nutsche filter. Slurry inlet (1), filtrate outlet (2), nitrogen gas inlet (3), inlet and outlet of heating jacket (4a and 4b), electrical scale (5), and filtration chamber (6).

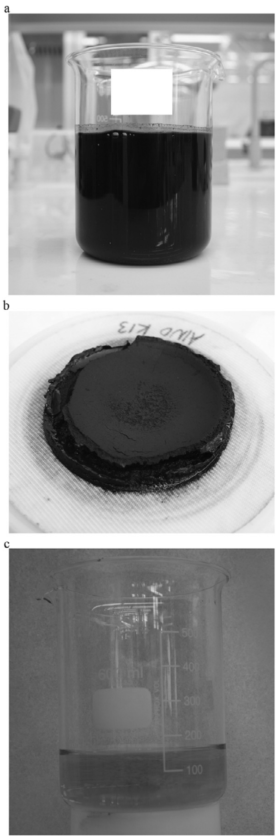

Fig. 2. a) Green liquor sludge, b) Pressed cake (dregs), c) Filtrate (green liquor).

The filtration tests with the Nutsche filter were carried out in a temperature range from 20 °C to 80 °C. The sludge was heated to the filtration temperature in a heating bath prior to being poured into the filtration chamber. In the Nutsche filter, the sludge was forced through the filter media under the force of pressurized nitrogen gas. Fig. 2 shows photos of the sludge, the cake (compressed and air-dried in Labox-100) and the filtrate.

Fig. 2 (b) is a photo of the cake that was formed by filtration, compression and air drying. As can be seen in this photo, the edge of the filter cake is broken due to the pressure in the compressing stage and removal of liquor from the porous structure of the cake during the air-drying stage. The experiments were done in a series to find the effect of the filtration variables on the filterability of both green liquor sludges. The variables of the tests and the utilized apparatus are listed in Table 4.

Except for the studied variables, all other conditions were kept constant to ensure comparable results. The effect of the variables on the filtration characteristics of green liquor sludge and the properties of the formed cake such as average specific resistance and compressibility were investigated following the experimental plan described in Table 4.

2.3. Elemental analysis of filtration samples

The concentration of various elements in the sampled cake and filtrate were measured to find the effect of the studied filtration variables on their recovery. This measurement also helped to find the distribution of elements between the cake and the filtrate. Elemental analyses of the samples were carried out with a Thermo Fisher Scientific ICAP6500 Duo (Thermo Fisher Scientific Inc., Cambridge, UK) inductively coupled plasma optical emission spectrometer (ICPOES). Prior to analysis, the solid samples (cakes) were digested using the US EPA method 3051. The wet digestion of solids was done in a mixture of HCl (3 ml) and HNO_3 (9 ml) in a CEM Mars 5 microprocessor-controlled microwave oven with HP 500 Teflon vessels (CEM corp., Matthews, USA) [45]. The concentration of each element was given by analysis of the cake samples ($g_{\text{element}}/g_{\text{dried solid}}$) and filtrate ($g_{\text{element}}/l_{\text{filtrate}}$). The results were then used in mass balance calculations to find the recovery percentages (wt%). The results of this calculation show the percentages of the total existing elements in the green liquor sludge that were recovered by the filtrate or the cake in the filtration experiments.

Table 4
Experimental plan and applied conditions.

Variable	The range of variable	Filtration apparatus	Type of used filter cloth	Sample
Air permeability of filter cloth ($m^3\ m^{-2}\ min^{-1}$)	0.08, 0.20, 1.00, 2.50, 3.00	Labox-100[1]	AINO K11, AINO K10, AINO K13, AINO T30, AINO T32	A, B1
Filtration temperature (°C)	20, 40, 60, 80	Nutsche[2]	T 1000 cellulosic depth filter sheet	B2
Storage period (months)	0 (fresh), 8 (stored)	Labox-100[3]	AINO K13	A

[1] Applied filtration pressure: 6 bar.
[2] Applied filtration pressure: 2, 4 and 6 bar.
[3] Applied filtration pressure: 4 and 6 bar.

3. Measurements and calculations

The classical filtration theory was applied for the calculation tasks in the current study. This theory is derived from Darcy's law, which explains the relation between the filtrate flowrate and pressure drop through a porous medium [28,46]. In the beginning of conventional cake filtration, solids that are not able to pass through the filter medium start to build a filter cake on its surface. Prior to the formation of the cake, the filter medium causes initial resistance, which increases due to the cake formation. In constant pressure filtration, the pressure difference through the cake and the medium is kept constant throughout the filtration stage [47,48]. In the filtration experiments of this study, the same method was applied to allow determination of the cake properties. Stable pressure in the filtration chamber is assumed to be reached at time t_s (s), and the volume of the filtrate is V_s (m^3) at this point. Using t_s and V_s as starting points in the integration of the general filtration equation gives Eq. (1) according to Svarovsky [28]:

$$\frac{t - t_s}{V - V_s} = \frac{\alpha \mu c}{2A^2 \Delta p}(V + V_s) + \frac{\mu R}{A \Delta p} \tag{1}$$

where c is the mass of solids per unit volume of the filtrate ($kg_{solids}/m^3_{filtrate}$), V is the volume of the filtrate (m^3), α is cake-specific resistance (m/kg), R is the medium resistance (1/m), A is the filtration area (m^2), and Δp (Pa) is the pressure difference through the filter medium and the filter cake. The constant dynamic viscosity of the filtrate is μ (Pa s), which depends on the temperature, composition and concentration of the dissolved solids in the filtrate. As the experiments included filtrates with different properties, the dynamic viscosities of the filtrates were found according to the temperature and measured concentration of sodium carbonate [49]. The cake-specific resistance and medium resistance can be determined experimentally. By using the collected filtrate volume and time in Eq. (1), a linear graph of $(t - t_s)/(V - V_s)$ (vertical axis) against $V + V_s$ (horizontal axis) was plotted. As an example, the recorded mass of the filtrate versus time during the filtration of GLD sludge by the Nutsche filter at different temperatures (20 °C, 40 °C, 60 °C and 80 °C) were utilized to draw the linear graphs in Fig. 3.

However, the formed cakes are mostly compressible, which means that their resistance is also affected by the pressure drop across the cake. For this reason, the cake-specific resistance in Eq. (1) is usually replaced by its average (α_{av}). The average specific cake resistance (m/kg) was calculated by using the obtained slope (a) of the linear graph in Eq. (2). This method has also wide application in scale-up calculations for filters [28,47,50].

$$\alpha_{av} = \frac{2aA^2 \Delta p}{\mu c} \tag{2}$$

Eq. (3) is the relation between cake-specific resistance and applied pressure drop. This is an experimentally-based empirical equation that is applicable in a limited range of pressures:

$$\alpha_{av} = \alpha_0 (\Delta p_c)^n. \tag{3}$$

In Eq. (3), $\alpha_0$is the specific resistance at unit applied pressure drop across the cake (Δp_c). The compressibility index n was obtained by repeating the filtration test with the same parameters at different pressures and constructing a graph of Δp (horizontal axis) against α_{av} (vertical axis). The average specific resistance of the compressible cake will change as a consequence of pressure changes. By fitting a power-type trend line, the compressibility index is obtained as the exponent [28,47].

4. Results and discussion

Laboratory-scale pressure filters were utilized in filtration tests of green liquor sludge, and the effect of filter cloth permeability on the filtrate flow rate was investigated. The effect of filtration temperature on the properties of the cake and filtrate was also

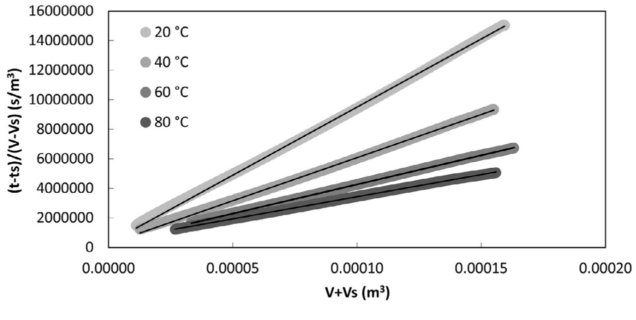

Fig. 3. Plotted linear graphs for filtration experiments by a Nutsche filter on GLD sludge at the temperatures of 20 °C, 40 °C, 60 °C and 80 °C with the constant filtration pressure of 4 bar.

studied. Elemental analyses of the collected filtrates and cakes provided information about the distribution of elements between the solid and liquid phases. The effect of storage of the sludge on the filtration properties of Sample A was also investigated.

4.1. Effect of filter cloth permeability on the filterability of sludge

Different types of filter cloths with different air permeabilities were used in the filtration tests with the Labox 100 apparatus. During the filtration, heated and well-mixed sludge was pumped into the filtration chamber at a pressure of 6 bar. In other words, the feeding pump provided the driving force for the filtrate to pass through the formed cake and filter cloth. Variations in the feed properties were minimized by continuous heating and mixing of the sludge. In each test, the filtration stage was ended by closing the feed valve after 400 g of filtrate had been obtained. Parameters such as temperature, pressure (6 bar) and amount of filtered sludge were kept constant to ensure comparable results with respect to the effect of filter cloth permeability. The cumulative mass of filtrate versus time is plotted in Fig. 4 for several cloths with different air permeabilities.

Fig. 4 (a) shows that more filtration time was required for Sample A when tighter filter cloths (0.08 and 0.2 ($m^3\ m^{-2}\ min^{-1}$)) were used. Yet, with other types of filter cloths (1.00, 2.50 and 3.00 ($m^3\ m^{-2}\ min^{-1}$)) similar filtration times were needed to obtain the same amount of filtrate. Less permeable filter cloth has higher resistance and accordingly reduces the filtrate flow rate. The same filter cloths and conditions were applied in the filtration of Sample B1. As can be seen in Fig. 4 (b), the highest filterability was not seen with the cloth with the highest permeability (2.50 ($m^3\ m^{-2}\ min^{-1}$)). It is interesting that the filter cloth with air permeability of 1.00 ($m^3\ m^{-2}\ min^{-1}$) had the best performance in the filtration of Sample B1. Thus, the pore size of the medium is not the only effective factor in filtration of green liquor but other parameters like surface treatment and the chemicals used in manufacturing should also be considered. Furthermore, comparison of Fig. 4 (a) and (b) shows that filtration of Sample B1 was faster than that of Sample A with the same filtration variables. This also shows how the filtration properties of GLD could change due to the sampling site.

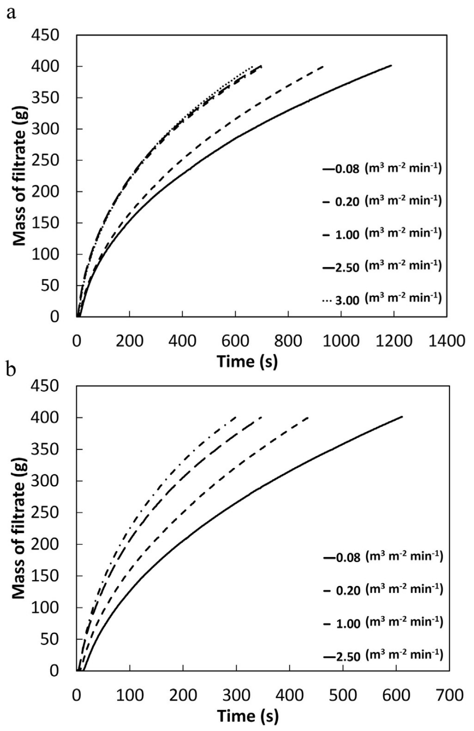

Fig. 4. Accumulated mass of filtrate during the filtration stage with a pressure of 6 bar. Different air permeabilities ($m^3\ m^{-2}\ min^{-1}$) of filter cloths were used in a Labox-100 filtration apparatus for the filtration of Sample A (a) and Sample B1 (b).

4.2. Effect of temperature on filtrate flow rate and cake properties

In order to clarify the effect of the filtration temperature on the filterability, a laboratory-scale Nutsche filter with a heating jacket was utilized in further experimental work. Sample B2 (collected in the winter) was filtered at a different temperatures. The recorded weight of the filtrate during the filtration in each test is illustrated versus time in Fig. 5. The only variable here was the temperature, and other factors such as the pressure of filtration (4 bar), the amount of sludge (200 g) and the type of filter medium (T 1000) were not varied. In order to eliminate the effect of medium fouling in the filtration, a new medium was utilized in each test.

The higher temperature caused faster filtration of the green liquor sludge, as shown in Fig. 5. The green liquor sludge contains precipitated sodium and a higher temperature will increase its solubility [39,51]. Moreover, a higher temperature decreases the dynamic viscosity of the filtrate, which is taken into account in Eq. (5). However, at elevated temperatures, a greater amount of salts will dissolve in the filtrate, which has a reverse effect on the dynamic viscosity of the filtrate. Fig. 6 shows the calculated average specific resistance of cakes in different temperatures of filtration.

As can be seen from Fig. 6, the resistance of the cake was reduced at higher temperature. The cake resistance at 20 °C is $2.94 \cdot 10^{12}$ m/kg and it is reduced dramatically to $2.35 \cdot 10^{12}$ m/kg at 40 °C. Reduction in cake resistance is not considerable when filtration temperature is elevated to 60 °C from 40 °C. However, the

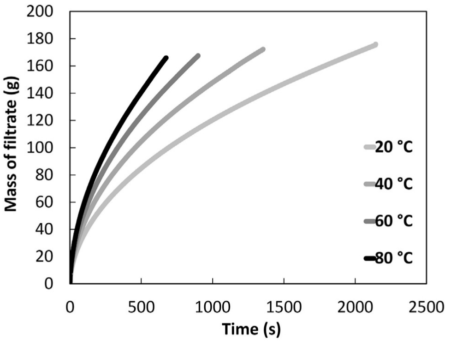

Fig. 5. Accumulated mass of filtrate during filtration at 4 bar pressure at different temperatures.

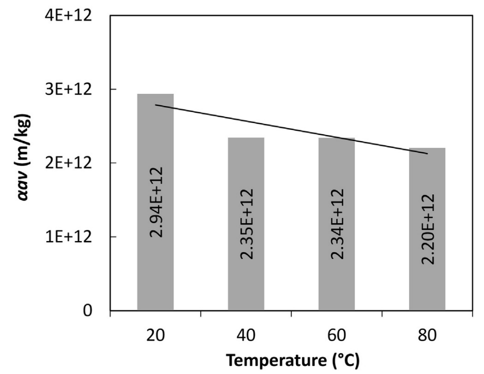

Fig. 6. Average specific resistance of formed cake at different temperatures of filtration (20 °C, 40 °C, 60 °C and 80 °C) and filtration pressure of 4 bar in a Nutsche filter.

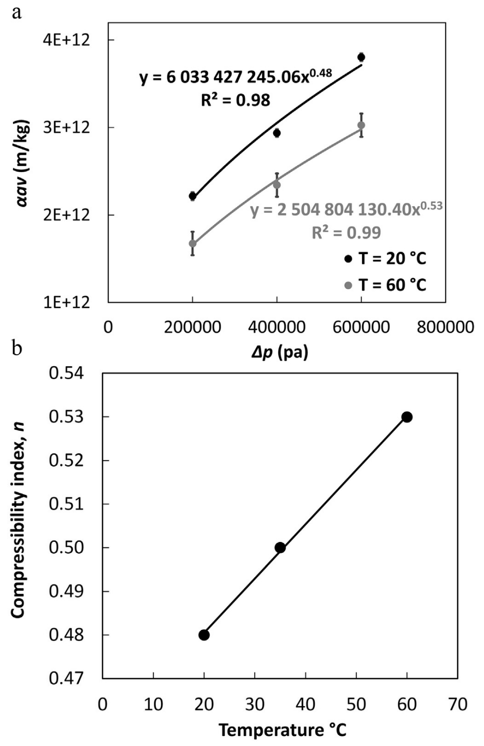

Fig. 7. (a) Compressibility of the cake at the filtration temperatures of 20 °C and 60 °C in the filtration of Sample B2 with the Nutsche filter. (b) Compressibility index of the filter cake (Sample B2) at different temperatures (20 °C, 35 °C and 60 °C).

least resistance of cake is $2.20 \cdot 10^{12}$ m/kg that obtained at 80 °C. The PSD of the solids in the sludge may depend on the temperature because of the possible effect of temperature variations on the formation of many particles and crystals. In addition to the effect of temperature on the size of solid particles, the dynamic viscosity of the filtrate is reduced at higher temperature [47]. These reasons may explain the dependency of cake resistance on temperature variations in the sludge like green liquor, which contains a significant amount of dissolved solids. The same type of filter medium (T 1000) and constant pressure of filtration (4 bar) was used in the tests (Fig. 6), so the only factor affecting cake resistance was the temperature. The results show that cake resistance in the filtration of green sludge has an inverse relation to temperature. It should be noted, however, that when the sludge contains soluble salts, temperature changes can promote the formation of a crystallized ore precipitated scale layer on the medium surface. Therefore, cake resistance alone may not be responsible for the lower filtrate flow rate.

The same filtration tests were done with a higher and lower filtration pressure (6 bar and 2 bar, respectively) at the temperatures of 20 °C and 60 °C to find the influence of heating on cake compressibility. A graph for the determination of the compressibility index in these tests is given in Fig. 7 (a). In another series of experiments with the same sample (Sample B2) using Labox-100, the compressibility index was calculated at the temperature of 35 °C. Filtration pressures of 2, 3, 4, 5, 6 bar were applied in this series of tests, while the other factors such as temperature (35 °C) and filter cloth (AINO K13) remained unaltered. The obtained compressibility index in this test is compared with the previously found one in the Nutsche test series in Fig. 7 (b).

The increasing trend of cake compressibility at higher temperature can be seen in the results presented in Fig. 7 (b). This means that the resistance of the resultant cake at higher temperature of filtration is more sensitive to pressure changes. These kind of changes in cake compressibility probably occurs because of changes in the rigidity of suspended particles at different temperatures.

4.3. Relation between filtrate properties and filtration temperature

After finishing the tests with the Nutsche filter and Sample B2, the samples of the filtrates and cakes were collected for further measurements to find the effect of temperature on their properties. Observable changes in the color of the filtrate, in particular between 20 °C (lighter yellow) and higher temperatures (darker yellow), was a sign of differences in their chemical properties. The densities and dissolved solid contents of the filtrates in tests with the same filtration pressure (4 bar), sludge (Sample B2) and filter cloth (T 1000) but at different filtration temperatures (20 °C, 40 °C, 60 °C and 80 °C) were measured. The filtrates obtained from the Nutsche filter were free of suspended solids. Consequently, the total dissolved solids content of the filtrate was measured by drying (in an oven at a temperature of 180 °C for 24 h) without need for further separation of suspended solids. The density was measured after heating each filtrate sample to its filtration temperature. The results of these measurements are presented in Fig. 8, together with the measured density of the filtrate.

The results show a higher dissolved solid content at elevated filtration temperatures, which indicates that heating of the sludge helps a higher amount of dissolved salts to pass through the cake. Hence, the recovery of chemicals as filtrate or cake is controllable by changing the filtration temperature. It is possible that the higher temperature caused greater solubility of the total dissolved solid content, but this effect may not be equal for all dissolved elements. In order to find the effect of temperature on the recovery of

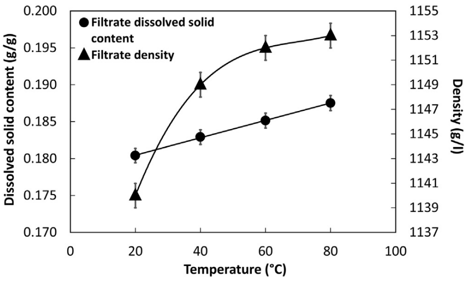

Fig. 8. Density and total dissolved solid content of filtrates obtained by filtration of Sample B2 with a Nutsche filter at fixed pressure (4 bar) and different temperatures.

Table 5
Recovery of elements by solid or liquid phase as weight percentage (wt%).

	Sample A, recovery (wt%)		Sample B1, recovery (wt%)	
	Filtrate	Cake	Filtrate	Cake
Al	0.25	99.75	0.24	99.76
B	85.66	14.34	93.44	6.56
Ba	2.00	98.00	8.05	91.95
Ca	0.09	99.91	0.11	99.89
Cd	<0.10	>99.90	<0.10	>99.90
Cu	1.22	98.78	0.77	99.23
Fe	0.17	99.83	0.12	99.88
K	90.95	9.05	94.88	5.12
Mg	0.17	99.83	0.16	99.84
Mn	0.18	99.82	0.14	99.86
Na	90.68	9.32	93.15	6.85
P	14.88	85.12	44.33	55.67
S	83.79	16.21	85.35	14.65
Zn	0.13	99.87	0.11	99.89

some important elements in the filtrate, elemental analysis was done on the filtrate and cake samples. The results of this measurement are presented in Fig. 9.

As can be seen in Fig. 9, changes in filtration temperature do not have a great effect on the recovery of Na, S, K and B from the filtrate. However, a temperature of 60 °C is slightly more effective in the recovery of Na, K and B from the dregs. Furthermore, if greater recovery of the sulfur content in the filtrate is desired, the temperature of 40 °C should be applied in the filtration of the green liquor sludge.

4.4. Distribution of elements in the cake and filtrate

Elements in the solid and liquid phases of the green liquor sludge were analyzed to ascertain their origin. For this purpose, elemental analysis was done on stored samples of the cake and filtrate from the filtration test with Labox-100. Table 5 shows the weight percentage (wt%) of each element separated as filtrate or cake.

The results show efficient recovery (> 90 wt%) of sodium as filtrate in both cases, even without applying a washing stage in the filtration. This is of importance, as higher sodium recovery in the filtrate is a key aim in green liquor handling [1]. The main dissolved salts of sodium in green liquor are sodium sulfide and sodium carbonate [6]. In addition to sodium, other chemical elements such as boron (B), potassium (K) and sulfur (S) were mostly recovered as filtrate (more than 83 wt%). However, a great part of other elements remained in the solid phase, because they were partially soluble in the filtration condition.

Table 5 also shows that dregs (GLD) contain most of the heavy metal content in the green liquor sludge, e.g. cadmium (Cd). GLD with low heavy metal content can be recycled to the forest to return its nutrient content to the ecosystem [52]. Previous leaching studies done by Manskinen et al. [11] have shown that heavy metals are not easily leached out from dregs. The existing heavy metals in the dregs form complexes, for example, with chloride, that need specific conditions to leach. Heavy metals are mostly leachable from the solid phase by oxidation. The leachability of some heavy metals in dregs becomes easier at lower pH, and the primary pH of landfilled GLD before exposure to environmental conditions is high [11,53,54]. The leachates of landfilled GLD can seep by percolation of rain and snow melting water and release their toxicity to the soil and water resources [55]. However, a study made by Österås et al. [56] showed that the concentrations of heavy metals in the stems of spruce trees (in Sweden) were not elevated under the effect of leached heavy metals from GLD.

4.5. Effect of storage on the filtration properties of green liquor sludge

As a part of the current study, the effect of storage of sludge was investigated by comparing the filtration properties of a fresh and a stored sample of the green liquor sludge. For this purpose, the same filtration tests were repeated on Sample A after eight months of storage at room temperature. Plastic buckets were utilized as storage containers, because of the high pH (approximately 13) of the samples. The filtration test was repeated with the Labox-100 equipment and the same model of filter cloth (AINO K13). The accumulated weights of the filtrate during filtration at 4 bar and 6 bar are compared in Fig. 10 (a). As it is clear from this graph, filtration of fresh sample happened faster than the stored sample in both filtration pressure of 4 bar and 6 bar. Thus, storage had a negative effect on the filterability of the green liquor sludge.

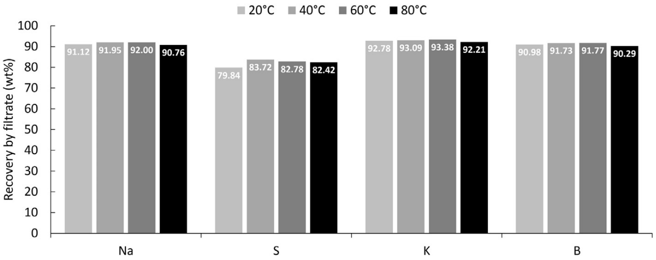

Fig. 9. Recovered weight percentage (wt%) of some elements (Na, S, K, B) in filtrate obtained by filtration of Sample B2 with a Nutsche filter at fixed pressure (4 bar) and different temperatures.

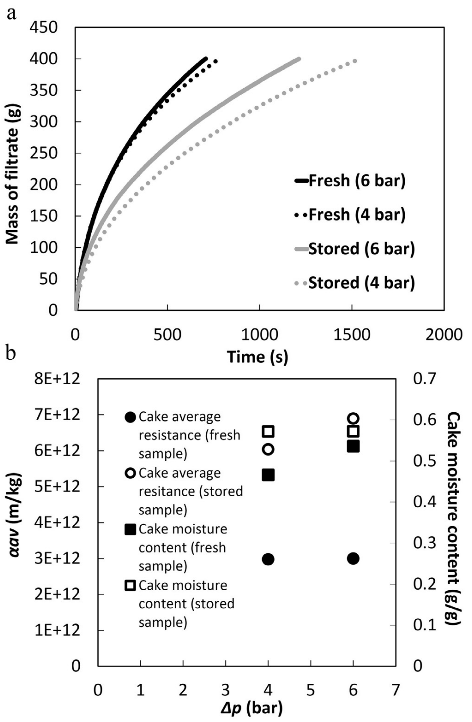

Fig. 10. (a) Accumulated mass of filtrate during filtration at a pressure of 4 bar and 6 bar of fresh and stored Sample A, (b) Average specific resistance and moisture content of the cake in filtration at a pressure of 4 bar and 6 bar of fresh and stored Sample A (Filtration temperature = 35 °C).

The properties of the filter cake in the tests are presented in Fig. 10 (b). The effect of pressure on the average specific cake resistance and filtrate flow was more clearly observable for the stored sludge than the fresh sample. This effect can be seen in Fig. 10 (a) and (b), which are in agreement with each other. The results show that the cake formed in filtration of the stored sludge was more compressible than the fresh sample. It is clear that the storage period had mostly a negative effect on the separation process. The effect of storage on the solubility of some existing salts in the sludge may be a reason for the change in filtration properties. A case study by Wannenmacher et al. [43] demonstrated that the solubility of aluminum and silicon in unclarified green liquor changed during storage.

5. Conclusions

This study investigated the effect of filtration variables on the filterability of green liquor sludge and the properties of the dregs cake. Green liquor sludge contains a considerable amount of dissolved solids. Thus, filtration variables like the temperature and storage affect their solubility and consequently the properties of the formed cake. In order to investigate the properties of the dregs cake, a series of filtration tests were made on three different industrial samples of green liquor sludge. The filtration temperature has direct influence on the filtrate flowrate, the average specific resistance and the compressibility of the cake. An elevated temperature eases the filtration of green liquor sludge by reducing the resistance of the cake. Moreover, heating increases the compressibility of the cake slightly. This means that the effect of pressure difference on cake resistance is clearer at higher filtration temperatures. In addition to its effect on the cake properties, higher temperature increased the concentration of the total dissolved solids in the filtrate, although it did not specifically increase the recovery of each element in the liquid phase. Regardless to the faster filtration and less resistance of cake at higher temperature, elements such as Na, K and B are mostly recovered from cake when temperature of filtration is 60 °C. Thus, the filtration temperature can be used to control the level of elements in dregs cake and filtrate. Use of lime mud as a precoat can improve the filterability of GLD, but the use of precoat leads to generate double size of solid wastes. The results of this study show that poor filterability of GLD can be improved by changing the filtration variables as well. So, optimized parameters for filtration can reduce the need for lime mud precoat in filtration of GLD, and consequently less amount of solid waste will be disposed. Based on elemental analysis of the cake and filtrate samples, it was found that the toxic metals such as Al, Cd, Fe, Mn and Zn are mostly insoluble (> 99.90 wt% of Cd remains in the cake) in green liquor against the sodium content. The analysis results show the recovery of more than 90 wt% of sodium content from the cake using the filtration apparatus applied in the experiments. As a matter of fact, the existence of toxic metals in the dregs results in accumulation of those metals in landfill zone.

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Publication III

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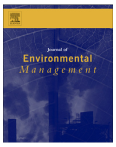

Research article

Extraction of hazardous metals from green liquor dregs by ethylenediaminetetraacetic acid

Mohammad Golmaei*, Teemu Kinnarinen, Eeva Jernström, Antti Häkkinen

LUT School of Engineering Science, Lappeenranta University of Technology, P.O. Box 20, FI-53851 Lappeenranta, Finland

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A B S T R A C T

Green liquor dregs are the major inorganic solid side stream of kraft pulp mills which contain environmentally hazardous metals. The presence of hazardous metals in this industrial residue brings statutory limits for its landfilling, although they are not easily mobilized from the solid phase. In this study, the chelating agent ethylenediaminetetraacetic acid (EDTA) is utilized to extract hazardous metals such as Cd, Pb and Zn from green liquor dregs. Furthermore, the influence of EDTA on the removal of Ca as the main mineral nutrient present in the green liquor dregs is studied. The effect of parameters such as EDTA dosage, L/S ratio and contact time on the removal rate of the elements is investigated. In addition, the experimental data are fitted to the Elovich model and the pseudo-first-order model to describe the desorption kinetics. The results show that 59 wt% of Cd, 13 wt% of Co, 62 wt% of Cu, 3 wt% of Mn, 12 wt% of Ni, 43 wt% of Pb, 16 wt% of Zn, and less than 1 wt% of Ca were extracted from green liquor dregs with EDTA dosage of 0.035 $g_{EDTA\ salt}/g_{dregs}$ and the L/S ratio of 6.25 ml/g. The current study opens up new possibilities to use the green liquor dregs for improving the soil fertility instead of landfilling.

1. Introduction

Green liquor dregs (GLD) are the main inorganic solid side stream of kraft pulp mills originating from the chemical recovery cycle (Pöykiö et al., 2006; Mäkitalo et al., 2012). This cycle is mainly responsible for the recovery of cooking chemicals such as sodium hydroxide (NaOH) and sulfide (Na_2S), which are utilized in lignin removal from wood chips (Sixta, 2006; Tran and Vakkilainen, 2007). The operation of the recovery cycle comprises the main stages of weak black liquor concentration in evaporators, combustion of black liquor in a recovery boiler, converting the Na_2CO_3 content of the smelt to NaOH in a recausticizing plant, and regeneration of reactive lime (CaO) by a lime cycle. GLD sludge is generated after dissolving the molten smelt of the recovery boiler, which contains mostly Na_2CO_3 and Na_2S in weak white liquor in a dissolving tank (Cardoso et al., 2009; Klugman et al., 2007; Sanchez, 2007; Tikka, 2008; Tran and Vakkilainen, 2007). Then the green liquor of GLD sludge is purified from suspended solids which are so called dregs by various methods, such as sedimentation, cross-flow filtration, cake filtration, and centrifugation (Golmaei et al., 2017). The purified green liquor is circulated back to the chemical recovery process, while the dregs are disposed at landfill after treatment in a series of washing and deliquoring stages (Tikka, 2008; Tran and Vakkilainen, 2007).

Dregs contain usually sodium hydroxide, carbonates of sodium and calcium, sulfides, and unburned carbon (Jia et al., 2013). In addition, this alkaline (pH > 10) inorganic solid residue contains non-process elements (NPEs) such as Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Ti, V, and Zn (Kinnarinen et al., 2016; Nurmesniemi et al., 2005). Owing to the presence of NPEs in GLD, its disposal is a way to remove these elements from the chemical recovery cycle (Sedin and Theliander, 2004). NPEs such as As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Ti, V, and Zn are present in the GLD as low water-soluble compounds, e.g. hydroxides and carbonates. Of these elements, considerable amounts of As, Ba, Cd, Cu, Cr, Mn, Ni, Pb and Zn are present in the form of oxidizable minerals, e.g. metal sulfides. It is supposed that the oxides of Fe and Mn are the most common forms of these elements in the GLD which are able to coat other elements, especially Ba, Co, Ni, V and Zn (Nurmesniemi et al., 2005). The recognized compounds of Al and Fe in dregs are silicate diopside ($CaMgSi_2O_6$), aluminosilicates pargasite ($NaCa_2Mg_3Fe^{2+}Si_6Al_3O_{22}(OH)_2$) and vermiculite ($Mg_{1.8}Fe^{2+}_{0.9}Al_{4.3}SiO_{10}(OH)_2\cdot 4(H_2O)$) (Taylor and McGuffie, 2007). In addition, calcium is accumulated in the dregs in the form of calcite

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* Corresponding author.
E-mail address: mohammad.golmaei@lut.fi (M. Golmaei).

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($CaCO_3$), calcite containing a small amount of magnesium ($Ca_{(1-x)}Mg_xCO_3$), calcium oxide (CaO), portlandite ($Ca(OH)_2$), anhydrite ($CaSO_4$), and dihydrate ($CaSO_4.2H_2O$) (Jia et al., 2013; Martins et al., 2007; Taylor and McGuffie, 2007).

Previous research by Nurmesniemi et al. (2005) on the extractability of NPEs from dregs by sequential leaching indicates that heavy metals are mostly available in the easily reduced fraction (extracted by $HONH_3Cl$) and oxidizable fraction (extracted by $H_2O_2 + CH_3COONH_4$). In the other study done by Mäkelä et al. (2016), the cyclone processing has been introduced as a potential method to reduce heavy metal content in green liquor dregs. It is also possible to extract the heavy metals from solids by using the chelating agents. One of the most commonly utilized chelating agents for the extraction of several divalent metals is ethylenediaminetetraacetic acid (EDTA) because of its strong ability to chelate (Di Palma and Mecozzi, 2007; Garrabrants and Kosson, 2000; Giannis et al., 2010; Nörtemann, 1992). Also, the relatively low price of EDTA (1.3 €/kg for technical grade) makes it an economically feasible choice for treatment processes (Leštan et al., 2008).

Contrary to the redox agents and strong acids which release metals by decomposition of the solid matrix, the chelating agents extract metals from the coordination sites (Manskinen et al., 2011). In general, the chelating agents donate their nitrogen and oxygen atoms for metal complexation, and their chelating strength is probably also determined by the number of these atoms (Kocialkowski et al., 1999). The chemical properties of the solid phase, such as pH and the presence of competing ions influence the extraction of metals. Also, the extraction efficiency of metals by chelating agents depends on the specific metal compound involved in the solid phase (Kim et al., 2003; Peters, 1999; Sun et al., 2001). In addition to chemical factors, physical factors like particle size, specific surface area, porosity, and the liquid-to-solid ratio influence the mobility of constituents from the solids (Sabbas et al., 2003; Virolainen et al., 2013). EDTA reacts with all present cationic metals in the solid phase, and consequently there is always a competition between these ions for complexation with EDTA (Kim et al., 2003).

Unfortunately, there is not much information about the influence of other present metals on the extractability of the target metal (Kim et al., 2003). Therefore, the order of metal mobility by the use of chelating agents needs to be studied case by case (Peters, 1999). Due to this and other incomparable conditions, the choice of the suitable chelating agent for the extraction of a specific metal is extremely difficult (Kocialkowski et al., 1999). The environmental risk in using EDTA for industrial residue treatment is the accumulation of its low biodegradable complexes with heavy metals in the aquatic environment like ground waters, rivers and lakes. The main complexed species of this chelating agent existing in natural waters are Ca-EDTA, Zn-EDTA, and Fe(III)-EDTA (Nowack and Sigg, 1996).

The utilization of GLD as a forest soil improving material is a way to return the nutrients lost through the harvesting of trees to the ecosystem (Mahmoudkhani et al., 2004). Only in Finland, 64200 metric tons of GLD solids were landfilled in 2012 (Kinnarinen et al., 2016). This high figure indicates that the reuse of this industrial residue as a fertilizer would be a considerable achievement towards circular economy. GLD contains macronutrients, such as less soluble salts of Ca and Mg, and easily soluble salts of Na and K (Mahmoudkhani et al., 2004; Nurmesniemi et al., 2005; Pöykiö et al., 2006). However, the presence of heavy metal elements, such as Cd, Cr, Cu, Ni, Pb and Zn in GLD would probably contaminate the soil (Alloway and Ayres, 1997; Kasassi et al., 2008). Of these pollutant metals, Pb is mostly present in the non-mobile fraction, and it can only be released to water resources as a result of weathering as a very long-term effect (Nurmesniemi et al., 2005).

The present study is the first one in which a chelating agent has been used to extract hazardous metals from GLD. The sample of GLD for the experimental part of the study was provided by a kraft pulp mill located in Finland. In this research, Cd, Pb and Zn represent the target pollutants. Moreover, the extractability of Ca as the main mineral nutrient of GLD and other metals such as Co, Cr, Cu, Mn and Ni are investigated. The removal of hazardous metals from GLD is still an unresolved issue for the industry. Using conventional acids for leaching from GLD at its highly alkaline pH is not feasible for industrial scale. The current research proposes a practical method for hazardous metals removal from green liquor dregs, while keeping their main nutrients. With this method, GLD could be utilized to improve soil fertility instead of landfilling, and consequently minimize the waste production in kraft pulp mills.

2. Materials and methods

2.1. Preparation and characterization of dregs

The sample of GLD sludge was collected from the reject side of X-Filter at a Finnish kraft pulp mill. The X-Filter is a falling film cross-flow filter that consists of a pressure vessel and vertically mounted filter elements (Keskinen et al., 1995). The required solid sample of dregs for extraction tests was prepared through GLD sludge filtration, dregs drying and crushing. In the first step, the GLD sludge was filtered by a laboratory scale press filter, PF 0.1 (manufactured by Outotec Oy, Finland) to separate the solid phase of dregs from the green liquor. The filtration was followed by pressing at the same equipment, but the resulted cake was not washed with water. Then, the cake of dregs with the moisture content of 33 wt% was dried in an electrical oven, after which the dried cake was crushed by a laboratory planetary ball mill to produce a homogeneous solid mixture for extraction experiments. The approximate volumetric particle size distribution (PSD) of the prepared dregs was measured with a Mastersizer 3000 particle size analyzer (manufactured by Malvern Co, UK). The PSD of the solids was calculated according to the Fraunhofer model.

The total concentrations of the elements in the dregs were measured with a Fisher Scientific ICAP6500 Duo (Thermo Fisher Scientific Inc., Cambridge, UK) inductively coupled plasma optical emission spectrometer (ICP-OES). The solids were digested completely prior to the analysis by using the method 3051 introduced by the US Environmental Protection Agency (1995). The SEM images were taken and energy-dispersive X-ray spectroscopy (EDS) mapping of the samples performed with a Hitachi SU 3500 scanning electron microscope, with a carbon tape background.

2.2. Preparation of extractant solutions

The extractant solutions were prepared by dissolving the ethylenediaminetetraacetic acid disodium salt dihydrate ($EDTA\cdot 2Na\cdot 2H_2O$) as the chelating agent in Millipore water. After the complete dissolution of the chelating agent, the pH of the solution was adjusted to 4.5. The desired pH of the solution was obtained by adding hydrochloric acid solution (HCl 0.1 M). In the experiments, various amounts (Table 1) of the chelating agent were dissolved in water, and the pH was in all cases slightly higher than 4.5. Therefore, only some droplets of the acidic solution were enough to adjust the pH of the extractant solution to 4.5.

2.3. Batch extraction

The pH-adjusted extractant solution containing a specified dosage of the chelating agent was added to 4 g of the dregs in plastic bottles. The extractant solutions were prepared in a higher volume than required for each extraction test, and a certain volume (10–25 ml) of it was taken by pipette and added to the solid sample. The flow diagram in Fig. 1 illustrates the procedure of a batch extraction test.

The suspension was shaken in an orbital shaker (VWR DS-500 Digital Orbital Shaker) for 24 h at ambient temperature (20 ± 0.5 °C). After each extraction test, the suspension was centrifuged at 4000 rpm (3082 g) and temperature of 20 °C for 30 min in a Jouan GT 422 centrifuge in order to separate the clear supernatant from the suspended solids. Then the supernatant was filtered through a syringe filter (Phenex RC 0.45 μm) and sent for elemental analysis by Agilent 7700 inductively coupled plasma mass spectrometry (ICP-MS) according to the SFS-EN ISO 17294-2: 2016.

2.4. Experimental method

The experiments were designed according to the principles of statistical factorial designs in order to study the effect of variables, such as the dosage of the added chelating agent to the suspension and liquid-to-solid (L/S) ratio ($\mathrm{ml_{Extractant\ solution}/g_{\ dregs}}$) on the extractability of Ca and other metals such as Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn from the dregs. The dosages of the chelating agent were determined by the dimensionless mass ratio of the EDTA salt ($\mathrm{EDTA{\cdot}2Na{\cdot}2H_2O}$) to the mass of dregs in each batch of extraction. The variables of batch extraction tests and their values are presented in Table 1.

Different mass ratios of the EDTA salt to dregs from 0.00025 to 0.23 were used by the L/S ratio of 6.25 ml/g. Also, the L/S ratio varied from 2.5 ml/g to 6.25 ml/g for all the applied dosages of the chelating agent between 0.005 $\mathrm{g_{EDTA\ salt}/g_{dregs}}$ and 0.23 $\mathrm{g_{EDTA\ salt}/g_{dregs}}$. The calculated molar ratios of EDTA to the hazardous metal (sum of the moles of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) content of the dregs prepared for extraction experiments are listed in Table 1. Furthermore, the extraction of elements over time were studied in a series of tests by using the highest applied dosage of chelating agent (0.23 $\mathrm{g_{EDTA\ salt}/g_{dregs}}$) and L/S ratio of 3.75 ml/g. For this series of tests, separate bottles of the suspension were prepared and each one was shaken for a duration of 30, 60, 120, 300, 720, 1440 and 2160 min. At the end of each experiment, the supernatant phase was sampled as described above and sent for elemental analysis to determine the concentration of elements.

3. Results and discussion

3.1. Characteristics of dregs

The particle size distribution (PSD) and a scanning electron microscope (SEM) image of the dregs are shown in Fig. 2.

The measured pH of the dregs at 1:5 mass ratio of dregs to Millipore water was 10.3. A possible reason for the alkaline pH of the dregs was the presence of soluble basic compounds, such as alkali metal carbonates, hydroxides and oxides (Nurmesniemi et al., 2005).

The measured total concentration ($\mathrm{mg/kg_{dregs}}$) of the elements, except for the major elements of O and S in the dregs, are presented in Table 2. In addition, the distribution of Ca, Fe, Mg, Mn, Na, O, S and Zn, as well as SEM images of dregs particles are presented in a supplementary file.

The analysis results show relatively high concentrations of nutrients such as Ca, Mg, Na and K. Table 2 shows the concentrations of elements in unwashed dregs, which means that the concentrations of easily soluble elements, such as Na and K, would be lower in a washed sample. In addition to nutrients, some Fe, Mn and Zn, together with traces of Cd, Co, Cr, Cu, Ni and Pb, which are referred to as heavy metals, could be found in the dregs. It is worth mentioning that metals like Cu and Zn are also known as nutrients in the soil (Pöykiö et al., 2006). The term heavy metal is mostly defined for the elemental form of a metal with a density greater than 5 $\mathrm{g/cm^3}$, which is, however, not confirmed by the International Union of Pure and Applied Chemistry (IUPAC) (Duffus, 2002).

3.2. Effect of EDTA dosage on the extraction

Different dosages of EDTA, from 0.00025 $\mathrm{g_{EDTA\ salt}/g_{dregs}}$ to 0.035 $\mathrm{g_{EDTA\ salt}/g_{dregs}}$, were used with the L/S ratio of 6.25 ml/g for batch extraction tests which were continued for 24 h. The extracted weight percentages (wt%) of Ca, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn from the dregs were calculated by using the determined concentration of these elements in the supernatant phase. In Fig. 3, the extracted weight percentages (wt%) of each element for different dosages of EDTA salt are shown. Standard deviations from the mean values of three-times repetition for one test for the extraction (wt%) were 1.2% for Ca, 0.8% for Cd, 0.6% for Co, 1.9% for Cr, 0.8% for Cu, 0.7% for Mn, 0.8% for Ni, 2% for Pb, and 0.9% for Zn. The results showed a clear increase of extraction for the elements except Cr

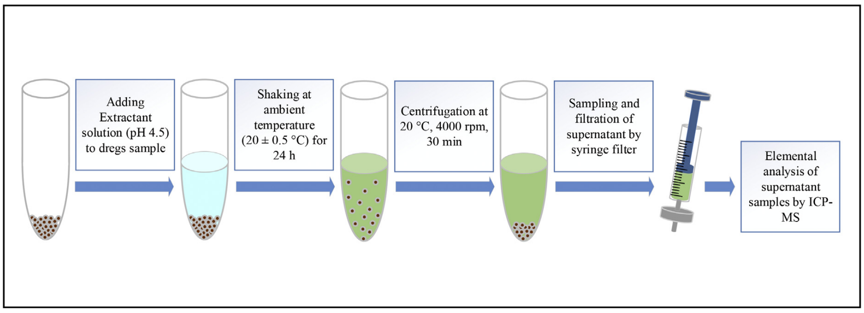
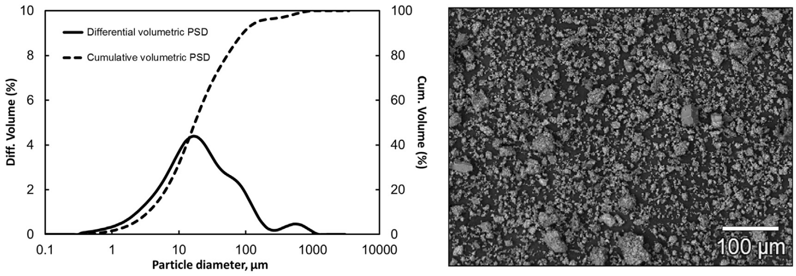


Fig. 1. The procedure of batch extraction tests.

Table 1
Variables and values for the batch extraction tests. The metals* included in the calculated molar ratios are Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn.

EDTA salt/dregs mass ratio (−)	EDTA/metals* molar ratio (−)	L/S ratio (ml/g)			
0.00025	0.003	–	–	–	6.25
0.0005	0.005	–	–	–	6.25
0.001	0.01	–	–	–	6.25
0.002	0.02	–	–	–	6.25
0.003	0.03	–	–	–	6.25
0.005	0.05	2.50	3.75	5.00	6.25
0.009	0.09	2.50	3.75	5.00	6.25
0.014	0.14	2.50	3.75	5.00	6.25
0.019	0.20	2.50	3.75	5.00	6.25
0.023	0.24	2.50	3.75	5.00	6.25
0.035	0.36	2.50	3.75	5.00	6.25
0.23	2.4	2.50	3.75	5.00	6.25



(a) (b)

Fig. 2. a) Differential and cumulative volumetric particle size distribution (PSD) of the dregs, b) SEM image of particles in the dregs.

Table 2
Total concentrations of elements in the dregs.

Element	Concentration mg/kg$_{dregs}$
Ca	$183\cdot10^3$
Cd	9.4
Co	7.7
Cr	102
Cu	158
Fe	1844
K	8498
Mg	43907
Mn	12713
Na	$105\cdot10^3$
Ni	38
P	2611
Pb	11
Zn	1558

with the increasing EDTA dosage. As can be seen in Fig. 3, EDTA was not able to mobilize a considerable amount of the Ca, since more than 99 wt% of this element remained in the dregs at the EDTA dosage of 0.035 $g_{EDTA\ salt}/g_{dregs}$. However, at the same dosage, EDTA removed efficiently 59 wt% of Cd, 62 wt% of Cu and 43 wt% of Pb from the dregs. Also, remarkable amounts of other metals, such as 13 wt% of Co, 3 wt% of Mn, 12 wt% of Ni and 16 wt% of Zn were mobilized from the dregs when 0.035 $g_{EDTA\ salt}/g_{dregs}$ of the chelating agent was utilized in the extraction. For the 1:1 metal-EDTA complexes at the same ionic strength, the stability constant (log K) of the complex formation for Ca is lower than other metals such as Cd, Cu, Mn, Ni, Pb and Zn (Martell and Smith, 1974; Sun et al., 2001). Therefore, a considerably smaller amount of Ca was released from the dregs compared to the other metals. It should be noted that the efficacy of metal-EDTA complexation depends on the metal speciation in a given solid matrix, as well as the stability constant (Leštan et al., 2008). The extraction of Cd mostly happened by an initial increase in the concentration of EDTA, and its removal was slightly improved when the used EDTA dosage was higher than 0.003 $g_{EDTA\ salt}/g_{dregs}$. The extraction of Pb and Zn was gradually increased by the higher dosages of EDTA. The most suitable dosage of EDTA for the optimum removal of all target pollutant metals including Cd, Pb and Zn is 0.009 $g_{EDTA\ salt}/g_{dregs}$.

Fig. 4 shows elevated extraction of the elements resulting from increasing the EDTA dosage from 0.035 $g_{EDTA\ salt}/g_{dregs}$ to 0.23 $g_{EDTA\ salt}/g_{dregs}$. The elevated extraction represents the released amount of the elements (wt%) by increasing the EDTA dosage from 0.23 $g_{EDTA\ salt}/g_{dregs}$ to 0.035 $g_{EDTA\ salt}/g_{dregs}$. In this experiment, an excessively high concentration of EDTA (0.23 $g_{EDTA\ salt}/g_{dregs}$) was used to investigate its effect on the extraction of Ca and other metals. This test was also done with the L/S ratio of 6.25 ml/g for 24 h of batch extraction. As presented in Table 1, the molar ratio of EDTA to the sum of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn present in the dregs was 2.4 at the EDTA dosage of 0.23 $g_{EDTA\ salt}/g_{dregs}$. It is not realistic to assume that all metals are available for EDTA, as the availability depends remarkably on the mineral composition, porosity, and the size of the particles. As shown in the supplementary file, metals such as Fe, Mg, Mn and Zn are not enriched in coarser particles.

These results showed that an unrealistically high dosage of EDTA (0.23 $g_{EDTA\ salt}/g_{dregs}$) was not able to improve the extraction of Cd and Pb considerably, while this effect was clear for the other elements. Specially, the removal of metals such as Co, Cu, Mn, Ni

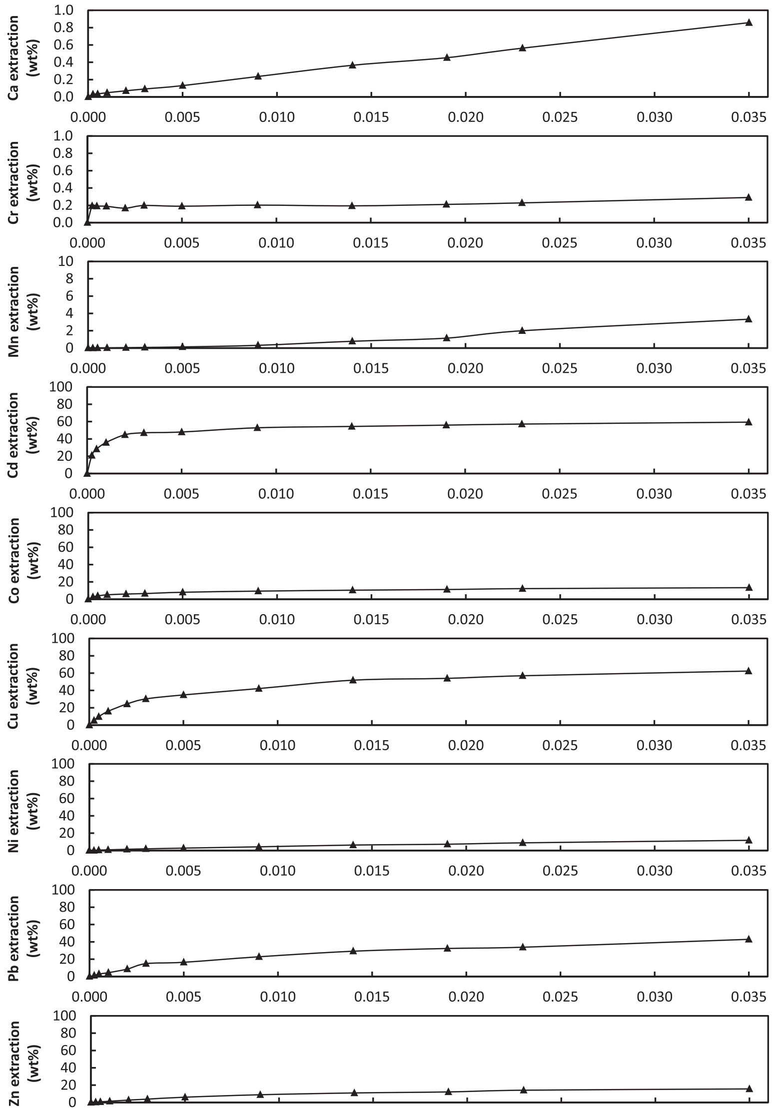


Fig. 3. Effect of EDTA dosage on the extractability of Ca, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn at a constant L/S ratio of 6.25 ml/g. The batch extraction was continued for 24 h. The y-axes for Ca, Cr and Mn have different ranges.

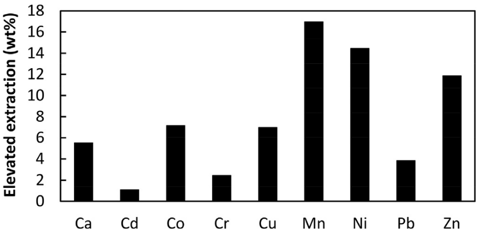


Fig. 4. Elevated extraction by the increase of EDTA dosage from 0.035 $g_{EDTA\ salt}/g_{dregs}$ to 0.23 $g_{EDTA\ salt}/g_{dregs}$ at L/S ratio of 6.25 ml/g. The batch extraction was continued for 24 h.

and Zn from solid phase was considerably improved by the mass ratio of 0.23 $g_{EDTA\ salt}/g_{dregs}$. Furthermore, the usage of this high EDTA dosage obviously reduced the concentration of Ca in the dregs. Although the extra amount of EDTA improved the release of hazardous metals, the excessive use of this chelating agent should be avoided for environmental reasons.

3.3. *Effect of L/S ratio on the extraction*

The ratio of the extractant solution to the solids is another important factor which influences the extractability of elements. The effect of this factor on the removal of the elements from dregs by EDTA was investigated by performing batch extraction tests with various liquid-to-solid (L/S) ratios of the extractant solution to the solids. Through these series of tests, L/S ratios of 2.5, 3.75, 5 and 6.25 ml/g were applied for 24 h of batch extraction with various dosages of EDTA, from 0.005 $g_{EDTA\ salt}/g_{dregs}$ to 0.035 $g_{EDTA\ salt}/g_{dregs}$. The results of these tests are presented in Fig. 5.

In general, increasing the L/S ratio had on average a negative effect on the mobilization of Mn and Ni against the other elements. The Ca release was mostly reduced at L/S ratios higher than 3.75. As can be seen in Fig. 5, the extractability of Ca and Cr was slightly affected by the L/S ratio. The effect of the L/S ratio could be clearly seen in the mobilization of Cd, Co, Cu, Pb and Zn, although this effect was not the same for all the applied dosages of EDTA. For the EDTA dosage of 0.019 $g_{EDTA\ salt}/g_{dregs}$ and 0.005 $g_{EDTA\ salt}/g_{dregs}$, the highest extraction of Cd was obtained with the L/S ratio of 5 ml/g. However, the extraction of Cd at the other applied EDTA dosages was likely enhanced by the higher L/S ratio. In addition, the effect of L/S ratio on the extractability of Cu was tangible for the EDTA dosage of 0.019 $g_{EDTA\ salt}/g_{dregs}$. The most significant increase of Pb removal occurred where the L/S ratio was increased to 6.25 ml/g at the EDTA dosage of 0.035 $g_{EDTA\ salt}/g_{dregs}$. Also, the effect of the L/S ratio on the extraction was studied for the excessively higher EDTA dosage of 0.23 $g_{EDTA\ salt}/g_{dregs}$, and the results are presented in Fig. 6.

As shown in Fig. 6, the extraction of Mn, Pb and Zn was

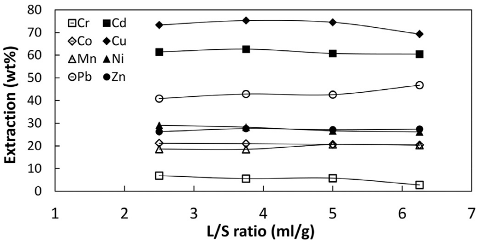


Fig. 6. The effect of L/S ratio (ml/g) on the extractability of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn for the EDTA dosage of 0.23 $g_{EDTA\ salt}/g_{dregs}$. The batch extraction was continued for 24 h.

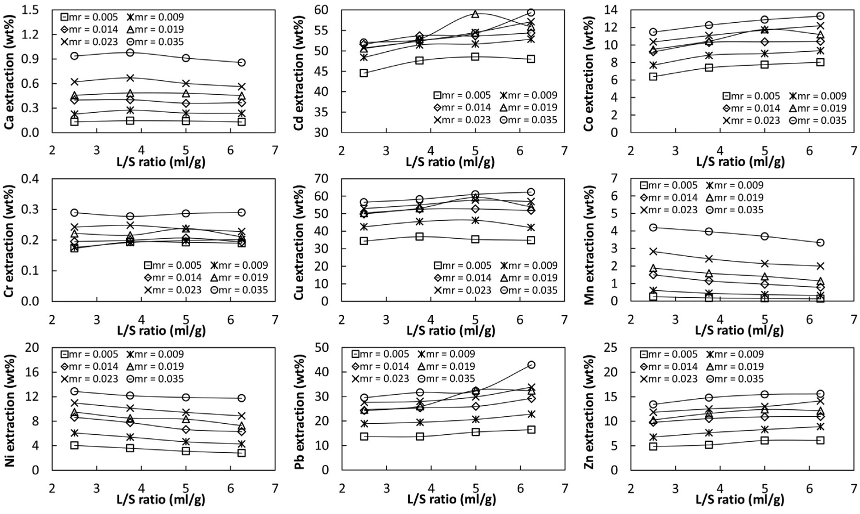


Fig. 5. The effect of L/S ratio (ml/g) on the extractability of Ca, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in different mass ratios (mr) of EDTA·2Na·$2H_2O$ to the dregs. The batch extraction was continued for 24 h. The y-axes have different ranges.

improved by the higher L/S ratio, while the increase of the L/S ratio had a negative effect on the extraction of Cr and Ni at the EDTA dosage of 0.23 $g_{EDTA\ salt}/g_{dregs}$. But in general, the L/S ratio had not considerable effect on the extraction at this EDTA dosage.

3.4. *The effect of contact time on metal release and desorption kinetic models*

The removal of different elements was investigated over the time by varying the duration of the batch extraction between 30 and 2160 min. The suspensions were prepared with the EDTA dosage of 0.23 $g_{EDTA\ salt}/g_{dregs}$ and L/S ratio of 3.75 ml/g. The EDTA dosage for the contact time experiments was selected on the basis of results of previous experiments in which the highest amounts of target hazardous metals were released with a reasonable L/S ratio. Fig. 7, which shows the removal of elements over time can give an impression of extraction kinetics.

The results showed that the elements under investigation were mostly mobilized during the first 30 min of extraction. This phenomenon happened because of fast formation and release of Ca-EDTA and other metal-EDTA complexes from the dregs (Zhang et al., 2010). In a longer period, the trend of the extraction became linear for Ca and Cr, while slight increase could be seen for Cd, Co, Mn and Ni. These slight changes in the extraction of metals after the primary period could happen due to their smaller availability in exchangeable form for complexation with EDTA (Kocialkowski et al., 1999). In addition, during the extraction period, those metal-EDTA complexes which may not be at equilibrium can be exchanged with other metals (Tandy et al., 2004).

The experimental results were fitted to two kinetic models to find out which model would be suitable for describing the desorption kinetics. The kinetic models used in this study are the pseudo-first-order and the Elovich model, expressed by Eq. (1) and Eq. (2), respectively (Kołodyńska, 2011; Ren et al., 2011; Saha et al., 2005):

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{1}$$

$$q_t = \frac{Ln(ab) + Ln(t)}{b} \tag{2}$$

where q_t *and* q_e are the quantities of desorbed metal from dregs after extraction time t (min) and at equilibrium (mg_{metal}/kg_{dregs}), k_1 is the first-order desorption rate constant (min^{-1}), a is the initial release rate (mg kg^{-1} min^{-1}), and b is the release constant (kg mg^{-1}). The time variation of EDTA sorption capacity for different metals is fitted to the abovementioned kinetic models in Fig. 8.

The parameters of kinetic models for desorption of Ca, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn from dregs and coefficients of determination (R^2) are presented in Table 3.

According to the R^2 values presented in Table 3, the Elovich model can be regarded as the best fitting model to the desorption data of Cd, Pb and Zn. The faster release rate of metals is indicated by a higher initial release rate and/or a lower release constant (Zahedifar et al., 2010). According to the parameters of the Elovich model in Table 3, the release of Ca is faster than that of the other metals. The higher first-order desorption rate constants suggest easier metal release (Ren et al., 2011). The first-order desorption rates presented in Table 3 show that the quantity of released Ca was surprisingly larger than that of other metals.

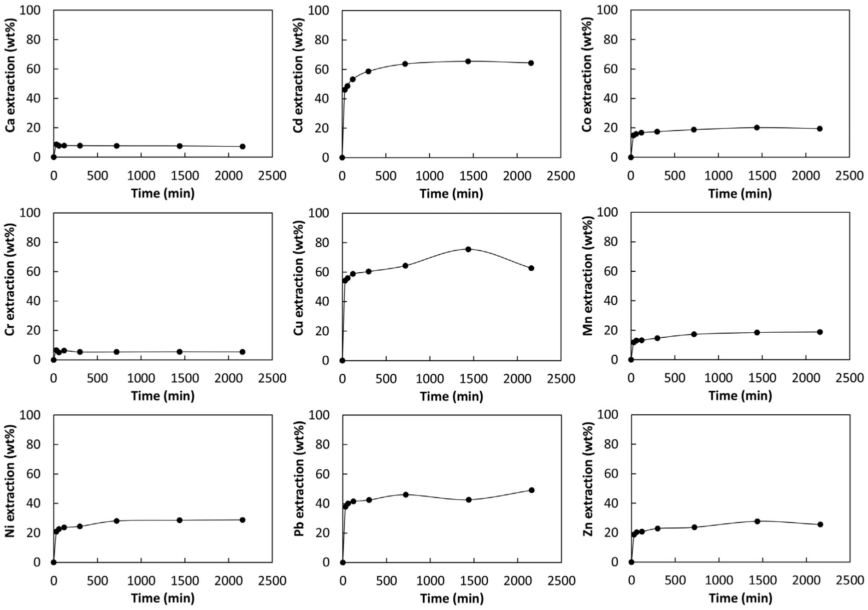


Fig. 7. Extraction of Ca, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn as a function of time at EDTA dosage of 0.23 $g_{EDTA\ salt}$/gdregs and L/S ratio of 3.75 ml/g.

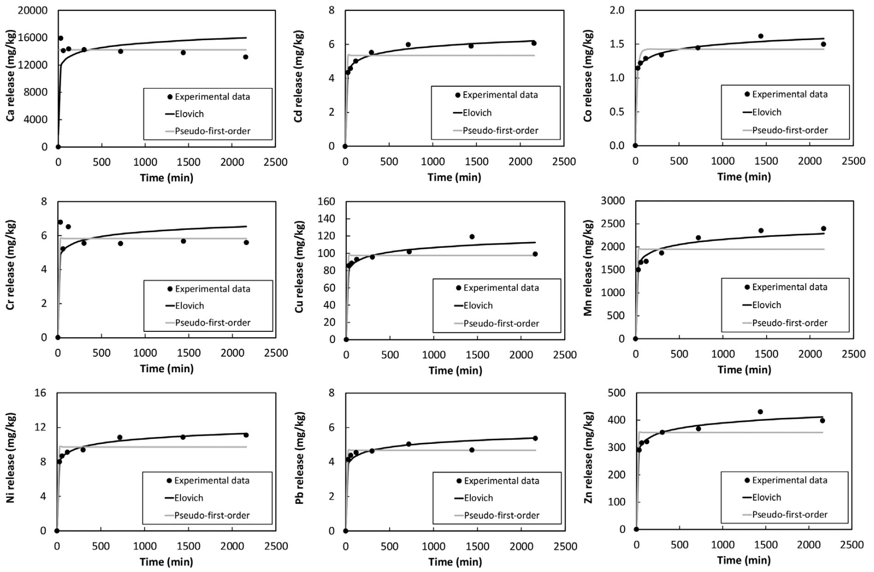


Fig. 8. Time variation of metal release from dregs for Ca, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn at EDTA dosage of 0.23 $g_{EDTA\ salt}$/gdregs and L/S ratio of 3.75 ml/g. The experimental data are fitted to the Elovich model and the pseudo-first-order model.

Table 3
The parameters of the Elovich model and the pseudo-first-order model for the desorption of Ca, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn from dregs, and the coefficients of determination (R^2). The extraction experiments were performed at EDTA dosage of 0.23 $g_{EDTA\ salt}$/gdregs and L/S ratio of 3.75 ml/g.

	Elovich			Pseudo-first-order		
	a	*b*	R^2	q_e	k_1	R^2
Ca	$5.97 \cdot 10^6$	$1.03 \cdot 10^{-3}$	0.802	$1.43 \cdot 10^4$	9418	0.977
Cd	$4.29 \cdot 10^2$	2.35	0.995	5.34	0.98	0.894
Co	$1.21 \cdot 10^2$	9.30	0.991	1.43	0.05	0.952
Cr	$2.49 \cdot 10^3$	2.51	0.767	5.83	9.05	0.937
Cu	$1.06 \cdot 10^4$	0.13	0.963	97.64	0.82	0.919
Mn	$1.04 \cdot 10^5$	$6.18 \cdot 10^{-3}$	0.980	1950	0.94	0.809
Ni	$8.15 \cdot 10^2$	1.30	0.996	9.72	0.84	0.903
Pb	$5.76 \cdot 10^2$	2.80	0.974	4.69	0.78	0.951
Zn	$2.76 \cdot 10^4$	0.04	0.989	354.6	3.95	0.883

4. Conclusion

In this study, the extraction of elements, such as Ca, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn, from GLD by the use of EDTA as the chelating agent was researched. The experiments were designed to investigate the effect of variables such as the EDTA dosage ($g_{EDTA\ salt}/g_{dregs}$), L/S ratio ($ml_{Extractant\ solution}/g_{dregs}$) and extraction time (min) on the removal of Ca and hazardous metals from the dregs. The results showed efficient extraction of two hazardous metals such as Cd (59 wt%) and Pb (43 wt%) at the EDTA dosage of 0.035 $g_{EDTA\ salt}/g_{dregs}$ with the L/S ratio of 6.25 ml/g. Also, by the same values of the variables, 13 wt% of Co, 62 wt% of Cu, 3 wt% of Mn, 12 wt% of Ni and 16 wt% of Zn with traces of Cr (0.3 wt%) and Ca (less than 1 wt%) were extracted from the dregs. Even the excessively higher EDTA dosage of 0.23 $g_{EDTA\ salt}/g_{dregs}$ did not have a remarkable effect on the removal of Cd against Co, Cu, Mn, Ni and Zn. On the other hand, the effect of an elevated L/S ratio was on average positive for the extraction of all elements, except Mn and Ni. Also, most of the investigated elements were removed from the dregs during the first 30 min of extraction. The Elovich model was successfully applied in describing the release of hazardous metals from the dregs. The parameters of the pseudo-first-order kinetic model showed that Ca was released from the dregs in larger quantities than the other metals. In a wider view, the results showed that EDTA is able to extract hazardous metals from GLD while keeping most of Ca.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jenvman.2018.01.078.

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Appendix A. Supplementary data related to Publication III

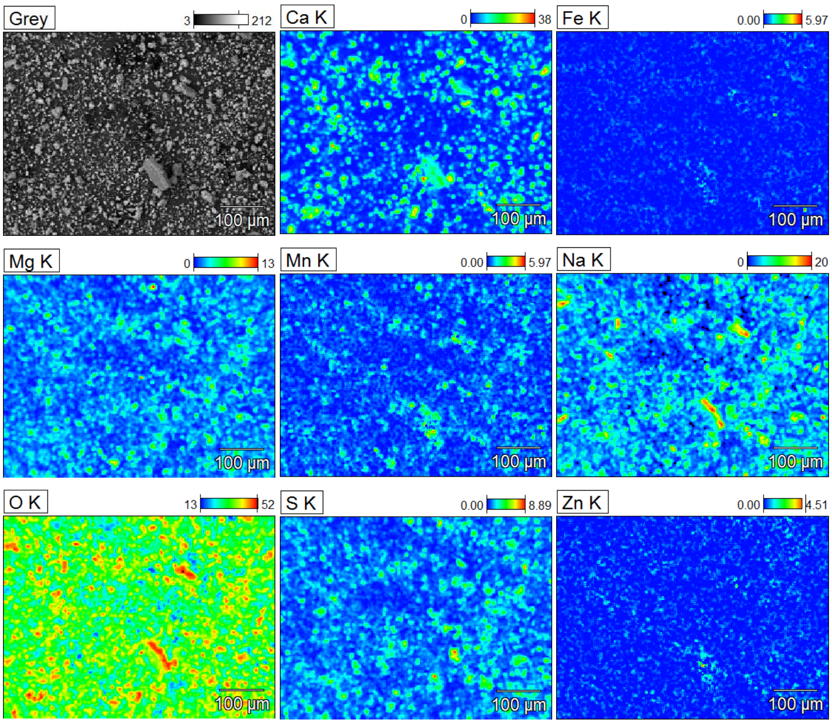

Fig. S1. SEM-EDS elemental mapping (wt%) by 200X magnification on a carbon tape background for dregs used in the extraction tests. Elemental mapping shows the relative concentrations of Ca, Fe, Mg, Mn, Na, O, S and Zn.

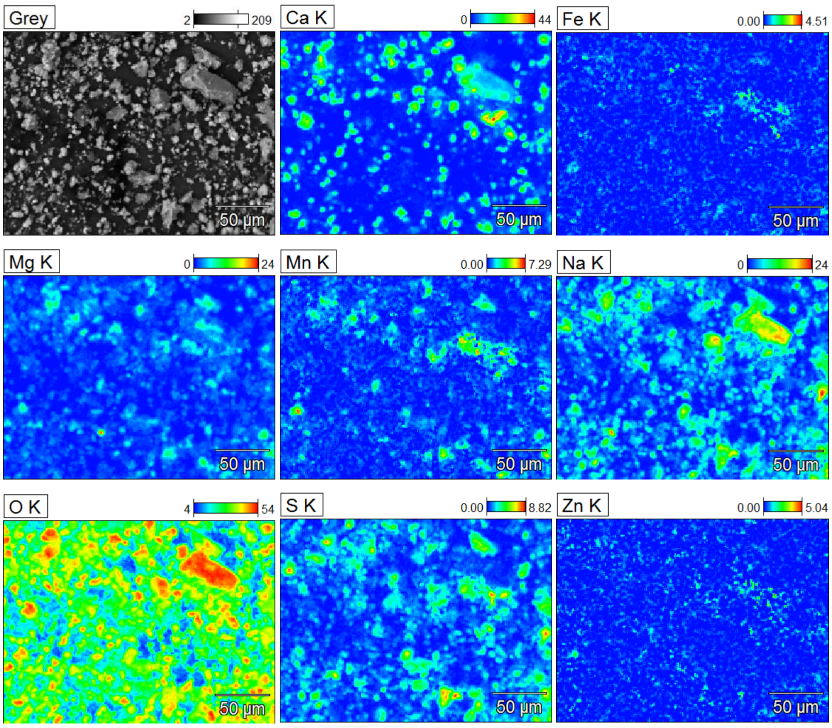

Fig. S2. SEM-EDS elemental mapping (wt%) by 500X magnification on a carbon tape background for dregs used in the extraction tests. Elemental mapping shows the relative concentrations of Ca, Fe, Mg, Mn, Na, O, S and Zn.

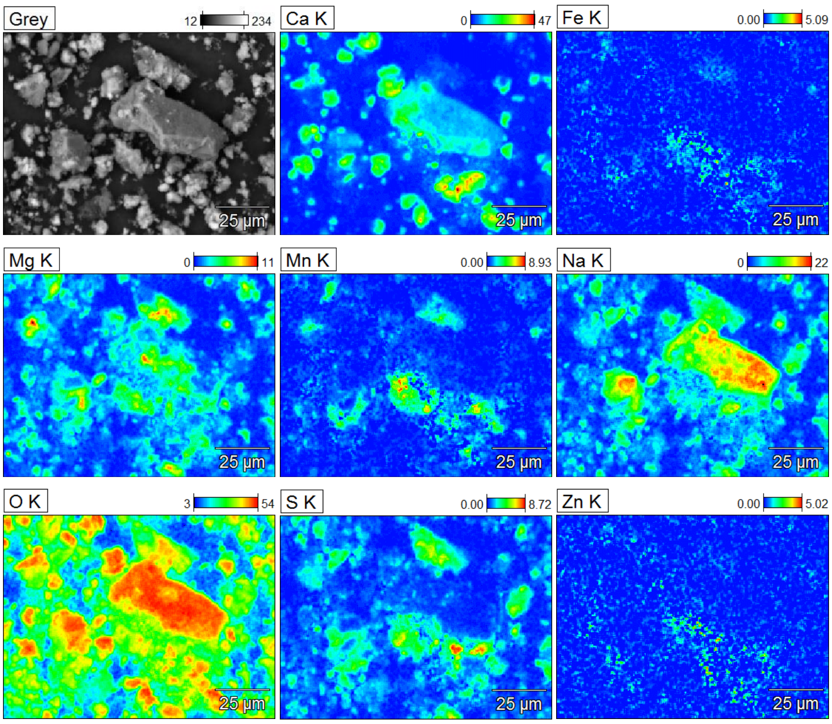

Fig. S3. SEM-EDS elemental mapping (wt%) by 1000X magnification on a carbon tape background for dregs used in the extraction tests. Elemental mapping shows the relative concentrations of Ca, Fe, Mg, Mn, Na, O, S and Zn.

Publication IV

Golmaei, M., Kinnarinen, T., Jernström, E., Häkkinen, A.
Efficient separation of hazardous trace metals and improvement of the filtration properties of green liquor dregs by a hydrocyclone

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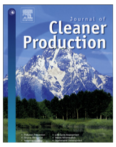

Efficient separation of hazardous trace metals and improvement of the filtration properties of green liquor dregs by a hydrocyclone

Mohammad Golmaei*, Teemu Kinnarinen, Eeva Jernström, Antti Häkkinen

LUT School of Engineering Science, Lappeenranta University of Technology, P.O. Box 20, FI-53851, Lappeenranta, Finland

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A B S T R A C T

The treatment of green liquor dregs (GLD), the main inorganic solid residues of kraft pulp mills, is a major concern in the industrial scale. In this study, the effect of hydrocyclone classification on the filtration properties of GLD and the separation of hazardous trace metals, such as Cd, Ni, Pb and Zn, rare earth elements, and other trace metals was investigated. The experiments were designed to find the influence of parameters such as the overflow to the underflow outlet diameter ratio and inlet pressure on the separation efficiency of a hydrocyclone. The results showed that a lower total filtration area was required for the separation of underflow and overflow fractions than for the original GLD sludge. Also, hazardous trace metals were effectively separated into finer overflow fractions, enhancing the possibilities to utilize the purified underflows e.g. in fertilizers and soil amendment. By using the diameter ratio of 3.70 and the inlet pressure of 1 bar, 90.1 wt-% of Cd, 70.1 wt-% of Ni and 91.4 wt-% of Zn were separated into the overflow, collecting 30 wt-% of the dregs in this fraction. The concentrations of rare earth elements (REEs) in the underflow solids were lower than the ones in the original sludge. Unlike the trace metals and REEs, Ca was accumulated in coarser particles that were separated by underflow fractions. Therefore, a majority of the dregs, enriched by Ca, was separated by underflow fractions. The possibility of categorizing the underflow fractions in CE-marked fertilizing products was also studied.

1. Introduction

The kraft pulping process accounts for the largest share of the world's virgin pulp production, but still its main inorganic waste fraction, the so-called green liquor dregs (GLD), is landfilled (Mäkitalo et al., 2012; Pöykiö et al., 2006; Tran and Vakkilainen, 2007). This solid residue originates from the chemical recovery cycle, which is employed to recover the effective cooking chemicals sodium hydroxide (NaOH) and sodium sulfide (Na_2S). For this reason, the chemical recovery cycle plays a crucial role in making the kraft pulping process economically feasible. The mixture of cooking chemicals is called white liquor and is utilized to remove lignin from wood chips. After the delignification process, the process liquor becomes black liquor, which contains the degraded lignin (Sixta, 2006; Zumoffen and Basualdo, 2008). In the chemical recovery cycle, the solids content of black liquor is increased in evaporators to elevate its heat value before feeding it to the recovery boiler. In the recovery boiler, steam is generated by using the released heat from the combusted organic contents of the black liquor, besides producing a smelt of inorganic salts enriched by Na_2S and Na_2CO_3 (Cardoso et al., 2009; Hupa, 2002; Tran and Vakkilainen, 2007). The GLD sludge is formed by dissolving the smelt in weak white liquor in a dissolving tank. The undissolved content of the smelt will remain as solid particles called dregs, whereas the dissolved Na_2CO_3 content of the sludge will be converted to NaOH in the causticizing process (Sanchez, 2007; Tikka, 2008). Since the green liquor should be free of suspended solids, the dregs are separated in the green liquor purification stage. The most commonly applied separation methods at this stage are sedimentation, centrifugation, cake filtration, and cross-flow filtration (Golmaei et al., 2017; Kinnarinen et al., 2016). The separated dregs contain some amounts of green liquor. In order to reduce the dependency of the process on the make-up of cooking chemicals, it is necessary to recover the green liquor efficiently. Therefore, the dregs are washed and dewatered, for instance with precoat drum filters, before landfilling (Beer et al., 2006; Sanchez and Tran, 2005).

The dregs contain non-process elements (NPEs), such as Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Ti, V, and Zn

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* Corresponding author.
E-mail address: mohammad.golmaei@lut.fi (M. Golmaei).

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0959-6526/

(Nurmesniemi et al., 2005). The disposal of the dregs is, therefore, a practical way to remove those elements from the loop of chemical recovery (Sedin and Theliander, 2004). The dregs are highly alkaline ($pH > 10$) with a great buffering capacity and low hydraulic conductivity. The main compounds of their solid phase are calcium carbonate $CaCO_3$, sodium carbonate Na_2CO_3, unburned carbon (char), magnesium hydroxide $Mg(OH)_2$, sodium sulfide Na_2S, and metal sulfides, e.g. FeS (Jia et al., 2013; Kinnarinen et al., 2016; Mäkitalo et al., 2012; Martins et al., 2007; Sanchez and Tran, 2005). In addition to the carbonate form, other compounds of calcium, such as calcium oxide (CaO), portlandite ($Ca(OH)_2$), calcite containing a small amount of magnesium ($Ca_{(1\text{-}x)}Mg_xCO_3$), anhydrite ($CaSO_4$), and dihydrate ($CaSO_4.2H_2O$) can be found in the dregs (Jia et al., 2013; Martins et al., 2007; Taylor and McGuffie, 2007). In a study made by Taylor and McGuffie (2007) on green liquor clarifier deposits and dregs, Al and Fe were recognized in compounds such as silicate diopside ($CaMgSi_2O_6$), aluminosilicates pargasite ($NaCa_2Mg_3Fe^{2+}Si_6Al_3O_{22}(OH)_2$) and vermiculite ($Mg_{1.8}Fe^{2+}{}_{0.9}Al_{4.3}SiO_{10}(OH)_2\cdot 4(H_2O)$). In the studies by Bennett et al. (1982) and Frederick (1984), it is reported that Al and Mg may form insoluble hydrotalcite in the GLD sludge and accumulate in the dregs.

The production rate of GLD varies from 3 to 4 kg of dregs/ton of pulp in newer boilers working at a designed capacity to 6–9 kg of dregs/ton of pulp in older overloaded recovery boilers (Beer et al., 2006). Finland is among the five dominating countries in the world's wood pulp production (Klugman et al., 2007), and solely in this country 64200 metric tons of GLD solids were disposed of in landfills in 2012 (Kinnarinen et al., 2016). This high figure means a big potential for making products from this residue. Macronutrients are present in GLD as easily soluble salts of Na and K and less soluble salts of Ca and Mg. It also contains micronutrients such as Cu, Fe, Mn and Zn (Mahmoudkhani et al., 2004; Nurmesniemi et al., 2005; Pöykiö et al., 2006). In addition to high alkalinity, the high concentration of hazardous metals cause challenges for the utilization of GLD. It is possible to produce e.g. fertilizers and soil amendments from GLD after reducing the concentration of hazardous metals, such as Cd. On the other hand, the high buffering capacity and low hydraulic conductivity of GLD make it a suitable alkaline barrier against oxygen (Jia et al., 2013; Mäkitalo et al., 2012), which enables the prevention of acid rock drainage in the mining industry. According to studies by Mäkelä et al. (2012) and Rothpfeffer (2007), GLD has also a good liming potential and even the ability to replace commercial agricultural limestone.

The performance of the hydrocyclone is mainly determined by operating and design variables. The design variables affecting the performance of the hydrocyclone are the overflow to the underflow diameter ratio, the cone angle, the diameter of the cylindrical part, and the length of the vortex finder. On the other hand, operating variables such as viscosity and the solids concentration of the feed, pressure drop and feed flow rate affect the performance (Cilliers, 2000; Ghadirian et al., 2015). The efficiency of light particle recovery is increased at a lower diameter ratio of overflow to underflow. Also a higher feed flow rate improves the performance of the hydrocyclone by forcing the larger particles to move faster towards the central axis (Ghadirian et al., 2015).

In this study, the effect of hydrocyclone parameters, such as feed flow rate and the overflow to the underflow diameter ratio on the fractionation of nutrients and hazardous metals in GLD is investigated. Additionally, the fractionation of rare earth elements (REE) and other trace metals in the overflow and underflow streams are studied. The concentrations of NPEs, such as Cd, Ni and Pb, in the underflow fractions are assessed regarding categorizing them in CE-marked fertilizing products. This class of fertilizing products was determined by the European Commission in March 2016 to have uniform standards all around the European Union (EC-European Commission, 2016). Furthermore, the effects of hydrocyclone classification on the filtration properties of the resulting GLD sludges are studied.

2. Theory and calculations

The hydrocyclone is a static device which is able to perform continuous classification of the solid particles by centrifugal force, according to their size and density. This equipment is highly useful for the industry, due to its relatively low capital, operating and maintenance costs (Cilliers, 2000; Ghadirian et al., 2015). The suspension is fed to the hydrocyclone head through a tangential inlet to generate a centrifugal field by a downward helical vortex moving close to the wall of the hydrocyclone. When the vortex approaches the underflow outlet, a reverse helical flow in the axial direction towards the vortex finder is generated. The vortex finder is a tube that is installed axially from the top of the hydrocyclone towards the lower edge of the suspension entry. The overflow stream containing finer particles is directed by the vortex finder to the overflow outlet (Cilliers, 2000; Cullivan et al., 2004; Svarovsky, 2000). The total separation efficiency (E_t) of the hydrocyclone can be calculated with Eq. (1):

$$E_t = \frac{m_u}{m_i} \cdot 100\% \tag{1}$$

where m_u is the mass of solids collected in the underflow and m_i is the mass of solids in the feed flow. The relationship between kinetic energy per volume and pressure drop across the hydrocyclone can be expressed by the hydrocyclone characteristic Euler number. This dimensionless number is defined by Eq. (2) (Vieira and Barrozo, 2014):

$$Eu = \frac{\pi^2 D_C^4 (\Delta P)}{8 \rho Q^2} \tag{2}$$

where D_C is the hydrocyclone diameter (m), ΔP is the pressure drop (Pa), ρ is the density of the liquid (kg m^{-3}) and Q is the feed volumetric flow rate (m^3 s^{-1}). A higher energy consumption is required to operate a hydrocyclone with the larger Euler number (Vieira and Barrozo, 2014).

As it was mentioned before, solid particles are classified into the overflow and the underflow according to their size. The so-called Sauter mean diameter D[3,2] of solids is an average of particle size which can be achieved by the conversion of volumetric distribution to surface area distribution. The Sauter mean diameter is defined by Eq. (3), where D is the diameter of a particle (m) and v_i is the proportion of particles in the size fraction (Allen, 2003):

$$D[3,2] = \frac{\sum_{i=1}^{n} D_i^3 v_i}{\sum_{i=1}^{n} D_i^2 v_i} \tag{3}$$

The Rosin-Rammler-Bennett (RRB) model was fitted to the measured volumetric particle size distribution (PSD) of dregs in different overflow and underflow fractions to calculate the function parameters of the size parameters (X_R(μm)) and dimensionless uniformity index (n_R). The general expression of the RRB model is expressed by Eq. (4) (Rosin and Rammler, 1933):

$$F(x) = 1 - \exp\left[- \left(\frac{X}{X_R} \right) \right]^{n_R} \tag{4}$$

where $F(x)$ is the distribution function, and X is the particle size (μm). In conventional cake filtration, the driving force for passing the filtrate through a porous medium is pressure difference. Darcy's law explains the relation between the filtrate flowrate and pressure drop through a porous medium (Darcy, 1856). Although Darcy's law is known to have some limitations, the "classical filtration theory" has been derived from this law (Svarovsky, 2000). During filtration, the initial pressure drop caused by the filter medium increases due to the resistance of the formed cake by trapped solids on the surface of the medium (Tarleton and Wakeman, 2007; Wakeman and Tarleton, 2005). In this study, the pressure difference over the cake and medium was kept constant throughout the filtration stage to allow determination of the cake properties. According to Svarovsky (2000), when the filtration pressure is constant, the integral function of the filtrate volumetric flow rate and time can be determined by Eq. (5):

$$\frac{dt}{dV} = \alpha\mu c\,\frac{V}{A^2\Delta p} + \frac{\mu R}{A\Delta p} \tag{5}$$

where α is the specific cake resistance (m/kg), μ is the dynamic viscosity of the filtrate (Pa s), c is the mass of solids per unit volume of the filtrate ($\mathrm{kg_{solids}/m^3_{filtrate}}$), V is the volume of the filtrate ($\mathrm{m^3}$), A is the filtration area ($\mathrm{m^2}$), Δp (Pa) is the pressure difference through the filter medium and the filter cake, and R is the medium resistance (1/m). Eq. (6) is an integration of Eq. (5):

$$\frac{t - t_s}{V - V_s} = \frac{\alpha\mu c}{2A^2\Delta p}\,(V + V_s) + \frac{\mu R}{A\Delta p}. \tag{6}$$

In Eq. (6), t_s and V_s are used as starting points in the integration. It is assumed that stable pressure in the filtration chamber is achieved at time t_s (s), and the volume of the filtrate is V_s ($\mathrm{m^3}$) at this point. As the resistance of compressible cakes is affected by the pressure drop during filtration, the specific resistance of the cakes in Eq. (6) is usually replaced by its average, α_{av}. In the calculation part of this study, the medium resistance and average specific cake resistance were determined experimentally. A linear graph of $(t\text{-}t_s)/(V\text{-}V_s)$ (vertical axis) against $V + V_s$ (horizontal axis) were plotted by the use of collected filtrate volume and time in Eq. (6). Then, the obtained gradient (a) of the linear graph was used in Eq. (7) to calculate the average specific cake resistance (Kinnarinen et al., 2013; Svarovsky, 2000; Tarleton and Wakeman, 2007).

$$\alpha_{av} = \frac{2aA^2\Delta p}{\mu c} \tag{7}$$

Also the medium resistance was calculated by using the intercept value of linear graph in Eq. (8):

$$R = \frac{bA\Delta p}{\mu} \tag{8}$$

The required filtration area for each sample was calculated by using the same volume of filtrate for a specific time in Eq. (6). As the other variables were already calculated for each cake, the filtration area was obtained by solving the derived quadratic equation from Eq. (6).

3. Materials and methods

In the experimental part of the study, GLD sludge collected from the reject side of a GLD X-Filter operating at a Finnish kraft pulp mill was classified by using a narrow-angle hydrocyclone in a single-pass process. The GLD sludge did not contain precoat material and its total suspended solids content (TSS) was 5 wt-% and the total dissolved solids content (TDS) of sludge was 21 wt-%. In the classification experiments, a standard narrow-angle hydrocyclone with a relatively long and narrow cylindrical part was utilized to facilitate the classification. The hydrocyclone experiments were carried out by using different overflow to underflow outlet diameter ratios (Do/Du) by varying the diameter of the underflow outlet. The tests were performed at inlet pressures of 1 and 1.5 bar. The underflow diameter was varied between 3 and 8 mm, while the overflow diameter was 11.1 mm in all tests. The applied variables and their values are listed in Table 1.

The sludge was fed the hydrocyclone by a screw-type positive-displacement pump from the feed tank. Before and during each test, the same pump was utilized to circulate the sludge in the feed tank. The circulation of GLD sludge in the feed tank was necessary to prevent the solids from settling and to provide a homogeneous feed for the hydrocyclone. After changing the diameter of the underflow outlet for each test, the hydrocyclone pressure was adjusted to the desired level. Prior to taking samples from the overflow and underflow, the hydrocyclone was kept in operation for 15 min to stabilize the pumping pressure. In addition to collecting overflow and underflow samples for exactly the same period of time, their mass flow rates were measured in a straightforward way, by using a stopwatch and a digital scale. The overflow and underflow samples were then stored for further measurements and filtration experiments. The approximate volumetric particle size distribution (PSD) of the suspended solids in the overflow and underflow samples were measured by a Mastersizer 3000 particle size analyzer (manufactured by Malvern Co, UK). Fig. 1 illustrates the schematic diagram of the process and the hydrocyclone dimensions.

The constant pressure filtration tests were carried out at room temperature with a laboratory-scale Nutsche pressure filter with the filtration area of approximately 20 $\mathrm{cm^2}$. The filter medium used in this pressure filtration apparatus was a cellulosic filter sheet of grade T 120, produced by Pall Filtersystems GmbH (Germany). After pouring 140 g of well mixed sludge into the Nutsche chamber, the feed valve was closed and nitrogen gas was introduced to the filter chamber at a constant pressure difference of 6 bar. Due to the pressure difference, the liquid was forced to pass through the filter medium, causing a gradual growth of cake on its surface. A data recording system was connected to the filter to record the

Table 1
Plan for hydrocyclone experiments.

	Sample code	Underflow diameter (mm)	Overflow to underflow outlet diameter ratio (Do/Du)	Hydrocyclone pressure (bar)
Test 1	UF3P1	3	3.70	1
Test 2	UF5P1	5	2.22	1
Test 3	UF6.5P1	6.5	1.71	1
Test 4	UF8P1	8	1.39	1
Test 5	UF3P1.5	3	3.70	1.5
Test 6	UF5P1.5	5	2.22	1.5
Test 7	UF6.5P1.5	6.5	1.71	1.5
Test 8	UF8P1.5	8	1.39	1.5

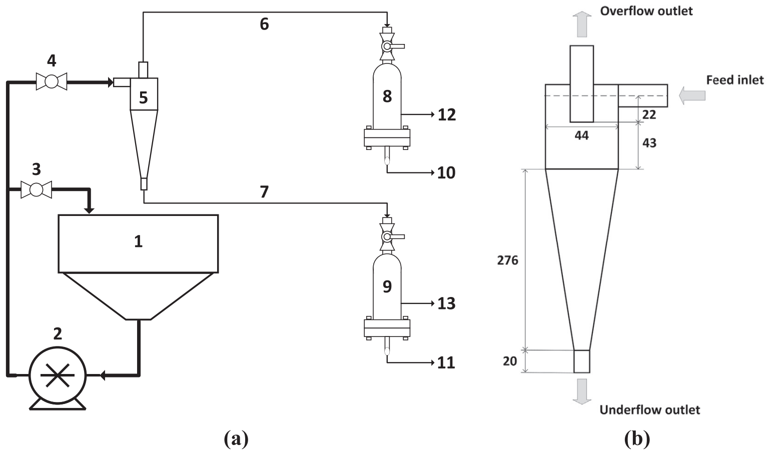


Fig. 1. a) Process schematic diagram. Hydrocyclone feed tank (1), hydrocyclone feed pump (2), recycling valve (3), hydrocyclone inlet valve (4), hydrocyclone (5), overflow fraction (6), underflow fraction (7), Nutsche pressure filter (8 and 9), filtrate (10 and 11), overflow cake (12), and underflow cake (13). b) The dimensions of the hydrocyclone are in millimeters, the cone angle is 7° and the wall thickness of the column is 5 mm.

cumulative mass of the filtrate and the pressure difference once a second. After recognizing the first gas bubble at the filtrate outlet, the gas valve was closed and the filtration was stopped. The moisture content of the cake was then measured by drying the cake in an electric oven at 105 °C for 24 h. Additionally, the total dissolved solids content of the filtrate was measured similarly, but at an elevated temperature (180 °C).

The concentration of elements in the solid samples (dried cakes) were measured with a Thermo Fisher Scientific ICAP6500 Duo (Thermo Fisher Scientific Inc., Cambridge, UK) inductively coupled plasma optical emission spectrometer (ICP-OES). The solids were digested in a mixture of HCl (3 ml) and HNO_3 (9 ml) in a CEM Mars 5 microprocessor-controlled microwave oven with HP 500 Teflon vessels (CEM corp., Matthews, USA) according to the US EPA method 3051, before ICP-OES analysis (US Environmental Protection Agency, 1995). The results of the ICP-OES analysis were used to calculate the fractionation of elements between the overflows and underflows.

Additionally, scanning electron microscope (SEM) images were taken from the dried cake samples (GLD sludge, UF3P1-underflow and overflow), and energy-dispersive X-ray spectroscopy (EDS) mapping of the samples was performed with a Hitachi SU 3500 scanning electron microscope, with a carbon tape background. The SEM images and EDS mapping are presented in Supplementary file.

4. Results and discussion

4.1. Particle classification with the hydrocyclone

The effect of the overflow (OF) to the underflow (UF) outlet diameter ratio (*Do*/*Du*) on the separation efficiency of hydrocyclone classification was evaluated on the basis of dimensionless split ratios of suspended solids, i.e. the fraction of material collected in the underflow and overflow. The TSS contents of the overflows varied between 2.2 wt-% and 1.5 wt-% and the TSS contents of the underflows are presented in Table 2.

According to the data presented in Table 2, the TSS content in underflows increased with the *Do*/*Du* diameter ratio. In this case, the separation efficiency of the solids was defined as the mass ratio of the solids collected in the underflow. These results are presented in Fig. 2 for the inlet pressures of 1 and 1.5 bar.

The graphs presented in Fig. 2 show that the total separation efficiency of the suspended solids decreased with the diameter ratio. This trend can be seen at both inlet pressures. In other words, decreasing the diameter of the underflow outlet made the underflow fraction thicker and reduced the concentration of the suspended solids in the overflow. However, the volumetric flow rate of feed was reduced at both inlet pressures as the diameter ratio was increased. Fig. 2 reveals that the increase of the diameter ratio from 2.22 to 3.70 had a more tangible effect on the separation efficiency

Table 2
The TSS contents of the underflows.

Diameter ratio (*Do*/*Du*)	Hydrocyclone inlet pressure (bar)	Suspended solids content of underflow (wt-%)
3.70	1	45.7
2.22	1	26.0
1.71	1	15.4
1.39	1	12.1
3.70	1.5	50.5
2.22	1.5	26.8
1.71	1.5	14.8
1.39	1.5	12.4

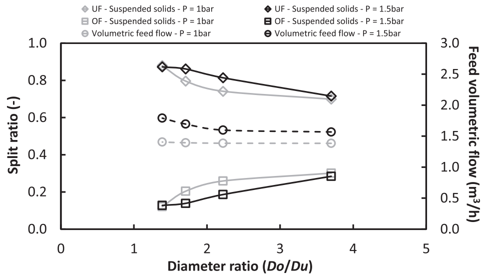


Fig. 2. Effect of the overflow to the underflow outlet diameter ratio (*Do*/*Du*) on the feed volumetric flow and suspended solids split ratio to the fraction of underflow (UF) and overflow (OF), when the hydrocyclone pressure was 1 bar and 1.5 bar. The overflow diameter was 11.1 mm for all tests.

of the solids, when the higher inlet pressure was applied. According to the studies done by Frachon and Cilliers (1999), the increase of inlet pressure improves the recovery of suspended solids into the underflow. In Fig. 3, the hydrocyclone characteristic Euler Numbers for various overflow to underflow outlet diameter ratios (*Do*/*Du*) at the inlet pressures of 1 bar and 1.5 bar are presented.

According to the data presented in Fig. 3, the Euler Number increased with the overflow to underflow outlet diameter ratio (*Do*/*Du*) at both applied pressures, but this trend was intensified at the higher inlet pressure. The data presented in Fig. 3 shows that the Euler Number was greater at the higher pressure, where the diameter ratio (*Do*/*Du*) was larger than 1.71. This means that the energy consumption of the hydrocyclone increases at a higher applied pressure.

The cumulative volumetric particle size distributions (PSD) of the solids in the overflow and underflow samples, together with those of the GLD sludge, are presented in Fig. 4, where the effect of the *Do*/*Du* diameter ratio on the size distribution of the particles present in each fraction is illustrated. Additionally, the particle size distribution of each sample is fitted to the Rosin-Rammler-Bennett (RRB) model and the parameters are presented in the legend of Fig. 4.

The most significant observation regarding the particle size distributions and obtained size parameters (X_R) of the overflows and underflows (Fig. 4) is that effective classification of the suspended solids was obtained with the hydrocyclone. The cumulative particle size distributions presented in Fig. 4 show that the finer particles were mainly collected with the overflow, while the coarser particles migrated to the underflow. It is clear in Fig. 4 that the separation efficiency of finer particles was improved by the increase of the diameter ratio at both inlet pressures. This result means that the separation efficiency of finer particles by overflow increased with increasing the diameter ratio.

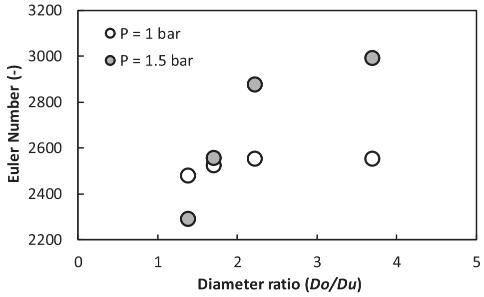


Fig. 3. Calculated hydrocyclone characteristic Euler Numbers for different overflow to underflow outlet diameter ratios (*Do*/*Du*) at the inlet pressures of 1 bar and 1.5 bar.

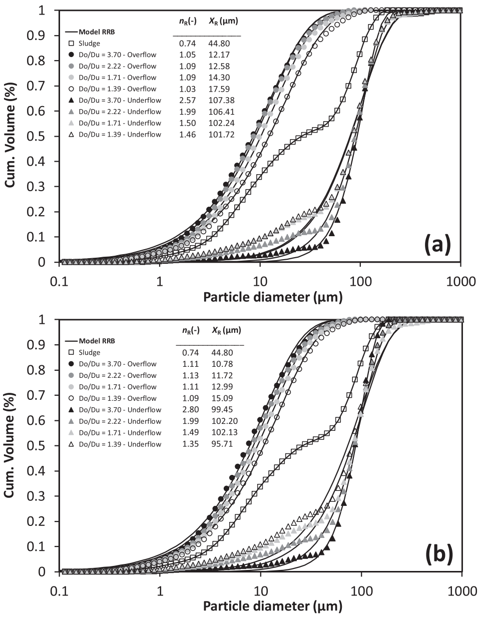


Fig. 4. Effect of the overflow to underflow outlet diameter ratio (*Do*/*Du*) on the particle size distribution in the overflow and underflow at the inlet pressure of 1 bar (a) and 1.5 bar (b). The Rosin-Rammler-Bennett (RRB) model is fitted to the measured PSDs, uniformity indexes (n_R) and size parameters (X_R) are presented in the legends.

According to the literature (Cilliers, 2000; Hwang et al., 2008), by using a smaller underflow diameter, coarser particles will be collected into the underflow. Additionally, the pumping pressure can intensify the effect of the diameter ratio on the separation efficiency of fine particles. The presented data of the RRB model in Fig. 4 show that the particle size parameters (X_R) in the overflow fractions were reduced at the higher hydrocyclone inlet pressure. It was also found by Frachon and Cilliers (1999) that a higher inlet pressure improves the separation of finer particles into the overflow.

4.2. Filtration characteristics of overflow and underflow streams

The overflow and underflow samples collected during the hydrocyclone tests were filtered, together with the original sludge by using a Nutsche pressure filter, to investigate the effect of classification on the filtration characteristics of the fractions. The cumulative mass of the filtrate during the filtration of the original sludge and the overflow and underflow fractions are presented in Fig. 5. The filtration periods of the underflow fractions were shorter than those of the original sludge and overflows, due to their lower

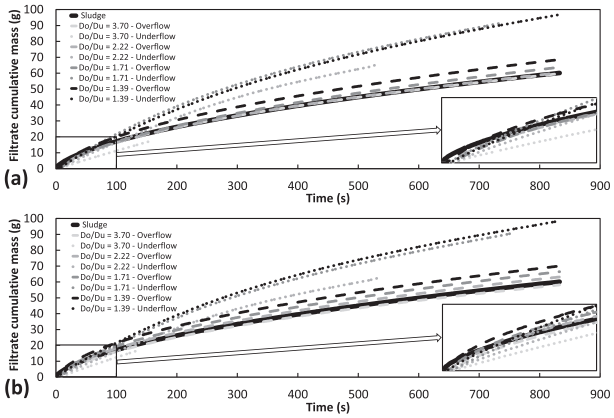


Fig. 5. The cumulative mass of filtrates during the filtration of overflow and underflow fractions at hydrocyclone inlet pressure of 1 bar (a) and 1.5 bar (b). The filtration pressure was 6 bar in all tests.

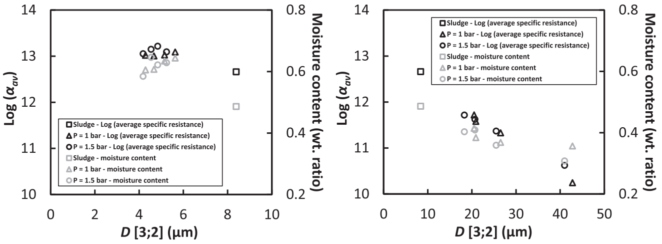
liquid contents. This can also be seen in Fig. 5, where the filtration of the underflows was finished early, while the filtration of the sludge and overflows still continued. Therefore, the cumulative masses of the filtrate for the original sludge and overflows are presented in Fig. 5 until a certain filtration time, not until the end of each experiment. As can be observed in Fig. 5, the filtration rate of the overflow fractions containing finer particles was slower. The filtration rate was also affected negatively by the use of a bigger diameter ratio. The same effect of particle size on the filterability of the samples can be seen for underflow fractions as well. As can be seen Fig. 5, the filtration rates of underflow fractions were faster than in the case of the original sludge and the overflow fractions, except the one obtained by using the biggest diameter ratio. Additionally, the results show an improvement in the filterability of the overflow fractions, compared to the original sludge. This is an interesting result, and it is discussed in closer detail with respect to the required filtration area in the end of this section.

The correlation plots between the Sauter mean diameters of suspended solids ($D[3;2]$) and the average specific cake resistances (α_{av}), as well as the final moisture contents of the filter cakes are shown in Fig. 6. Fig. 6 (a) shows that the presence of finer particles in the overflow fractions, compared to the original sludge, results in the formation of filter cakes with higher average specific resistances and moisture contents. However, the average specific resistances and moisture contents of the overflow filter cakes were not dependent on the changes of the Sauter mean diameters of particles, as much as in the case of underflow filter cakes.

The reducing trend of average specific resistance and moisture content of cake resulting from the increase in the particle size can be seen in the data of underflow fractions.

The suspended solid contents of the underflow fractions increased when bigger diameter ratios were used. The diameter ratio was increased in this study by using a smaller underflow diameter, and the fixed size of 11.1 mm was used for the overflow. As a consequence, thicker filter cakes were formed from the underflow fractions obtained by applying bigger diameter ratios. Correspondingly, the diameter ratio had an opposite effect on the suspended solids contents of the overflow fractions and consequently on the thickness of the filter cakes. The thickness of the underflow cakes was increased from 10.6 mm to 34.7 mm with the increase of the diameter ratio, while the cake thickness was reduced from 1.4 mm to 0.8 for the corresponding overflows.

In order to perform a more reasonable comparison of filterability, the required filtration areas for a fixed feed rate of 16.7 t/h were calculated. The required filtration areas for the original sludge and overflows and underflows for 16.7 t/h of hydrocyclone feed



(a) (b)

Fig. 6. Moisture content and logarithm of average specific resistance of cakes (Log(α_{av})) according to the Sauter mean diameter of suspended solids ($D[3;2]$ (μm)) in overflows (a) and underflows (b). The filtration pressure was 6 bar in all tests.

with 4 wt-% of dregs at two different pressures are presented in Fig. 7. The feed rate of the GLD sludge was approximated with certain assumptions for a pulp mill producing 2000 tons pulp/day and having a GLD production rate of 8 kg_{GLD}/ton_{pulp}.

As can be seen in Fig. 7, the total required filtration area for the underflows and overflows was increased when a bigger overflow to underflow diameter ratio was used in the hydrocyclone. The most important result shown in Fig. 7 is that the total filtration area required for the separation of the GLD sludge could be reduced when hydrocyclone classification was used as the pretreatment method. From the technical point of view, a smaller required filtration area means a reduction in the capital and operating cost of the process. In the industrial scale, the clogging of the filter medium may be a big concern, which could be mitigated by reducing the required filtration area by classification.

As the presented filtration results show, particle size distribution affects the filterability of the sludge and the characteristics of the filter cake. This effect can be explained by the specific surface area of the particles. The finer particles have bigger specific surface areas, which increases the friction between the fluid flow and filter cake structure, and consequently reduces the filtration rate. The negative effect of finer particles on the filtration rate results in filter cakes with higher moisture contents. Also the porosity of the filter cake is a function of particle size distribution, which affects its permeability and specific resistance (Svarovsky, 2000; Wakeman, 2007). The inverse effects of particle size distribution on the cake specific resistance have been recently studied by Kinnarinen et al. (2017) as well.

4.3. Elemental classification into overflow and underflow

The concentrations of elements in the suspended solid content of the overflows and underflows were measured with ICP techniques as described above. The analysis results were used to investigate the classification of each element by the hydrocyclone. The fractions (wt-%) of the suspended solids and elements such as Al, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, and Zn, classified into overflows are presented in Fig. 8. As Fig. 8 shows, the separation efficiency of finer particles and the target elements by the overflow fractions was improved by the increase of the overflow to the underflow outlet diameter ratio (*Do*/*Du*). The majority of hazardous metals, such as Cd, Ni and Zn, and a relatively small fraction of suspended solids were collected by the overflows. Therefore, the concentrations of hazardous metals in the underflow fractions were significantly lower than those in the original GLD sludge. In other words, hydrocyclone classification resulted in overflows rich in hazardous metals and underflows with reduced concentrations of these metals.

The concentration of REEs and other trace metals, such as Ag, Th, U, Co, Li, Pb, Rb, Ti and Zr in the total suspended solids (TSS) of the original GLD sludge, and the obtained fractions from the hydrocyclone test with the diameter ratio of 3.70 (*Do*/*Du*) at the pressure of 1 bar are presented in Table 3. In addition, the distribution of Al, Ca, Cu, Fe, Mg, Mn, O, S, Si, and Zn, as well as SEM images of particles in the crushed dry cake of the samples are presented in Supplementary file 1.

As can be observed in Table 3, the REEs and trace metals such as Ag, Th, U, Co, Li, Rb, Ti, and Zr are mostly accumulated in the overflow fractions. It can also be seen that the concentration of another hazardous metal, Pb, in the underflow fraction is much lower than in the original sludge of GLD.

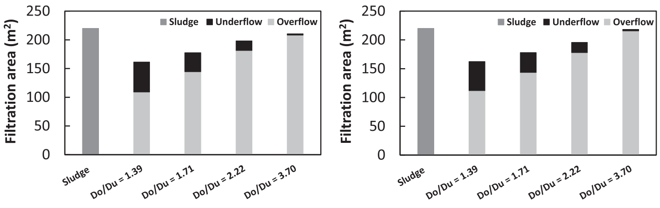
The results confirm that the hazardous metals Cd, Ni, Pb and Zn, other trace metals, and REEs are mostly found in the finer particles of the dregs. Therefore, the hydrocyclone classification of dregs according to their size is a practical method to separate a considerable amount of these elements by overflow fractions which contain a smaller share of suspended solids in the original GLD sludge. Contrary the other elements, Ca, which is the most abundant nutrient element in the dregs is accumulated in the underflow fractions.

4.4. Assessing the utilization of underflow as a soil fertilizer

The underflow fractions, with low concentrations of hazardous metals and enriched by Ca, can be potentially used as soil fertilizers. Different product function categories (PFC) of CE-marked fertilizing products were determined by European commission in March 2016, to have uniform standards all around the European Union (EC-European Commission, 2016). In this section, the concentrations of hazardous elements in GLD are studied by categorizing them as CE-marked fertilizing products, according to the above-mentioned standards. The maximum allowed concentrations of hazardous trace elements in all the mentioned CE-marked products are listed in Table 4.

In Table 5, the concentration of hazardous trace metals, micronutrients and macronutrients in the dregs content of the non-classified GLD sludge are presented. The concentrations are presented with respect to the total solids (TS) and suspended solids (TSS) of the filter cake. The concentration of elements in suspended solids has been calculated for washed dregs cakes that are free of dissolved solids.

As can be seen in Table 5, efficient cake washing of dregs increases the concentration of listed elements which are almost insolube in water. A high cadmium content of dregs has usually been regarded as the main obstacle to their utilization for any value-added purpose. By comparing the data presented in Tables 4 and 5, it can be seen that the concentration of Cd in the dregs used in this study are higher than the maximum allowed concentration



(a) (b)

Fig. 7. Required filtration area for the original sludge and underflows and overflows at the filtration pressure of 6 bar, when 16.7 (t/h) of sludge is fed into the hydrocyclone at the pressure of 1 bar (a) and 1.5 bar (b) by using different overflow to underflow diameter ratios (*Do*/*Du*).

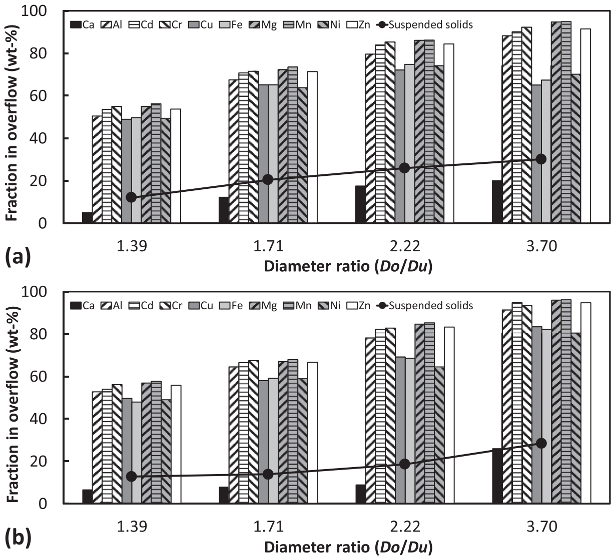


Fig. 8. The fraction (wt-%) of Ca, Al, Cd, Cr, Cu, Fe, Mg, Mn, Ni, and Zn with suspended solids collected by overflows at different overflow to underflow outlet diameter ratios (*Do*/*Du*) and the hydrocyclone pressure of 1 bar (a) and 1.5 bar (b).

in all CE-marked fertilizing products. The concentration of Ni in the dregs should be reduced to categorize them as (PFC 1(A)) and (PFC 3(A)). The concentrations of other hazardous trace elements are already lower than the maximum allowed values for all CE-marked

Table 3
Concentrations of rare earth elements (REE) and other trace metals in the total suspended solids (TSS) of the original GLD sludge, as well as the overflow and underflow fractions of the hydrocyclone operated by using the highest diameter ratio (*Do*/*Du* = 3.70) and the inlet pressure of 1 bar.

Symbol of element	Name of element	Concentration (mg/kg $_{TSS}$)		
		Sludge	Overflow	Underflow
Rare earth elements (REE)				
Er	Erbium	0.07	0.11	0.02
Eu	Europium	0.05	0.05	0.02
Gd	Gadolinium	0.14	0.23	0.06
Ho	Holmium	0.02	0.04	<0.01
La	Lanthanum	1.6	1.8	0.7
Lu	Lutetium	<0.01	0.02	<0.01
Nd	Neodymium	0.9	1	0.4
Pr	Praseodymium	0.3	0.3	0.1
Sm	Samarium	0.14	0.2	0.06
Tb	Terbium	0.02	0.03	<0.01
Tm	Thulium	<0.01	0.02	<0.01
Yb	Ytterbium	0.06	0.1	0.01
Y	Yttrium	0.86	1.43	<0.2
Other trace metals				
Ag	Silver	2.2	4.1	<0.2
Th	Thorium	0.2	0.2	<0.1
U	Uranium	0.2	0.4	<0.1
Co	Cobalt	8.84	15.4	<2
Li	Lithium	5.39	9.99	5.5
Pb	Lead	16.9	22.6	<10
Rb	Rubidium	44.1	79.3	19.4
Ti	Titanium	51.9	96.2	23.9
Zr	Zirconium	<2	2.85	<2

Table 4
Maximum allowed concentrations of hazardous trace elements in different product function categories (PFC) which can be used as CE-marked fertilizing products (EC-European Commission, 2016).

Product function category	Maximum allowed concentration (mg/kg dry matter)				
	As	Cd	Hg	Ni	Pb
Organic fertilizer (PFC 1(A))	-	1.5	1	50	120
Liming material (PFC 2)	120	3	2	90	200
Organic soil improver (PFC 3(A))	-	3	1	50	120
Inorganic soil improver (PFC 3(B))	-	1.5	1	100	150
Growing medium (PFC 4)	-	3	1	100	150

Table 5
Concentration of elements in the total solid (TS) and total suspended solids (TSS) of dregs separated from GLD sludge by pressure filtration at 6 bar. The final moisture content of the wet dregs cake was 36 wt-%.

Element	Concentration (mg/kg TS)	Concentration (mg/kg TSS)
Al	1380	1651
As	<3	-
Ca	112000	134028
Cd	7.1	8.5
Co	6.3	7.5
Cr	93	111
Cu	420	503
Fe	2220	2657
Mg	32700	39131
Mn	8420	10076
Ni	60	72
Pb	12	14
Zn	1140	1364

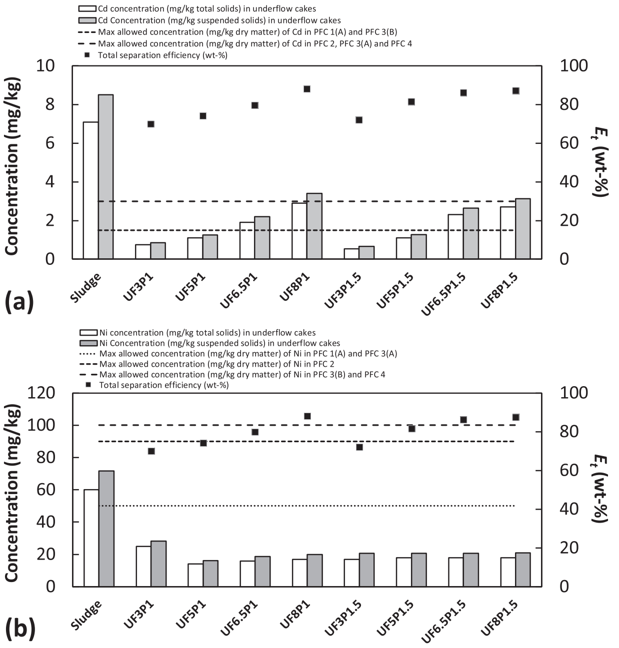


Fig. 9. Concentration of Cd (a) and Ni (b) in suspended and total solids of the cakes obtained from filtration of the GLD sludge and the underflow samples at 6 bar – The total separation efficiency (E_t) - The maximum allowed concentration of Cd determined by the European commission regulations for CE-marked fertilizing products (2016/0084 (COD)) in product function categories (PFC).

fertilizing products. The concentrations of Cd and Ni in the underflow fractions obtained by hydrocyclone classification are compared to their maximum allowed concentrations in CE-marked fertilizing products in Fig. 9.

As can be seen in Fig. 9 (a), the concentration of Cd in the dregs content of underflows obtained in experiments UF3P1, UF3P1.5, UF5P1 and UF5P1.5, are lower than the maximum allowed concentration of Cd in all the CE-marked fertilizing products presented in Table 4. Also, the dregs content of the underflow fractions of UF6.5P1 and UF6.5P1.5, as well as the unwashed dregs of UF8P1 and UF8P1.5 can be categorized in PFC 1(A) and PFC 3(B) according to their level of Cd. The concentration of Ni in dregs is allowed for all CE-marked fertilizing products, except for PFC 1(A) and PFC 3(A). Fig. 9 (b) shows that hydrocyclone classification reduced the concentration of Ni in the dregs content of the underflow effectively, and thus they would be categorized even in PFC 1(A) and PFC 3(A).

5. Conclusions

The effect of hydrocyclone classification on the filtration properties of green liquor dregs and the separation efficiency of hazardous trace metals Cd, Pb, Ni and Zn into the overflow and underflow fractions were studied. The main conclusions can be summarized with a few bullet points:

- In the hydrocyclone classification experiments, the finer dregs were for the most part separated by the overflow fraction, while the coarser dregs migrated rather to the underflow. In addition, most of the suspended solids were separated by the underflow fraction. The separation efficiency of finer particles was improved by increasing the overflow to the underflow outlet diameter ratio (Do/Du). Although the higher inlet pressure improves the separation efficiency of the finer particles, it is not always applicable due to an increase in the energy consumption of the hydrocyclone.
- The filter cakes of the overflow fractions, containing finer particles than the underflows and the feed sludge, had higher moisture contents and higher average specific cake resistances, α_{av}. The increase of the Sauter mean diameter $D[3,2]$ of the dregs had a reducing effect on the α_{av} of the cakes in the case of underflows. However, the total required filtration area for a certain feed flow rate of the GLD sludge was reduced by hydrocyclone classification, which is a very promising result regarding industrial implementation of the dregs classification process.
- The results showed that hazardous metals Cd, Ni, Pb and Zn, other trace metals and REEs are mostly found in the finer overflow fractions. The increase of the overflow to the underflow outlet diameter ratio (Do/Du) had a positive effect on the separation efficiency of finer particles, and therefore also the hazardous metals into the overflows. The results showed that 90.1 wt-% of Cd, 70.1 wt-% of Ni and 91.4 wt-% of Zn were separated by the overflow, collecting 30 wt-% of dregs and 19.9 wt-% of Ca in this fraction by using the diameter ratio of 3.70 at the

inlet pressure of 1 bar. The increase of the inlet pressure to 1.5 bar improved the separation of these elements into the overflow.

The concentrations of Cd and Ni in the dregs are usually higher than the maximum allowed concentrations in CE-marked fertilizing products. The results of this study showed that the concentrations of these two critical elements in the underflows could be reduced to a level lower than the maximum allowed for CE-marked fertilizing products, while concentrating Ca in the underflows. In other words, the results showed that over 80 wt-% of dregs could be separated by hydrocyclone classification into the underflow, i.e. the fraction of solids which could possibly be used as all CE-marked fertilizing products discussed in this study. The utilization of these residues as sustainable products is an achievement as regards material utilization in the circular economy, as well as an important step towards cleaner pulp mills. Further studies on the topic could focus on investigating technical details, such as the effect of feed concentration and additional classification stages on the separation efficiency of hazardous metals.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jclepro.2018.02.123.

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Appendix A. Supplementary data related to Publication IV

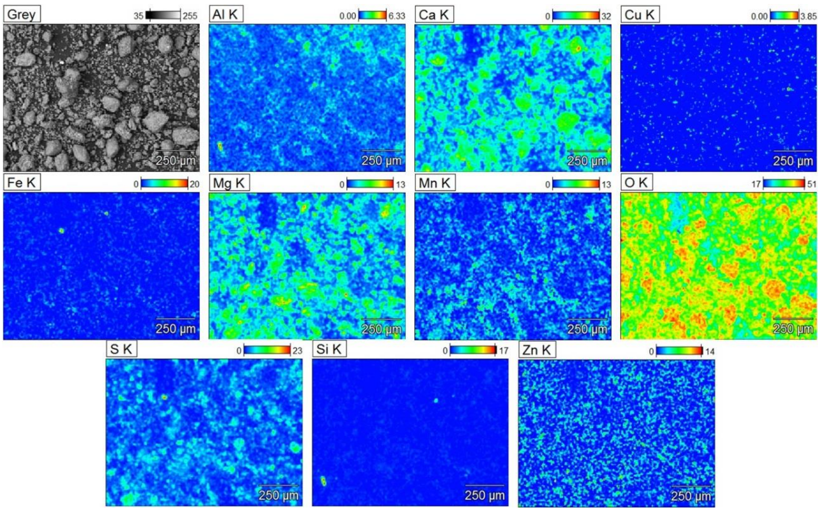

Fig. S1. SEM-EDS elemental mapping (wt%) by 100X magnification on a carbon tape background for crushed dry cake of original GLD sludge. Elemental mapping shows the relative concentration of Al, Ca, Cu, Fe, Mg, Mn, O, S, Si and Zn.

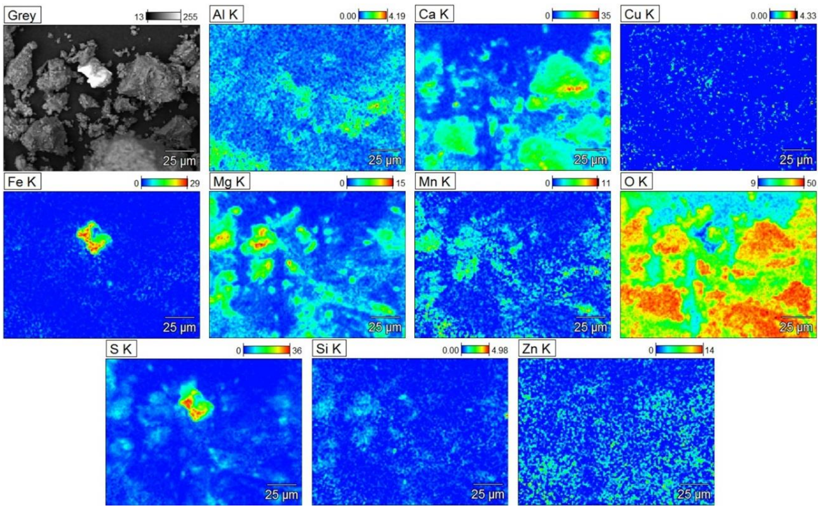

Fig. S2. SEM-EDS elemental mapping (wt%) by 750X magnification on a carbon tape background for crushed dry cake of original GLD sludge. Elemental mapping shows the relative concentration of Al, Ca, Cu, Fe, Mg, Mn, O, S, Si and Zn.

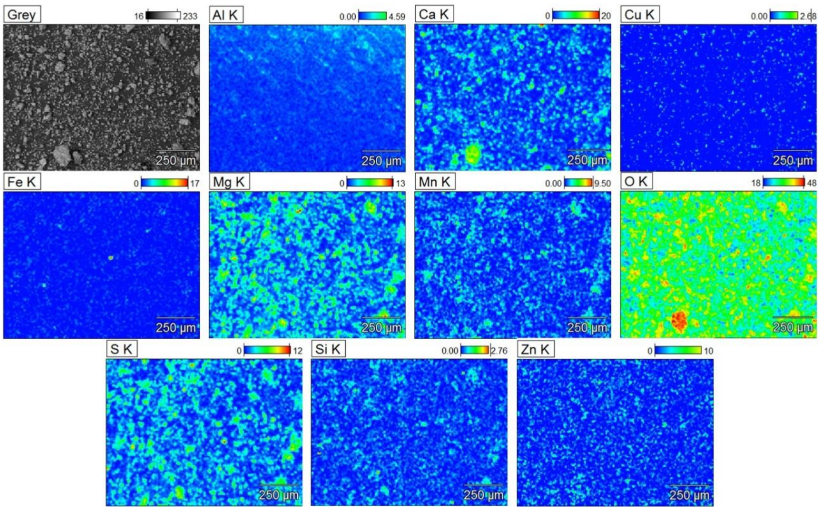

Fig. S3. SEM-EDS elemental mapping (wt%) by 100X magnification on a carbon tape background for crushed dry cake of overflow fraction obtained by using overflow to underflow outlet diameter ratio of 3.7 and the inlet pressure of 1 bar. Elemental mapping shows the relative concentration of Al, Ca, Cu, Fe, Mg, Mn, O, S, Si and Zn.

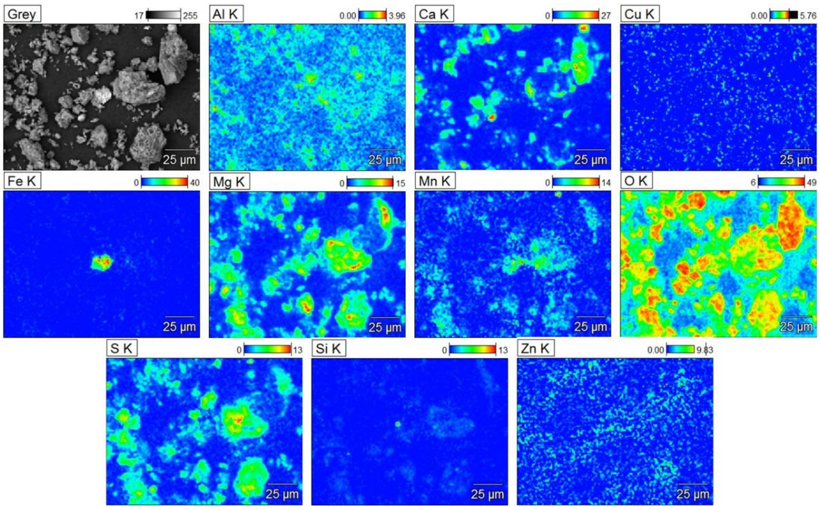

Fig. S4. SEM-EDS elemental mapping (wt%) by 750X magnification on a carbon tape background for crushed dry cake of overflow fraction obtained by using overflow to underflow outlet diameter ratio of 3.7 and the inlet pressure of 1 bar. Elemental mapping shows the relative concentration of Al, Ca, Cu, Fe, Mg, Mn, O, S, Si and Zn.

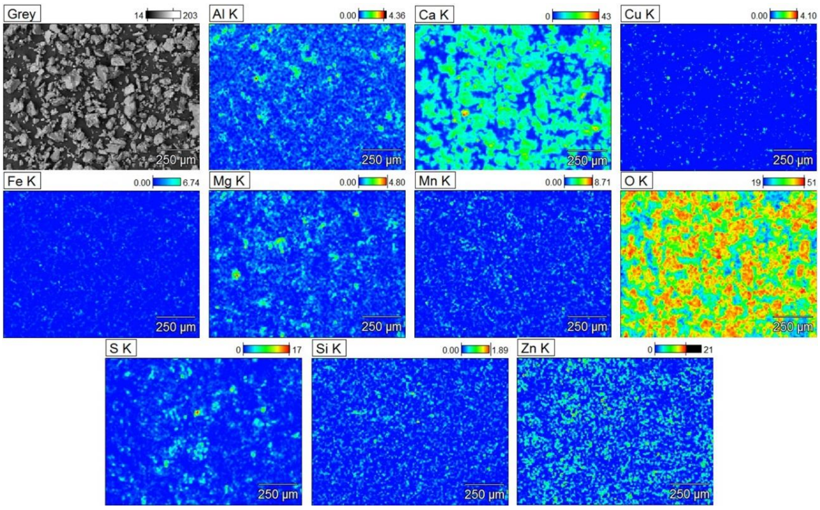

Fig. S5. SEM-EDS elemental mapping (wt%) by 100X magnification on a carbon tape background for crushed dry cake of underflow fraction obtained by using overflow to underflow outlet diameter ratio of 3.7 and the inlet pressure of 1 bar. Elemental mapping shows the relative concentration of Al, Ca, Cu, Fe, Mg, Mn, O, S, Si and Zn.

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