

Mia Bredenberg

WASTE TO PROCUCT-IMPROVING THE UTILIZATION POTENTIAL OF GREEN LIQUOR DREGS BY USING FROTH FLOTATION

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 24 November, 2014.

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FOREWORDS

This thesis was written for my Master degree in Environmental Technology within Process Industry at Aalto University School of Chemical Technology under assignment of Stora Enso Pulp Competence Centre and Stora Enso Imatra Mills during fall 2013 and spring 2014. The laboratory experiments were carried out at the department of Material Science and Engineering. The purpose of this thesis was to evaluate a froth flotation technique for treatment of green liquor dregs, a solid waste product produced at kraft pulp mills, in order to improve its utilization potential. This thesis consists of a literature part, which briefly discusses the theory of froth flotation and the legislation governing utilization of waste, and an experimental part, in which froth flotation for treatment of green liquor dregs from the Imatra Mills is studied in laboratory and pilot scale experiments.

I would like to thank following people. My instructors Timo-Pekka Veijonen and Juha Oksanen, and the people at Stora Enso research center and Imatra mills, for the support and opportunities given in this Master's thesis. I want to thank Nóra Schreithofer for her help and advices in the laboratory flotation experiments. I would also like to thank my Professor Olli Dahl and supervisor Mikko Martikka for their suggestions and guidance in writing of this thesis. Finally, I would like to thank my family and friends for their constant support during the time I studied.

Espoo 24 November 2014

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Number of pages: 89 + 11 Language: English

Author: Mia Bredenberg

Title of thesis: Waste to Product-Improving the Utilization Potential of Green Liquor Dregs by Using Froth Flotation

Department: Department of Forest Products Technology

Professorship: Environmental technology within process industry Code of professorship: Puu-127

Thesis supervisor: Professor Olli Dahl

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Date: 24.11.2014

Abstract

Froth flotation was studied as a separation technique for treatment of green liquor dregs (GLD) in order to improve its utilization potential. GLD consist mainly of poorly soluble calcium carbonates (calcites), which can be utilized i.e. as construction material or as soil amendment agents. GLD contain also small amounts of hazardous trace elements (HTEs), which in some cases may exceed the limit values set for utilization of waste. In this thesis a froth flotation procedure, where calcite and unburned carbon are separated from GLD by using air-bubbles and certain flotation agents, was studied for treatment of GLD from the Stora Enso Imatra Mills.

In the experimental part, laboratory and pilots-scale experiments were carried out for both unfiltered and pre-coat filtered GLD in order to study the performance and scale-up potential of the flotation process. During the experiments, it was recognized that the studied flotation procedure was highly affected by the composition of the GLD. Especially, high concentrations of unburned carbon in the GLD was recognized to improve the flotation process. In the pilot-scale experiments, the separation of calcite from unfiltered GLD was relatively poor due to the low content of unburned carbon (0.6%) and high concentrations of water soluble compounds (80%) in the studied GLD. The results from the pilot-scale experiments with pre-coat filtered GLD indicated that calcite could be efficiently separated from pre-coat filtered GLD that contain primarily water insoluble compounds (>90%) and has relatively high unburned carbon content (>1%). However, the daily variations in the composition of the GLD may complicate the optimization of the slurry properties. Consequently, the qualities of the flotation fractions vary according to the elemental composition of the GLD, which complicates the utilization of these fractions.

Keywords Green liquor dregs, froth flotation, waste utilization, environmental protection



| Tekijä: Mia Bredenberg | | |
|--|----------------------------|---------------------------|
| Työn nimi: Jätteestä tuotteeksi- Viherlipeäsakan kä | isittely vaahdotustekniika | lla hyötykäyttöä varten |
| Laitos: Puunjalostustekniikan laitos | | |
| Professuuri: Prosessiteollisuuden ympäristötekniikka Profe | | Professuurikoodi: Puu-127 |
| Työn valvoja: Professori Olli Dahl | | |
| Työn ohjaajat: DI Timo-Pekka Veijonen, DI Juha Ok | sanen | |
| Päivämäärä: 24.11.2014 | Sivumäärä: 89 + 11 | Kieli: Englanti |

Tiivistelmä

Diplomityössä tutkittiin vaahdotustekniikan soveltuvuutta viherlipeäsakan käsittelyssä sen hyötykäyttöä varten. Viherlipeäsakka koostuu pääosin niukkaliukoista kalsiumkarbonaatista (kalsiitista), jolle on useita hyötykäyttökohteita. Viherlipeäsakka sisältää myös pieniä määriä raskasmetalleja, joiden pitoisuudet tapauskohtaisesti ylittävät jätteen hyötykäytölle asetetut raja-arvot. Vaahdotusmenetelmällä oli tarkoitus erottaa viherlipeäsakasta kalsiitti yhdessä tai erikseen palamattoman hiilen kanssa vaahtokerrokseen ilmakuplia ja vaahdotuskemikaaleja hyväksi käyttäen. Diplomityön tarkoituksena oli tutkia soveltuuko vaahdotusmenetelmä Stora Enson Imatran Tehtaiden viherlipeäsakan käsittelyyn.

Vaahdotustekniikan soveltuvuutta tutkittiin suodattamattomalle suodatetulle ja pre-coat viherhilpeäsakalle laboratorio- ja pilottikokeiden avulla. Kokeiden aikana huomattiin, että viherlipeäsakan laatu vaikuttaa suuresti vaahdotusprosessin tehokkuuteen. Palamattoman hiilen ja kalsiitin erotus tutkitusta suodattamattomasta viherlipeäsakasta osoittautui haasteelliseksi johtuen sen alhaisesta palamattoman hiilen pitoisuudesta (0, 6 %) ja korkeasta vesiliukoisten yhdisteiden määrästä (80 %). Tulokset pilottikokeista osoittavat että kalsiittia voidaan tehokkaasti erottaa pre-coat suodatetusta viherlipeäsakasta, joka koostuu pääasiallisesti niukkaliukoisista yhdisteistä (>90 %) ja jonka palamattoman hiilen pitoisuus on melko korkea (1,2 %). Vaahdotusprosessin käyttöä hankaloittaa viherlipeäsakan koostumuksen päivittäinen vaihtelu, sillä laiteparametrit ja kemikaaliannokset määritetään lietteen ominaisuuksien perusteella. Tämän takia myös erotettujen vaahdotusfraktioiden koostumukset vaihtelevat, mikä vaikeuttaa näiden hyötykäyttöä.

Avainsanat Viherlipeäsakka, vaahdotustekniikka, jätteen hyötykäyttö, ympäristönsuojelu

List of Definitions

| BWR | basic work requirements |
|---------|--|
| Calcite | calcium carbonate |
| CPR | Construction Products Regulation |
| D.S | dry solids content |
| EoW | end of waste criteria |
| ETA | European Technical Assessment |
| FFI | Finnish Forest Industry |
| GLD | green liquor dregs |
| hENs | harmonized product standard |
| HTEs | hazardous trace elements |
| ICP-OES | inductively coupled plasma optical emission spectrometer |
| ISO | International Organization for Standardization |
| NPEs | non process elements |
| REACH | Registration, Evaluation, Authorisation and Restriction of Chemicals |
| S.S | suspended solids concentration |
| XRD | X-ray diffraction |

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I LITERATURE PART

1. INTRODUCTION

1.1 Background

Industries are encouraged to minimize their waste production through legislation, economic benefits and social influences. The quantity of waste going to landfills should be minimized firstly by prevention of the production of waste and secondly by recycling and recovery of the produced waste. The disposal of waste in landfills should be the last solution and completely eliminated if possible. Due to directives and regulations designed to conserve the environment, the cost of landfill disposal has increased significantly. Additionally, waste can represent a loss of valuable resources in the form of both materials and energy. (Nurmesniemi, Pöykiö et al. 2007)

Green liquor dregs (GLD) are one of the biggest solid waste fractions produced at kraft pulp mills. It has been estimated that the pulp industry in Finland produces about 80 000 tonnes of GLD per year, of which approx. 85% are disposed in landfills. Currently, about 15% of the produced GLD are utilized, mainly as neutralizing agents in treatment of wastewaters and as construction material in the hydraulic barrier layer of landfills. The utilization of GLD is challenging due to its alkali nature and varying composition. According to the national waste act, GLD are considered as waste, thus its utilization is directed by various environmental legislations and regulations. (Manskinen, Nurmesniemi et al. 2011)

GLD consist mainly of poorly soluble or insoluble calcium carbonates (calcites), which are suitable for utilization. However, GLD contain also small amounts of hazardous trace elements (HTEs), which may at some kraft pulp mills exceed the limit values set for utilization of waste. To meet the criterion set by the legislation and the application, it is necessary to separate environmental contaminants and technical pollutants from reusable calcites.

The thesis is based on findings from a VISA-research project, where different separation techniques were studied for treatment of GLD in order to increase its utilization potential. The results from this project indicated that HTEs and magnesium could be efficiently removed from GLD by using froth flotation.

VISA Project

The object of the VISA project was to develop a treatment method for GLD in order to separate useful material for utilization, thus decrease the waste quantities requiring landfill disposal. The project was carried out by the University of Joensuu for Finnish Forest Industry (FFI) during the years 2005-2009. In the first part of the VISA project, different separation techniques used in the mining industry including, froth flotation, electrical dissolving, saline extraction, and extraction based on specific gravity, were studied as treatment techniques for GLD. From the studied techniques, froth flotation gave the best results, thus the technique was chosen for further investigation in the second part of the VISA project.

Two flotation methods, referred as the two-step method and the one-step method, were developed and tested with laboratory and pilot-scale experiments. In the two-step method unburned carbon and calcite are separated in two flotation steps from unfiltered GLD, while in the one-step method carbon-calcite is separated from the unfiltered GLD in one flotation step.

Both flotation in columns and cells were studied in the experiments. The pilot-scale flotation experiments were carried out with a MicroCell[®] pilot column with an active volume of 5.7 litres and Outotec[®] OK-R pilot cells with active volumes of 50 litres. According to the results, the flotation column was more suitable for the one-step method and the cells for the two-step method. Additionally, the two-step method was suggested for GLD that contained high concentrations of unburned carbon. The best results from the column flotation experiments indicated that up to 70% of the dry solids from the GLD could be recovered in form of carbon-calcite. As its best, the recovery of calcium was up to 95%, whereas the concentrations of magnesium and HTEs in the carbon-calcite fraction were reduced to a half of their original concentrations. The potential utilization targets for carbon-calcite are bricks, cement, asphalt and stone wool. As the rest fraction from the flotation process was filtered without using of pre-coat, the waste needing landfill disposal decreased to 10-25%. (FFI 2006, FFI 2009)

1.2 The Objective of the Thesis

This thesis was done under assignment of Stora Enso Pulp Competence Centre and Stora Enso Imatra Mills during fall 2013 and spring 2014. Stora Enso is a global producer of the paper, board, biomaterials, and wood products. The wood based products provides a climate friendly alternative to many products made of competing non-renewable materials and have a smaller carbon footprint.

The object of this thesis was to investigate the suitability of the flotation procedure developed in the VISA project for treatment of GLD from the Stora Enso Imatra mills. Laboratory and pilot- scale experiments were carried out in order to study the performance and scale-up potential of the flotation process.

The laboratory experiments were carried out at the department of Material Science and Engineering at Aalto University. The scope of the laboratory experiments was to study the influences of slurry properties, quantity of reagents and machine variables on the flotation of unburned carbon and calcite from the unfiltered GLD.

The pilot-scale experiments were carried out with a 1 m³ Outotec TankCell[®] pilot flotation cell at the causticising plant at Stora Enso Imatra Mills in order to study the performance of the flotation procedure in mill conditions, where the composition and density of the GLD varies constantly according to the operation conditions at the mill.

2. GREEN LIQUOR TREATMENT

In chemical pulping, cooking chemicals are used to extract cellulose from the wood by removing the lignin that binds the cellulose fibers together. The most commonly used chemical pulping process in the world is kraft cooking, which uses a mixture of sodium hydroxide (NaOH) and sodium sulphide (Na₂S) to pulp wood. Used cooking chemicals along with the lignin from the wood will leave the digester as black liquor. The main purpose of the chemical cycle is to convert the chemicals in the black liquor to a form that they can be reused in the cooking process. Another important goal is to harness the heat from the recovery process and convert it into steam energy. Figure 1 shows a process scheme of the chemical recovery cycle. (Gullichsen, Fogelholm 1999)



Figure 1. Block flow diagram of the chemical recovery cycle. The liquor cycle is marked with unbroken lines and the solids cycle with broken lines

The spent cooking chemicals and the wash waters from the pulp washing stage are combined to form weak black liquor, which is concentrated through a series of evaporators to obtain a dry solids content of 70-80%. The strong black liquor from the evaporators is pre-heated and pumped through black liquor guns to the furnace. The black liquor is settled at the bottom of the boiler, where the water is vaporised and the solids combusted partially depending on the amount of primary air. The large amount of heat generated in the recovery boiler is used to produce high-pressure steam. In addition to the generation of energy, the main objective of the recovery boiler is to convert sodium sulphate (Na₂SO₄) to Na₂S. The reduction occurs when Na₂SO₄ and incompletely combusted carbon are in close contact with carbon monoxide in the reducing air. The reactions in the furnace are illustrated by Equations 1 and 2.

$$Na_2S + 2O_2 \rightarrow NaSO_4 \tag{1}$$

$$Na_2SO_4 + 2C + heat \rightarrow Na_2S + 2CO_2 \tag{2}$$

Additionally following chemical reactions takes place:

$$NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \tag{3}$$

$$Na_2O + CO_2 \to Na_2CO_3 \tag{4}$$

$$Na_2O + SO_2 + \frac{1}{2}O_2 \to Na_2SO_4$$
 (5)

$$H_2S + \frac{3}{2}O_2 \to SO_2 + H_2O$$
 (6)

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \tag{7}$$

The inorganic material from the bottom of the recovery boiler, i.e. smelt, is transported further to the smelt dissolver where it is dissolved in weak liquor from the causticising process to form green liquor. The main compounds in the green liquor are Na₂CO₃ and Na₂S. In addition to these compounds, green liquor contains also small amounts of other sodium compounds, such as NaOH, Na₂SO₄, Na₂S₂O₃ and NaCl, non-soluble compounds, such as unburned carbon from incomplete combustion, metal oxides from corrosion, silicates from the wearing of linings, and contaminants brought in with the wood or make up chemicals. (Gullichsen, Fogelholm 1999, Sanchez 2007)

The insoluble particles in the green liquor are referred as green liquor dregs (GLD) and they may cause problems in the causticising and lime burning processes if they are not properly removed. GLD are removed by clarification or filtration or a combination of these processes. The concentration of GLD in the green liquor before clarification is 800-1200 ppm and the aim is to decrease the concentration to below 100 ppm. In order to achieve a sufficient dregs removal, the residence time of the green liquor in the clarifiers is typically 2-4 hours. The dregs from the clarifiers are filtered and washed in order to remove the residual chemicals and to increase the solids content of the dregs for ease of disposal.

The clarified green liquor from the top of the clarifiers is pumped to the lime slaker for recausticising. In recausticising calcium oxide (CaO) first reacts with the water in the green liquor generating calcium hydroxide (Ca(OH)₂) according to Equation 8.

$$H_2O + CaO \to Ca(OH)_2 + heat \tag{8}$$

The generated $Ca(OH)_2$ then reacts with sodium carbonate (Na_2CO_3) in the green liquor to form NaOH and calcium carbonate ($CaCO_3$) i.e. lime mud according to Equation 9.

$$Ca(OH)_2 + Na_2CO_3 \leftrightarrow 2NaOH + CaCO_3 \tag{9}$$

The recausticising reaction is slow, always ending in equilibrium. The causticized green liquor is known as white liquor, which contains mostly NaOH and Na₂S and it is returned to the digester for reuse in pulping. The precipitated lime mud from the causticising reaction is washed and sent to the lime kiln, where it is heated to a high temperature to regenerate CaO according to Equation 10.

$$CaCO_3 \to CaO + CO_2 \tag{10}$$

In addition to the main element, CaCO₃, lime mud entering the lime kiln also contains some unreacted lime as CaO, water, small amounts of alkali and other impurities. The amount typically varies between 7 and 10% depending on the amount of impurities introduced in to the process with green liquor and make up lime. All washing liquors (from the washing of lime mud and GLD) are jointly collected into the weak white liquor tank from where the weak white liquor is pumped to the smelt dissolver. (Gullichsen, Fogelholm 1999, Sanchez 2007)

3. FORMATION AND COMPOSITION OF GREEN LIQUOR DREGS

The green liquor dregs (GLD) are a mixture of insoluble material that does not participate in the pulping or bleaching systems and so-called non-process elements (NPEs), e.g. potassium (K) magnesium (Mg), manganese (Mn), iron (Fe), aluminium (AI) and silicon (Si). The main compounds in GLD are calcium and magnesium carbonates, which may occur in form of calcite, pirssionite or gibbsite. Additionally, the GLD contain unburned carbon, soluble sodium salts, sulphur compounds, and small amounts of hazardous trace elements (HTEs). Table 1 shows approximate concentrations of the main elements present in GLD. (FFI 2006, Thun 1999)

| Flomont | Concentration | Concentration |
|-----------|------------------|---------------|
| Liement | mg/kg dry solids | % dry solids |
| Carbon | 76000-505000 | 7.6-50.5 |
| Calcium | 123000-339000 | 12.3-33.9 |
| Magnesium | 27000-97000 | 2.7-9.7 |
| Sodium | 6500-148000 | 0.65-14.8 |
| Sulphur | 7500-29000 | 0.75-2.9 |
| Potassium | 600-10700 | 0.06-1.07 |
| Zink | 240-4500 | 0.024-0.45 |
| Cadmium | 0.09-31 | <0.01 |
| | | |

Table 1. Approximate concentrations of the main elements in GLD at different Finnish pulp mills (FFI 2006, Thun 1999)

The physical and chemical properties of the GLD vary significantly depending on the process conditions in which they are formed. In cooking, lignin and metal compounds are dissolved in alkaline conditions. Most metals form in these alkaline cooking conditions sparingly-soluble compounds, such as sulphates, sulphides and carbonates. The same compounds enter the recovery boiler, where the sulphates are decomposed to sulphides and some of the carbonates to oxides in the reducing conditions at the bottom of the recovery boiler. However, also unreduced sulphate compounds may leave the recovery boiler with the smelt, since the conditions at the top of the boiler are oxidizing. Incomplete combustion of black liquor may lead to inert carbon particles that leave with the smelt, increasing considerably the carbon content of the produced GLD. (Gullichsen, Fogelholm 1999, Ek, Gellerstedt et al. 2009)

The smelt from the recovery boiler is dissolved in weak liquor, where the metals and their oxides are reforming carbonates, sulphides, sulphates and hydroxides. The weak liquor contains also small amounts of calcium carbonates from the lime mud and other impurities from purchased lime, which will leave with the green liquor to the dregs clarifier. Due to the alkalinity and ion saturation of the white liquor, also water soluble salts are precipitated. The precipitate, i.e., dregs, are separated by clarification and filtration and the water soluble salts, mainly sodium and potassium compounds, are removed by washing. The remaining compounds include: insoluble carbonates, sulphides and sulphates of NPEs and HTEs. (Martins, Martins et al. 2007, Manskinen, Nurmesniemi et al. 2011)

3.1 Dregs Filtration

The filtration of GLD is affected by several process variables including, total titrable alkali (TTA), liquor temperature, liquor density, dregs particle density, dregs particle diameter, and suspended solids content of the raw green liquor. (Törmälä 2013) The filtration method has a great impact on the composition and quantity of the produced GLD. According to a study, where GLD from 17 different Finnish pulp mills were studied, the concentrations of soluble sodium and potassium salts in the GLD were higher at mills that use pressure filters. Additionally, the GLD from these mills had higher concentrations of pirssonite and magnesium carbonate compared to the GLD from mills that used pre-coat filtration. The contents of calcium compounds, including calcite and calcium phosphate in the GLD, were lower in mills that used pressure filters, which indicates that the calcium phosphate originates from the lime mud. (FFI 2006, internal source)

3.1.1 Pre-coat Drum Filter

In the filtration of GLD, lime mud is generally used as pre-coat. Lime mud is much easier to filter, as the flow resistance through a cake of lime mud is much lower than that of a cake of GLD. Before beginning of the filtration a 10-15 cm thick pre-coat layer is applied on the drum. The dregs form a layer on top of the lime mud pre-coat and the liquor is filtered through this pre-coat with a suction pump influenced by the pressure difference. An advanced type of scraper scrapes off the washed and dried dregs together with a thin layer of the pre-coat material. This implies that the pre-coat layer of lime mud must be renewed after a certain period of time. (Ek, Gellerstedt et al. 2009) Figure 2 shows a schematic diagram of a rotary drum filter.



Figure 2 Schematic diagram of a rotary pre-coat drum filter (Sanchez 2007)

The pre-coat filter operates periodically. Depending on the load on the filter and the drum operating speed the pre-coat layer will last 8-16 hours. At the end of the pre-coat cycle, the filter is washed and a new layer of pre-coat is formed on the drum before more dregs can be filtered. (Sanchez 2007, Ek, Gellerstedt et al. 2009) The use of pre-coat filtration increases the amount of discharge going to landfills. Due to the cost of landfilling and the certain environmental requirements, alternative aid-free filtration methods has been applied for handling of GLD. (Fogelholm 1999)

3.1.2 Chamber Filter Press

Chamber filter presses are widely used in the mining industry. Currently, two types of chamber filter presses are available for filtration of GLD: horizontal filter presses and vertical filter presses. In the horizontal filter presses the filtering chambers lay horizontally and the filtering media is a movable cloth, while the vertically designed filter presses are generally automatic units with few moving parts. The filtration process itself for both filters is very similar. The pressurized sludge is fed to the filter chambers, where the filtrate passes through the filter cloth leaving the dregs in the chambers. The dregs trapped in the chamber are formed into a solid cake, which is washed by forcing water through the cake. The cake is dried by squeezing it with moving chamber walls and

the dried cake is discharged from the filter by opening the chambers. The press is then closed to repeat the cycle. Figure 3 shows a typical vertical filter press.



Figure 3 Outitec Larox FFP horizontal filter press (Outotec 2013)

The main benefits of using filter presses for treatment of GLD include: decreased amount of discharge going to landfills as a result of decreased or eliminated use of filter aids, lower disposal costs as the cake contains less liquid, better quality of the filtrate, and significantly lower consumptions of energy and water compared to conventional centrifuge filters. (Dickenson 1997, Fogelholm 1999, Outotec 2014)

3.1.3 Decanter Centrifuge Filter

Decanter centrifuges are basically circular settling tanks mounted on an axis and spun at high speed to produce separation of solids in the decanter. A rotating screw-type conveyor inside the decanter provides continuous discharge. The essential condition for the decanter centrifuge to function is that the concentration of the solids is higher than the concentration of the liquid. (Dickenson 1997) Figure 4 shows a shematic diagram of a typical decanter centrifuge filter.



Figure 4 Schematic diagram of a decanter centrifuge filter (GN solids control 2014)

The advantages of using a decanter centrifuge for filtration of GLD include: decreased amount of discharge going to landfills as a result of eliminated use of filter aids, minimized impacts on the landfills as the dregs from the centrifuge process are less bulky and better washed, and higher chemical recovery. (Andritz 2006, Alfa laval 2003)

4. FROTH FLOTATION

Froth flotation is widely used in the mining industry for separating valuable minerals from gangue minerals. The technique was initially developed for concentrating sulphides of copper, lead and zinc. The flotation techniques are continuously enhancing and today flotation is used for separating of e.g. platinum, nickel, and gold-hosting sulphides, oxides, oxidised minerals, and non-metallic ores, such as fluorite, phosphates, and fine coal. (Wills 2006)

4.1 General

Froth flotation is a physicochemical separation process, where particles are separated according to their surface properties. In flotation, hydrophobic particles are attach to air bubbles and transported upwards into a froth layer, while hydrophilic particles remain at the bottom of the flotation machine and are removed from the process through the tailings outlet. Figure 5 shows a typical flotation cell. In flotation concentration the valuable mineral is usually transferred to the froth i.e., concentrate or float fraction, leaving the undesired particles in the tailings. This type of flotation refers to direct flotation, while the opposite type of flotation, in which the undesired particles are separated into the float fraction, is called reverse flotation. (Wills 2006)



Figure 5. Illustration of a typical flotation cell (Wills 2006)

The theory of froth flotation is complex, involving three phases (solids, water, and air) with many sub processes and interactions. Particles are recovered from the flotation process according to three mechanisms:

- 1. **True flotation**, where hydrophobic particles and air bubbles are attached to each other due to their surface properties
- 2. **Entrainment**, where particles in the water phase between the bubbles are lifted to the froth layer
- 3. **Entrapment** (often referred to as "aggregation"), where particles trapped between bubbles are lifted to the froth layer

In industrial processes, the valuable particles are mainly recovered by true flotation. However, the selectivity of the flotation is also affected by entrainment and entrapment, since both desired and undesired minerals are recovered by these two mechanisms. Additionally, the recovery and grade are affected by drop back of particles from the froth to the slurry and the recovery of water molecules. (Wills 2006) The performance of the flotation process depends on many variables including, feed characteristics, machine type and design, and hydrodynamic conditions in the flotation machine. This thesis focuses on flotation chemistry and physics of fine particles. (Welsby, Vianna et al. 2010)

4.2 Flotation Chemistry

Minerals are classified according to their surface characteristics into polar or non-polar types. The surfaces of non-polar minerals do not readily attach to water dipoles and are therefore hydrophobic. Minerals of this type include graphite, sulphur, molybdenite, diamond, coal, and talc. Minerals with polar surfaces react strongly with water molecules and are therefore naturally hydrophilic. In general, the degree of polarity increases from sulphide minerals, through sulphates, carbonates, halites, phosphates, etc., then oxides-hydroxides, and, finally, silicates and quartz. (Wills 2006)

The froth flotation process is controlled by reagents, which are grouped into collectors, frothers and regulators. The type and amount of the reagents depends on the nature and particle size of the mineral. **Frothers** are surface-active and usually non-ionic reagents, which key functions are to create fine bubbles and aid froth stability in order to prevent drop back of particles. Very small quantities of a frother may have marked effects, thus the frother is often added in stages during the flotation to control the volume of the froth. However, in absence of particles frothers are only marginally effective. (Farrokhpay 2011)

Collectors are organic chemical compounds used in froth flotation in order to increase the hydrophobicity of certain minerals, thus facilitating bubble attachment. Collectors also determine the contact time needed to form a stable particle-bubble aggregate. (Mathe, Harris et al. 1998)

Regulators are used to control the flotation process by activating or depressing the mineral attachment to bubbles or to control the pH of the slurry. (Alexander 2006) pH regulators control the ionic composition of the slurry by improving the collector-mineral interactions and diminish the interactions with undesired minerals. (Wills 2006, Bulatovic 2007)

4.3 Flotation of Fine Particles

The particle size plays an important role in the flotation process, since the success of true flotation is highly dependent on the collision and adhesion of mineral particles onto air bubbles. Flotation can only be applied to particles within the size range of 5-300 μ m. For particles finer than 10-20 μ m, the flotation rate tends to decrease significantly as a result of the decreased probability of particle-bubble collisions as the particle size is reduced. Characteristics for fine particles are their high surface area per unit of mass. In the flotation process, fine particles tend to be more affected by the water chemistry and the ions in slurry than coarse particles, thus higher reagent doses are typically required. (Pease, Curry et al. 2006; Zhou, Xu et al. 1997)

Slurry density

The slurry density has a great impact on the recovery and grade of the mineral. For economic reasons, flotation is usually carried out in as dense slurry as possible, as a denser slurry requires less cell volume. Additionally, the overall reagent consumption is lower when higher slurry density is used, since the effectiveness of most reagents is a function of their concentrations in a solution. On the other hand, in applications where high grade is required, the selectivity of the flotation process can be improved by using a lower slurry density. (Wills 2006)

Mixing conditions

The main functions of the mixing include: keeping the slurry in suspension, dispersion of the air stream into bubbles, and promotion of collisions between particles and bubbles. Fast mixing is typically recommended for flotation of fine particles, since it increases the probability of particle bubble collisions. Fast mixing also keeps the slurry in suspension, which prevents sanding of the cell floor caused by settling of heavier particles. On the other hand, too fast mixing may affect the selectivity of the flotation, since also fine undesired particles are lifted to the froth. (Matis, Mavros 1991, Newell, Grano 2006, Gupta, Yan 2006)

Bubble size

Recent studies shows that flotation of fine particles could be improved by using smaller air bubbles, since smaller bubbles have higher specific surface area compared to conventional sized bubbles favouring the adsorption. According to these studies, the probability of particle bubble collisions is increased by using smaller bubbles resulting in higher recovery rate and possible better selectivity. (Stevenson 2012)

Air flow rate

The air flow rate is used for controlling of the froth depth, thus it affect greatly the recovery and grade of the mineral. The air flow rate should be sufficient to provide the bubble surface area needed to carry the hydrophobic particles to the froth layer. The recovery rate is typically improved by using higher air flow rates. However, too high air flow rate may increase the entrainment of particles, leading to a decrease in the grade of the mineral. Additionally, fine particles tend to follow water molecules more easily than coarse particles due to their lower momentum, thus less energy for bubble generation is needed in flotation of fine particles. (Mathe, Harris et al. 1998, Stevenson 2012)

Mean residence time

The mean residence time i.e., the average time a particle spends in the flotation cell, affects both the grade and recovery of the mineral. The mean residence time can be determined by using retention time distribution (RTD) testing or by using the Equation 11. (Wills 2006)

$$Mean residence time = V/Q \tag{11}$$

Where, V =active volume of the cell, Q =slurry flow rate to the cell.

Recovery

The recovery is the percentage of the valuable mineral in the feed that is recovered to the concentrate. The recovery can be calculated by using Equations 12. (Xu 1998)

$$Recovery = \frac{c(f-t)}{f(c-t)} \times 100\%$$
⁽¹²⁾

Where, c, f and t = concentrations of the valuable mineral in concentrate, feed and tailings

The recovery grade curve shows the attainable value of recovery for a concentrate grade. Any point of the curve is the same from the process perspective at a given operating conditions but it is not the same in the economic point of view. As can be seen from the curve in Figure 6, what is gained in recovery is lost in the grade of concentrate.



Figure 6 Typical recovery grade curve (Wills 2006)

The recovery of fine particles can be improved by increasing the residence time in the cell. However, a longer residence time will also increase the recovery of other particles present in the slurry, thus lower the selectivity. The number and size of the flotation cells should be adjusted to have the proper amount of time for flotation. (Bulatovic 2007)

Selectivity

Selectivity measures how well the undesired particles are maintained in the slurry and it depends greatly on the flotation process and the processes prior to the flotation, such as grinding and conditioning. The selectivity decreases when the availability of free hydrophobic particles decreases. The selectivity can be improved by increasing the froth depth, decreasing the turbulence at the slurry froth interface, decreasing the slurry density and by utilizing froth washing. (Wills 2006)

4.4 Flotation Machines

Flotation machines are generally divided into four classes including, mechanical cells, pneumatic machines, froth separators, and flotation columns. (Young 1982) The two main types, mechanical cells and flotation columns, are discussed in this thesis.

4.4.1 Mechanical Cells

Mechanical flotation cells are the most widely used flotation machines in the mining industry. A typical mechanical flotation cell consists of a cylindrical tank with a mixer-diffuser mechanism at the bottom of the tank which agitates the slurry and disperses air into small bubbles. The mechanical flotation cells can be divided into self-aerating and supercharged cells. In the self-aerating cells the air is introduced to the cell by the rotor, thus the maximum aeration rate is a function of the impeller speed. In the supercharged, or the so called forced air cells, air is fed to the cell by using an external blower, thus the aeration rate can be maximized independently from the rotor speed.

The conditioned slurry enters the cell from the feed inlet at the bottom of the cell, where it is mixed with the air forming particle-bubble aggregates. The formed bubble-particle aggregates are floated to the top of the cell forming a froth bed, which is skimmed by using natural overflow or mechanical scrapers. The remaining slurry leaves the process through the tailings outlet. (Young 1982, Wills 2006)

4.4.2 Flotation Columns

In the column flotation, valuable particles are separated from the slurry by using a counter current flow of air bubbles and solid particles. A flotation column consists of a vertical cylinder with a bubble generator, i.e., a sparger at the bottom of column. Figure 7 shows a typical structure of a flotation column.



Figure 7a Schematics of a flotation column (Wills 2006)

Figure 7b A Flotation column (Metso 2014)

The slurry is fed to the column from the feed inlet, which is located above the midpoint of the column. The mineral particles fall due to gravity through the rising swarm of bubbles. Hydrophobic particles collide with the bubbles generating particle-bubble aggregates that are transported to the cleaning zone. The collection zone in the flotation columns is almost the entire volume of the machine, thus the probability of bubble-particle collisions is increased. The rising froth bed above the feed point is washed down by a spray of water and clean froth is collected from the top of the column. Hydrophilic particles are removed from the bottom of the column through the tailings outlet. The main advantages of the flotation columns compared to the mechanical cell include, improved separation performance in fines, lower operational cost, and less plant space demand. The main disadvantages of flotation columns are: the mixing in the axis of the column, the blockage of spargers, and problems posed by the column height in installations. Additionally, the water requirements and consequently the frother requirements may be higher for the columns compared to the cells. (Jena, Biswal et al. 2008, Yianatos 1989)

4.5 Scale-up of a Flotation Cell

Scale-up studies are carried out in order to investigate whether or not a process developed in the laboratory can be transferred to industrial scale. Laboratory and pilot-scale data should provide the optimum conditions for froth flotation and the effect of a change in process variables. A flotation cell can be operated in different modes, such as batch, semi-batch or continuous. Batch and semi-batch test are often used in laboratory scale experiments. Batch test are simple to operate, thus the effect of a specific flotation variable on the flotation process is easy to determine. The batch test is carried out with a certain amount of slurry, hence the slurry characteristics and the reagent concentrations remains the same during the test. Consequently, the slurry level will sink as particles are leaving the process with the concentrate. In a semi-batch operation, water is added to the process to maintain the slurry level. However, the addition of water dilutes the slurry and the concentrations of reagents in it. In the continuous tests, the froth characteristics do not change with time for fixed operating conditions. Since commercial flotation cells generally operates with a continuous feed, continuous pilot-scale flotation tests are required in order to determine whether the flotation process will work in industrial scale. (Stevenson 2012)

As the machines get larger, care has to be taken in order to prevent possible loss of hydrodynamic capabilities already present in small machines. Small laboratory cells have generally higher turbulence than larger pilot or industrial cells. In scale-up of flotation cells, operational and geometrical factors are related to dimensionless numbers, such as air flow number, power number, etc. These numbers allow a comparison of the hydrodynamic conditions in different sizes of flotation cells. (Newell, Grano 2006, Jameson, Nguyen et al. 2007) The most common hydrodynamic numbers used for scale-up are presented in Table 2.

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| Specific airflow | $\frac{Q_g}{V_c}$ |
|------------------|---------------------|
| Power intensity | $\frac{P}{V_c}$ |
| Airflow number | $\frac{Q_g}{ND^3}$ |
| Tip speed | $\frac{\Pi ND}{60}$ |

Table 2 Typical hydrodynamic numbers for a flotation cell (Sripriya, 2003)

In this table, Q_g is the volumetric flow rate of air (m³/h), V_c is the Volume of the cell (m³), N is the impeller speed in RPM and D is the impeller diameter (m). The airflow number is the most frequently used parameter in scale-up of laboratory cells. The Specific airflow is essential for achieving high contact probability between the bubbles and the particles to be floated. The tip speed describes the speed of impeller taking into account the diameter of the impeller. (Sripriya, Rao et al. 2003)

5. LEGISLATION GOVERING THE UTILIZATION OF GREEN LIQUOR DREGS

The utilization of GLD is affected by various environmental legislations and regulations. The premise is that the utilization of the GLD including, processing, transporting, storing and other actions during and after the utilization, does not pose risks to the environment or human health. The environmental legislation does not set requirements for the technical properties of the material.

The Finnish waste legislation is largely based on EU directives and regulations. The most important Finnish environmental legislation concerning waste recovery and reuse are the Finnish Environmental Protection Act (86/2000), the Finnish Environmental Protection Decree (169/2000), the Finnish Waste Act (646/2011) and the Finnish Waste Decree (179/2012). According to the Finnish Waste Act (646/2011) GLD is regarded as waste, thus an environmental permit is required for an institutional or professional utilisation. In Finland, there are currently no generally accepted limit values for environmental eligibility evaluation of materials subject to authorisation. (Waste Decree 2012, Environmental Protection Act 2000)

According to the Government Decree on landfills (331/2013), industrial waste can be divided into inert, non-hazardous and hazardous waste. The classification of the waste depends on the origin and composition of the waste and it determine the whole treatment cycle of the waste from storage to transportation and disposal in landfills. The limit values for the different waste classes are presented in Table 3.

| Element | Inert waste L/S = 10 l/kg mg/kg dry substance | Non-hazardous waste L/S = 10 l/kg mg/kg dry substance | Hazardous waste L/S = 10 l/kg mg/kg dry substance |
|----------|---|---|---|
| As | 0,5 | 2 | 25 |
| Ва | 20 | 100 | 300 |
| Cd | 0.04 | 1 | 5 |
| Cr total | 0,5 | 10 | 70 |
| Cu | 2 | 50 | 100 |
| Hg | 0.01 | 0.2 | 2 |
| Мо | 0.5 | 10 | 30 |
| Ni | 0.4 | 10 | 40 |
| Pb | 0.5 | 10 | 50 |
| Sb | 0.06 | 0.7 | 5 |
| Se | 0.1 | 0.5 | 7 |
| Zn | 4 | 50 | 200 |
| Chloride | 800 | 15 000 | 25 000 |
| Fluoride | 10 | 150 | 500 |
| Sulphate | 1000 | 20 000 | 50 000 |
| DOC | 500 | 800 | 1000 |

Table 3. Limit values for inert, non-hazardous and hazardous waste set in the Government Decree on landfills (331/2013)

According to the EU regulations, materials are either waste or products. A waste material suitable for utilization can be productized, which means that the waste case to be waste and regulations from product and chemical legislation are applied. Registration of an industrial by-product to the Regulation (1907/2006/EC) concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) becomes compulsory if the by-product is planned to be brought onto the market. (EU Commission 2006, Pajukallio, Wahlström et al. 2011)

Waste can also be utilized if it fulfils the criterion for by-products or the End-of-Waste (EoW) criteria described in the Waste Framework Directive (2008/98/EC). According to the Directive, a substance or object from a production process, in which the primary aim is not the production of that item, may be regarded as by-product if the following conditions are met:

- (a) further use of the substance or object is certain
- (b) the substance or object can be used directly without any further processing
- (c) the substance or object is produced as an integral part of a production process

(d) further use is lawful, i.e. the substance or object fulfils all relevant product, environmental and health protection requirements for the specific use and will not lead to overall adverse environmental or human health impacts

According to the EoW criteria, waste cease to be waste, when it has undergone a recovery and complies with specific criteria developed in line with certain legal conditions, in particular;

- (a) The substance or object is commonly used for specific purposes
- (b) a market or demand exists for such a substance or object
- (c) the substance or object fulfils the technical requirements for the specific purposes and meets the existing legislation and standards applicable to products
- (d) the use of the substance or object will not lead to overall adverse environmental or human health impacts

The EoW criteria will most likely cover only the priority waste streams. Currently, the EoW criteria have been laid down for iron, steel and aluminium scrap. Planned waste streams for the EoW criteria include, copper scrap metal, recovered paper, glass cullet, plastics and biodegradable waste. (EU Commission 2008) The making of an EoW proposal to the Agency is a complex process due to factors, including the presence of contaminants, intended end uses, frequent quality control, and the possible requirement to comply with the REACH-regulation. The setting of shared limit values for environmental contaminants for the EoW products for all European countries may be challenging due to the differences in the existing national criterions and the different environmental weights and conditions among the countries. The limit values from the EU Directive (1999/31/EC) according the acceptance of waste at landfills may be applied in the determination of the environmental eligibility of the product. (Pajukallio, Wahlström et al. 2011)

5.1 Utilization of Inorganic By-products as Fertilizer Products

The Act of the Ministry of Agriculture and Forestry on Fertilizer Products (539/2006) regulates the production, marketing, import and export of fertilizer products. The Decree of the Ministry of Agriculture and Forestry on Fertilizer Products (24/11) regulates the requirements for the type designation list and the requirements for quality, marking, packaging, transporting, storage, usage and other requirements and the raw materials used in fertilizer products. (MMM 2006, MMM 2011) For commercialization of a fertilizer product, the fertilizer product must be either in the

national designation list or the EU designation list. Inorganic fertilizer products can be used as fertilizers in agriculture, horticulture, forestry and in landscaping of green areas (MMM 2006, MMM 2011). The Decree on fertilizer products (24/11) qualifies also inorganic by-products from industrial plants with fertilizing properties as fertilizer products. The requirement for this type of fertilizer is that the product has a growth promoting effect on plants, which is primary based on the amount of plant available nutrients present in the by-product. The total concentrations of primary nutrients must be at least 2.0% or the total concentrations of secondary nutrients at least 8%. The concentration of the nutrients in the product description of the fertilizer product. The permissible variations for different nutrients are described in detail in Decree on fertilizer products (24/11). The limit values for HTEs in inorganic fertilizer products and liming agents from Decree 24/11 are presented in Table 4. (MMM 2011, Appendixes II-IV)

Table 4. Limit values for hazardous elements in inorganic fertilizer products and liming agents when leached with nitric acidic from the Decree on fertilizer products 24/11 (MMM 2011, Appendix IV)

| Element | Maximum concentration mg/kg dry solids | |
|---------|---|-----------------------|
| | în General | In Forest fertilizers |
| As | 25 | 40 |
| Hg | 1 | 1 |
| Cd | 1.5 | 25 |
| Cr | 300 | 300 |
| Cu | 600 | 700 |
| Pb | 100 | 150 |
| Ni | 100 | 150 |
| Zn | 1500 | 4500 |

Soil amendment

A soil amendment is any material added to a soil to improve its physical properties, such as water retention, permeability, water infiltration, drainage, aeration, and structure. Soil amendments may contain considerably amounts of primary or secondary nutrients. The concentration of primary nutrients in the soil amendment product may vary with ±50% from the concentration declared in the product description. (MMM 2006, MMM 2011 Appendix II-III)

Liming agent

Liming agents are products containing calcium and/or magnesium applied to the soil in order to reduce soil acidity to a level that is optimal for plant growth. The neutralizing value in liming agents must be at least 10% (d.w. Ca; equivalents). The neutralizing value may vary with 2.0% and the nutrient content with ±20% from the values declared in the product description. Liming agents can be used as fertilizers in agriculture, horticulture or forestry and in landscaping of green areas. Commonly used liming agents include, calcium carbonate, calcium hydroxide and calciummagnesium carbonate. Additionally, by-products, such as wood ash, fly ash, and lime stabilized sewage sludge and cement kiln dust, may be used as liming agents. (MMM 2011 Appendixes I and III)

5.2 Utilization of waste as Construction Material

The key EU regulation concerning construction products is the EU Construction Products Regulation (CPR; 305/2011). The aim of the CPR is to ensure the availability of accurate and reliable information on the performance and properties of construction products across Europe. The basic work requirements (BWR) are related to the following:

- Mechanical resistance and stability
- Safety in case of fire
- Hygiene, health and the environment
- Safety in use
- Protection against noise
- Energy economy and heat retention
- Sustainable use of natural resources

CE-marking has now become mandatory in all EU countries for construction products that are covered by a harmonised product standard (hENs) or a construction product that conforms to a European Technical Assessment (ETA). The CE-mark states that the product is assessed before being placed on the market and meets EU requirements set for safety, health and environmental protection. The usage of construction materials and products are still controlled by national authoritative regulations. The national Act on the Approval of Certain Construction Products (954/2012) applies to the approval of construction products used for construction purposes in cases where the products in question are not covered by the hENs or ETA arrangement for the products does not exist. (EU Commission 2011, Wahlström et al. 2014)

II EXPERIMENTAL PART

The scope of the experimental work was to examine the performance and the scale-up potential of the froth flotation procedure developed in the VISA project. The elemental composition of the unfiltered and pre-coat filtered GLD from the Stora Enso Imatra mills was analysed in order to optimize the flotation process. The scope of the laboratory experiments was to study the influences of slurry properties, quantity of reagents and machine variables on the flotation of unburned carbon and calcite from unfiltered GLD. The data from the experiments were used for modelling the pilot-scale experiments. The pilot-scale experiments were carried out at the causticising plant at Stora Enso Imatra Mills in order to study the performance of the flotation procedure in mill conditions.

6. IMATRA MILLS

Stora Enso Imatra Mills in Kaukopää and Tainionkoski produce pulp on three production lines. The annual productions of the different pulps are: 900 000 t/a bleached pulp (72% hardwood and 28% softwood), 200 000 t/a unbleached softwood pulp and 200 000 t/a CTMP. The Imatra Mills produce annually approx. 1.1 million of tons of board (990 000 t/a) and paper (85 000 t/a) of which 97% is exported. The most important market is Europe, but a substantial share of exports also goes to South East Asia. The Kaukopää power plant produces all the heat the mills consume and more than half of the needed electricity. It also burns wood-based by-product fuels generated in the mills and takes care of the regeneration of cooking chemicals used in the pulp production.

The power plant produces process steam with two recovery boilers, one bark boiler, and four gas boilers. Fly ash from the electrostatic precipitators, economizers and ash funnels of the cooking piping are mixed in a mixing tank to the black liquor. The black liquor is pre-heated by indirect steam heating and pumped through black liquor guns to the furnace. The black liquor is settled at the bottom of the boiler, where the water is vaporised due to the high temperature and the solids are combusted partially depending on the amount of primary air. The smelt, which is accumulated at the bottom of the furnace, is then lead to the dissolver.

The two lined causticizing plant produces up to 9700 m³/d of white liquor. The process scheme of the Kaukopää causticizing plant is shown in Appendix 1. White liquor is produced from green liquor from the smelt dissolvers and lime from the lime mud reburning kiln. The green liquor from the dissolvers is pumped to the equalization tank. The purpose of the equalization tank is to even out the concentration, temperature and flow variations of the green liquor. The green liquor is pumped from the equalization tank to two green liquor clarifiers where the GLD are settled to the bottom of the clarifier and discharged periodically to the dregs handling. Approx. 12 ton/d GLD is pumped from the clarifiers to a pre-coat filter. In the beginning of each filtration cycle a 70 mm thick layer of pre-coat i.e. lime mud is applied on the drum. The duration of a filtration cycle is about 12h. (Stora Enso, internal material 2014)

7. CHEMICAL ANALYSIS OF UNFILTERED AND PRE-COAT FILTERED GREEN LIQUOR DREGS FROM IMATRA MILLS

Both unfiltered and pre-coat filtered GLD from Stora Enso Imatra Mills were studied for their elemental compositions, pH and dry solids contents. The unfiltered GLD composite sample, consisting of six individual one litre daily samples, was collected during one week in November 2013 from a sampling point after the dregs clarifier. The pre-coat filtered GLD composite sample was collected during one week in Mars 2014 from a sampling point after the pre-coat filter. The mill was operating normally during both of the sampling periods. The concentrations of the main elements in the unfiltered and pre-coat filtered GLD are presented in Table 5. The analysis methods are presented in Appendix 2.

| Element | Unfiltered GLD | | Pre-coat filtered GLD | |
|---------|----------------|-----------|-----------------------|-----------|
| | mg/kg | % | mg/kg | % |
| Na | 280000 | 28 | 13700 | 1.37 |
| С | 75900 | 7.59 | 94600 | 9.46 |
| S | 88000 | 8.8 | 27000 | 2.7 |
| Са | 42700 | 4.27 | 242000 | 24.2 |
| К | 40400 | 4.04 | 1800 | 0.18 |
| Mg | 6300 | 0.63 | 58400 | 5.84 |
| Mn | 2500 | 0.25 | 33300 | 3.33 |
| н | 1550 | 0.155 | 4300 | 0.43 |
| Si | 790 | 0.079 | 230 | 0.023 |
| Fe | 555 | 0.0555 | 7400 | 0.74 |
| AI | 540 | 0.054 | 6300 | 0.63 |
| Zn | 465 | 0.0465 | 5500 | 0.55 |
| Р | 410 | 0.041 | 2300 | 0.23 |
| N | >100 | >0.01 | 400 | 0.04 |
| Ва | 77.5 | 0.00775 | 1100 | 0.11 |
| Cu | 31.5 | 0.00315 | 260 | 0.026 |
| Cr | 23 | 0.0023 | 350 | 0.035 |
| Ni | 9.25 | 0.000925 | 140 | 0.014 |
| Мо | 2.85 | 0.000285 | 13 | 0.0013 |
| Cd | 2.2 | 0.00022 | 25 | 0.0025 |
| Se | 41671 | 0.00012 | 15 | 0.0015 |
| Sb | >1 | >0.0001 | 2.2 | 0.00022 |
| As | >0.75 | >0.000075 | <0,75 | >0.000075 |

According to the results, the main elements in the unfiltered GLD were sodium (28%), sulphur (8.8%), calcium (7.59%), and potassium (4.04%). Most of the sodium, sulphur and potassium are recovered in the weak wash, while the insoluble compounds are concentrated in the pre-coat filtered dregs. The main elements in the pre-coat filtered GLD are calcium (24.2%), magnesium (5.84%), manganese (3.33%) and sulphur (2.7%). Most of the NPE, including aluminium (6300 mg/kg), silicon (230 mg/kg), phosphorous (2300 mg/kg), chlorine, potassium (1800 mg/kg), magnesium (58400 mg/kg) and iron (7400 mg/kg) are concentrated in the pre-coat filtered GLD, thus leaving the chemical cycle. Additionally, small amounts of HTEs are concentrated in the GLD, of which zinc was the prominent (5500 mg/kg). The next prominent HTEs present in the pre-coat filtered GLD include chrome (350 mg/kg), copper (260 mg/kg), and nickel (140 mg/kg), while the concentrations of antimony (2.2 mg/kg), selenium (15 mg/kg) and cadmium (25 mg/kg) are relatively low in the pre-coat filtered GLD. The concentration of antimony in the unfiltered GLD and the concentrations of arsenic in the unfiltered and pre-coat filtered GLD were below the limit values of the determination.

7.1 Dry Solid Contents, Density and pH

The dry solids contents, pH and density for the unfiltered and pre-coat filtered GLD are presented in Table 6.

| Determination | Unfiltered GLD | Pre-coat filtered GLD |
|----------------------------|-------------------|--------------------------|
| Dry Sodids content % | 25.7 | 42.5 |
| рН | 12.8 | 11.2 |
| Density kg/dm ³ | 1.2165 | |

Table 6. Dry solids contents, pHs and the density of the unfiltered and pre-coat filtered GLD
7.2 Water Insoluble Elements

The concentrations of water insoluble elements in the unfiltered and pre-coat filtered GLD are presented in Table 7.

| Element | Unfiltered GL | D olids | Pre-coat filtered GLD | | |
|---------|---------------|------------|-----------------------|-------|--|
| | mg/kg | % | mg/kg | % | |
| Ca | 487250 | 48.73 | 363500 | 36.35 | |
| 0 | 314400 | 31.44 | 358100 | 35.81 | |
| Na | <5000 | < 0.5 | 13800 | 1.38 | |
| Mg | 86750 | 8.68 | 116800 | 11.68 | |
| Mn | 47850 | 4.79 | 58400 | 5.84 | |
| S | 15900 | 1.59 | 29400 | 2.94 | |
| Fe | 12500 | 1.25 | 14700 | 1.47 | |
| Zn | 9950 | 1 | 11500 | 1.15 | |
| Al | 6100 | 0.61 | 11400 | 1.14 | |
| Si | <5000 | < 0.5 | 14000 | 1.4 | |
| Р | <5000 | < 0.5 | <5000 | <0.5 | |
| Cl | 7800 | 0.78 | <5000 | <0.5 | |
| К | <5000 | < 0.5 | <5000 | <0.5 | |
| Ва | <5000 | < 0.5 | <5000 | <0.5 | |

Table 7. Concentrations of the main insoluble elements in the unfiltered and pre-coat filtered GLD

According to the results, 21.2% of the compounds in the unfiltered GLD were water insoluble, while the percentage of the water insoluble compounds in the pre-coat filtered GLD was 96.8%. The main compounds in the water insoluble fractions are carbonates of calcium and magnesium. The calcium particles present in the GLD can be divided into fine and coarse particles. Figure 8a and 8b shows micrographs of the coarse and fine particles present in the unfiltered GLD.



Figure 8a Micrograph of the coarse calcium particles present in the unfiltered GLD



Figure 8b Micrograph of the fine calcium particles present in the unfiltered GLD

According to the X-ray diffractogram (XRD) of the unfiltered GLD presented in Appendix 3, calcium was mostly present in form of calcium hydroxide in the unfiltered GLD. The results from the XRD-analysis were not completely accurate due to the high concentration of soluble sodium carbonate in the sample. In the insoluble fractions of the unfiltered and pre-coat filtered GLD calcium was mainly in form of calcium carbonate and magnesium as magnesium carbonates. The NPEs and the HTEs in the GLD are mainly present as insoluble carbonates and sulphates. The concentration of solition in the insoluble fraction of the unfiltered GLD and the concentrations of sodium, phosphorus, barium and potassium in the insoluble fraction of the unfiltered and pre-coat filtered and pre-coat filtered GLD were below the limit values of the determination.

7.3 Water Soluble Elements

The concentrations of water soluble compounds and elements in the unfiltered and pre-coat filtered GLD are presented in Table 8.

| Compound/ | Unfiltered GLD | | Pre-coat filtered GLD | | |
|---------------------------------------|----------------|------------|-----------------------|------------|--|
| Element | mg/kg | % | mg/kg | % | |
| Sulphide S ²⁻ | 62329 | 6.2 | <10000 | < 1 | |
| Soluble CO ₃ ²⁻ | 219550 | 22 | 61300 | kesä.13 | |
| Na | 292269 | 29.2 | 9778 | 0.98 | |
| Mg | 5.42 | 0.00054 | 11.73 | 0.0012 | |
| AI | 2.26 | 0.00023 | <0.5 | < 0.00005 | |
| Si | 390 | 0.039 | 32.76 | 0.0033 | |
| Р | 117 | 0.012 | 4.89 | 0.0005 | |
| Si | <5000 | <0.5 | 11244 | 1.124 | |
| к | 46320 | 4.63 | 1515 | 0.15 | |
| Ca | 45.18 | 0.0045 | 20.58 | 0.0021 | |
| Cr | <0.05 | < 0.000005 | 0.78 | 0.00008 | |
| Mn | 2.19 | 0.00022 | 2.15 | 0.0002 | |
| Fe | <0.55 | < 0.000055 | 0.54 | 0.00005 | |
| Ni | 0.15 | 0.000025 | <0.15 | < 0.000015 | |
| Ci | <.025 | < 0.000025 | <0.25 | < 0.000025 | |
| Zn | 0.37 | 0.000037 | 0.36 | 0.00004 | |
| As | <0.75 | < 0.000075 | <0.75 | < 0.000075 | |
| Se | <0.7 | < 0.00007 | <0.7 | < 0.00007 | |
| Мо | 2.96 | 0.0003 | 0.49 | 0.000049 | |
| Cd | <0.5 | < 0.000005 | <0.5 | < 0.000005 | |
| Sb | <1 | < 0.0001 | <1 | < 0.0001 | |
| Ba | 0.84 | 0.000084 | 0.1 | 0.00001 | |

Table 8. Concentrations of the main water soluble elements in the unfiltered and pre-coat filtered GLD

According to the results, 78.8% of the compounds in the unfiltered GLD were water soluble, while the percentage of the water soluble compounds in the pre-coat filtered GLD was 3. 2. The main water soluble elements in the unfiltered GLD are sodium and potassium, which are mainly present in form of carbonates or sulphides. The main water soluble elements in the pre-coat filtered GLD are silicates, sodium and potassium, while the concentrations of water soluble sulphides were below the determination values. The low concentrations of water soluble sodium and potassium in the pre-coat filtered GLD indicate that the filtration process was working properly during the sampling period.

7.4 Carbon

The concentrations of total carbon and non-carbonated carbon in the unfiltered and the pre-coat filtered GLD are presented in Table 9.

| Determination | Unfilte | red GLD | Pre-coat filtered GLD | | |
|--------------------------------------|---------|---------|-----------------------|------|--|
| | mg/kg | % | mg/kg | % | |
| Carbon (C) | 75900 | 7.59 | 94600 | 9.46 | |
| Non-CO ₃ ²⁻ -C | 6350 | 0.635 | 11800 | 1.18 | |
| CO3 ²⁻ -C | 69550 | 6.955 | 82800 | 8.28 | |

Table 9. Concentrations of carbon in the unfiltered and pre-coat filtered GLD

According to the results in Table 9, most of the carbon present in the GLD was in form of carbonates. In the unfiltered GLD, 91.6% of the total carbon was in form of carbonates, of which sodium carbonates was the prevalent compound. The concentration of total carbon was higher in the pre-coat filtered GLD than in the unfiltered GLD due to the absence of water soluble elements. The concentration of total carbon in the pre-coat filtered GLD was 9.46% of which 12.47% was in non-carbonated form. The carbon present in the pre-coat filtered GLD was mostly in form of calcium carbonate i.e. calcite and magnesium carbonate. The non-carbonated carbon in the GLD originates from incomplete combustion of organic material in the recovery boiler; since the concentrations of non-carbonated carbon was relatively low in the analysed GLD composite samples it can be assumed that the recovery boiler at the mill worked impeccably during the sampling periods.

8. FROTH FLOTATION IN TREATMENT OF GLD

The flotation experiments are conducted according to two methods, referred as the one-step method and the two-step method, where the unburned carbon is separated alone or together with calcite to the float fraction, leaving the undesired substances, including hazardous trace elements (HTEs), in the tailings.

The two-step method is recommended for carbon rich GLD. In this method, carbon and calcite are separated from the GLD separately, resulting in three fractions; calcite, carbon and waste. In the first step unburned carbon is floated with hexadecane, which is a gasoline derivative commonly used in flotation of fine coal, to the float fraction leaving carbonates and heavy metals in the tailings. The tailings, or so called carbonate fraction, are further treated in the second step, where the calcite is floated with tall oil to the float fraction, while HTEs and magnesium remain in the waste fraction and leave the process from the tailings outlet. In the one-step method the calcite is floated together with the carbon to the float fraction, leaving magnesium and heavy metals in the tailings. The process schemes for the one and two step methods are illustrated in Figures 9a and 9b.





Figure 9 b. Schematics of the one-step method

The one-step method is suitable for GLD with low carbon content, since the formation of carbon froth requires an adequate amount of carbon particles to form a stable froth. The one-step method is more advantageous compared to the two-step method according to material, cost and space efficiency. The two-step method produces three fractions requiring further treatment, such as filtration and washing steps, while the one-step method produces only two. On the other hand, the produced carbon-calcite product from the one-step method is more difficult to utilize than the calcite product from the two-step method.

The flotation separation technique was studied for both unfiltered and pre-coat filtered GLD. Flotation of unfiltered GLD was studied as the first option due to its economic and technological benefits. Firstly, the unfiltered GLD coming from the dregs clarifier is already in suspension, thus no pre-treatment is needed. Secondly, depending on the dry solids content in the unfiltered GLD, only 1:4-1:3 additional water is needed in the flotation process. Thirdly, the produced calcite or carbon-calcite fractions can be filtered with the existing dregs filter, thus only smaller filters for the waste and the carbon fractions are needed. On the other hand, the filtration of the different calcite fractions may affect the quality of the weak liquor, thus the chemical recovery. Figure 10 shows a process scheme of a flotation process, where carbon-calcite is separated from the unfiltered GLD according to the one-step method.



Figure 10. Process scheme of a flotation process, where carbon-calcite is separated from the unfiltered GLD according to the one-step method

Froth flotation of pre-coat filtered GLD was studied as a second option. The main benefit of placing the flotation process after the dregs filter is that the chemical cycle is not affected. Additionally, the carbon content is higher in the filtered GLD than in the unfiltered GLD, which makes the flotation of carbon more effective. On the other hand, the filtered GLD must be grinded and diluted with water before it can be pumped to the flotation cell, which consumes both water and energy. The produced flotation fractions require, according to the chosen method, 2-3 filters for water removal. Figure 11 shows the process scheme of a flotation process, where carbon-calcite is separated from pre-coat filtered GLD.



Figure 11. Process scheme of the flotation process, where carbon-calcite is separated from pre-coat filtered GLD according to the two-step method

9. LABORATORY EXPERIMENTS

The flotation experiments were conducted according to the one- and two-step methods described in Chapter 8. The scope of the laboratory experiments was to study the influences of slurry properties, quantity of reagents and machine variables on the flotation of carbon and calcite from the unfiltered GLD. The experiments were carried out with a laboratory flotation machine at the department of Material Science and Engineering at Aalto University. The unfiltered GLD used in the experiments was collected from a sampling point after the dregs clarifier at the Imatra Mills. The samples were stored in 30 I plastic tanks in room temperature during the five weeks of experiments.

9.1 **Process Description of the Batch Tests**

Several baseline flotation tests were performed to establish the slurry level and the manually performed scraping technique. Additionally, the effect of the mixing speed and the air flow rate were visually determined.

Preparation of the slurry

The unfiltered GLD was diluted with tap water in a 20 I mixing tank to a density of 45-60 g/l, corresponding a water:GLD ratio of 1:4-1:3. About 2-3 g/l of NaHCO₃ was added to the slurry to control the pH and the slurry was heated to a temperature of 80° C to simulate the mill conditions.

Flotation reagents

Hexadecane ($C_{16}H_{34}$), which is a gasoline derivative commonly used in flotation of coal, was used as collector and 1-metox-2-propanol, which is referred in this thesis by its commercial name Dowfroth250 (DF250), as frother for unburned carbon. Tall oil from Stora Enso Imatra Mills served both as collector and frother in the flotation of calcite. Additionally, NaHCO₃ was used for pH control.

Flotation of unburned carbon

Depending on the cell size, 1.5-3 l of the prepared slurry was measured into the flotation cell. The slurry was first agitated at tip speed 2.1 m/s for 2 min, after which 0.15-0.3 ml hexadecane was added to the slurry. The slurry was conditioned for 3 minutes and 0.6-1.2 ml DF250, was added and the slurry was conditioned for an additional 5 minutes. The tip speed was increased to 3.14 m/s companied with air addition of 1-1.5 l/min. The collection of the froth was started 5 minutes

after the formation of the froth to ensure that the froth was stable. The concentrate was scraped with a scraper from the top of the cell during 20 minutes. During the flotation experiment, tap water was added every five minute to the process to maintain the slurry level. The amount of make-up water varied, because the required amount of water depended on the slurry properties and reagents used in the flotation experiments.

Flotation of calcite

The flotation of calcite was carried out in a 1.5 I flotation cell, using the carbonate fraction from experiment 4, Trial 2. About 1 ml/l tall oil, which serves as frother and collector, was added to the slurry and the mixture was agitated with tip speed 2.1m/s for 10 minutes. After the conditioning phase, air was added 1 l/min, while the mixing speed was maintained. The concentrate was scraped with a scraper from the top of the cell during 20 minutes.

Sample handling

The collected samples of the concentrates and tailings were filtered the next day in room temperature by using a 7 bar pressure and S&S White ribbon 589/2filters. The concentrate samples were weighted to determine the recoveries, while only small quantities of the tailings samples were filtered to avoid plugging of the filter paper. The samples were dried in a 105 °C oven over night, weighted and pulverized for further analysis.

9.2 Results and Discussion

The flotation of unburned carbon was carried out according to the reverse flotation principle, in which the undesired particles, in this case unburned carbon, are floated to the carbon fraction leaving the from utilization perspective valuable calcites in the tailings. The object of this flotation step was to maximize the recovery of carbon, sulphur and HTEs to the carbon fraction, while keeping the recovery of calcium as low as possible. In the flotation of calcite, the aim was to maximize the recovery of calcite to the float fraction, referred as calcite fraction, while avoiding the recovery of HTEs. The performances of the flotation processes were examined according to the recoveries and residual concentrations of total carbon, calcium, sulphur and HTEs in the different flotation fractions.

9.2.1 The Effect of Machine Variables in Flotation of Unburned Carbon

In this thesis the effects of the machine variables were only visually studied. The optimal mixing speed, air flow rate and slurry level were determined according to the characteristics of the formed froth. The aim was to get a stable carbon rich froth, while avoiding recovery of water and calcite. Picture 12a, shows the carbon froth at the froth building stage, and Picture 12b the carbon froth after 10 minutes of scraping.



Figure 12a. Flotation of carbon after five minutes of froth building



Figure 12b. Flotation of carbon after ten minutes of scraping

The formation and properties of the froth depended highly on the mixing speed and the slurry level. The formation of the froth started only when the mixing speed was increased to over 2.72 m/s, while no significant visual change was seen in the froth characteristics when the air rate was increased from 1 l/min to 1.5 l/min. According to these observations the tip speed was established to 3.14 m/s and the air rate to 1 l/min. Due to the high impeller speed and the small cell sizes used in the laboratory experiments, the turbulence in the cell was relatively high, which increased the recovery of all particles present in the slurry. The slurry level had a great impact on the quality of the concentrate, since a shallow froth increases the risk of entailing slurry in the concentrate container. The scraping method and frequency had also great impacts on the quality of the concentrate, since too deep scraping increase the recovery of the slurry, while frequent scraping increase the water recovery.

9.2.2 The Effect of Slurry Density and Reagent Dose on Flotation of Unburned Carbon

The scope of experiments 1-3 was to study the influences of different reagent doses and slurry densities on the recovery of unburned carbon. The feed and the flotation fractions were analysed for their elemental compositions, results from the experiments are presented in Appendix 4. The slurry densities and quantities of the reagents are presented in Table 10.

| Experiment | Experiment 1 | | Experiment 2 | | | Experiment 3 | | | | | |
|-----------------|-------------------------|-----|--------------|-----------------------|------|--------------|-----------------------|-----|------|-----|------|
| details | slurry density 52.5 g/l | | 52.5 g/l | slurry density 60 g/l | | | slurry density 55 g/l | | | | |
| Trial nr. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Hexadecane ml/l | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.2 | 0.2 | 0.1 | 0.2 | 0.1 | 0.2 |
| DF250 ml/l | 0.4 | 0.4 | 0.8 | 0.4 | 0.4 | 0.8 | 0.8 | 0.4 | 0.8 | 0.4 | 0.8 |
| NaHCO3 g/l | 2.2 | 2.2 | 2.2 | 2.2 | 2.2 | 2.2 | 3.2 | 2.2 | 2.2 | 3.2 | 3.2 |
| Concentrate m-% | 5.6 | 5 | 8.8 | 7.9 | 11.8 | 7.7 | 10.4 | 6.9 | 5.4 | 7.6 | 6.4 |
| Tailings m-% | 94 | 95 | 91.1 | 92 | 88 | 92 | 89.6 | 93 | 94.6 | 92 | 93.6 |

| Table 10. Slurry densi | ties and the reagent of | doses in experiments 1-3 |
|------------------------|-------------------------|--------------------------|
|------------------------|-------------------------|--------------------------|

The mass-% of the carbonate fractions in Trials 1-3 varied between 5 and 11.8%. The slurry density was controlled by addition of water. The addition of water improves the flotation performance in several ways. The slurry density and dry solids content are decreased, thus lighter material are lifted to the froth. Additionally, alkali compounds are dissolved, which decreases the need of wash water and prohibits the crystallization of sodium compounds, which are harmful for the filtration process. The effect of the slurry densities and reagent doses on the total carbon concentrations in the feed and the flotation fractions are shown in Figure 13.



Figure 13. Concentrations of total carbon in the feed and the flotation fractions in Trials 1-11

The recoveries of unburned carbon, which represents the non-carbonated carbon present in the GLD, cannot easily be determined from Figure 13, since the fractions were only analysed for their concentrations of total carbon of which only approx. 8% are in non-carbonated form. The concentrations of total carbon were reduced in experiments 2 (Trials 1-3) and 3 (Trials 8-11) between 10 and 15%, which indicates that most of the unburned carbon present in the GLD was recovered in the carbon fraction. The recovery rate and selectivity of the process depends highly on the amount and nature of the particles in the slurry. The separation of unburned carbon was most effective in Trials 8-11, where the concentrations of total carbon in the carbonate fractions were reduced up to 15% from their initial concentrations. The better carbon separation was due to the higher concentration of total carbon in the feed, which indicates that flotation of unburned carbon is more suitable for carbon rich GLD. Experiment 2 (Trials 4-7) gave the best recoveries combined with the poorest selectivity. The selectivity was low especially in Trials 6 and 7, where the concentrations of the total carbon were reduced only by 4 and 6% in the carbonate fractions. The selectivity decreases as the recovery increases due to entrainment of other particles e.g. calcites. The quantity of the reagents did not have a significant effect on the recovery of unburned carbon.

The unfiltered GLD consists up to 80% of water soluble sodium and potassium carbonates and sulphides. According to the results in Appendix 4, the flotation of unburned carbon did not have a significant effect on the sodium and potassium compounds present in the GLD. Generally, the recovery of sodium and potassium were increased with increased carbon recovery, which indicates that sodium and potassium are recovered mainly through entrainment. The recoveries of carbon, calcium, sulphur and zinc in the carbon fractions are shown in Figure 14.



Figure 14. Concentrations of total carbon, sulphur, zinc, and calcium recoveries in the carbon fraction in Trials 1-11

The grade of the carbon fraction is affected by the recovery of other particles to the carbon fraction. Due to entrainment, the recoveries of other particles present in the slurry increase with increased carbon recoveries. Higher slurry densities give higher recoveries with lower grades, which can be seen from the results in Trials 4-7, where the slurry density was the highest. Recovery of calcium was an undesired feature in these experiments, since it increases the volume of the carbon fraction and causes loss in material in the carbonate fraction.

The GLD contained small amounts of HTEs, whereof zinc was the prominent. Figure 15 shows the concentrations of zinc in the feed and the flotation fractions.



Figure 15. Concentrations of zinc the feed and the flotation fractions in Trials 1-11

According to the results from Trial 1-11, zinc could be floated to the carbon fraction. The separation of zinc was highest in Trials 1-3, where the concentrations of zinc in the carbonate fractions were reduced by 14-26%. The better separation in these Trials might be due to the higher concentration of zinc in the feed combined with the lower slurry density. Furthermore, the higher doses of sodium bicarbonate in Trials 7, 10 and 11 seemed to increase the zinc concentrations in both the carbon and carbonate fractions, which indicate that the addition of sodium bicarbonate may affect the filtration process. Table 11 shows the floatability of the other prominent HTEs in the feed and the flotation fractions Trial 3.

| Element | Feed mg/kg | Carbon fraction mg/kg | Carbonate fraction mg/kg |
|---------|---------------|-----------------------------|--------------------------------|
| Zn | 2700 | 2900 | 2000 |
| Cd | 12 | 13 | 9.7 |
| Cr | 120 | 130 | 98 |
| Ni | 45 | 60 | 38 |
| Se | 5.3 | 6,2 | 4,1 |
| As | <0.75 | <0.75 | <0.75 |
| Cu | 220 | 180 | 170 |
| Мо | 0.83 | 0,85 | 0.86 |
| Sb | 1.1 | <1.0 | 1 |
| Si | 200 | 150 | 150 |

Table 11. Concentrations of main HTEs in the feed and the flotation fractions in Trial 3

According to the results from Trial 3, all of the studied HTEs present in the GLD are possible to float. The floatability of the different elements depends on the particle size and the form in which they are present in the slurry.

9.2.3 The Effect of Flotation Time on Flotation of Unburned Carbon

The effect of the flotation time on the recovery of total carbon and other elements present in the GLD was studied in Experiment 4. The slurry density was 45 g/l and the reagent doses were 0.1 ml/l hexadecane and 0.4 ml/l DF250. In Trial 1 the concentrate was collected during 20 minutes in one container to determine the overall flotation performance, while in Trial 2 the concentrate was collected in 4 individual containers during 5 minutes periods. Table 12 shows the concentrations of total carbon and calcium and the m-% of the flotation fractions in Trials 1 and 2.

| Experiment 4 | | | | | | | |
|--------------|--------|-----------|---------|----------|----------|----------|--|
| Trial | 1 2 | | | | | | |
| | Carbon | Carbonate | Carbon | Carbon | Carbon | Carbon | |
| Fraction | tot. | tot. | (5 min) | (10 min) | (15 min) | (20 min) | |
| С % | 20.1 | 9.9 | 30.1 | 20.7 | 15.3 | 13.2 | |
| Ca % | 16.2 | 23.3 | 18.5 | 23.7 | 21.2 | 25.5 | |
| m- % | 8.7 | 91.3 | 3.0 | 1.7 | 1.8 | 1.7 | |

Table 12. Concentrations and recoveries of total carbon and calcium in the flotation fractions in Trials 1 and 2

Figure 16 shows the concentrations of main elements in the feed and the flotation fractions from Trial 1.



Figure 16. Concentrations of main elements in the feed and the flotation fractions in Trial 1

Figure 16 shows that in addition to carbon, also sodium, sulphates and potassium are floated to the carbon fraction. The effects of the flotation time on the recoveries of these elements are shown in Figure 17.



Figure 17. Concentrations of main elements in the carbon fraction at different time intervals in Trial 2

In batch tests, the recovery rate decreases significantly after five minutes of flotation as the amount of floatable particles decreases. As can be seen from Figure 17, the recovery of total carbon was highest during the first five minutes of the flotation experiment. During these five minutes, also sulphur was floated to the carbon fraction, while the flotation of calcium was still relatively low. Due to the absence of unburned carbon particles and the recovery of calcium, both the recovery and the grade of the carbon fraction decrease after 5-10 minutes of flotation. After 15 minutes of flotation the recovery through entrainment, i.e. recovery of less hydrophobic particles such as sodium, increased significantly. Consequently, the concentration of total carbon in the carbon fraction decreased with almost 50% from the concentration achieved during the first five minutes of the flotation. During the last 5 minutes of the experiment, the recovery of total carbon continued to decrease, while the calcium concentration in the carbon fraction was increased to 25.5%. Additionally, the recovery of magnesium increased during the flotation, while the concentration of potassium persisted during the whole experiment. The concentrations of the prominent HTEs in the carbon fraction during the flotation process are presented in Table 13.

| Element | Feed | Carbon (5 min) | Carbon (10 min) | Carbon (15 min) | Carbon (20 min) |
|---------|-------|-------------------|--------------------|--------------------|--------------------|
| | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg |
| Zn | 2500 | 3200 | 3200 | 3100 | 4300 |
| Ва | 550 | 410 | 500 | 460 | 650 |
| Cd | 14 | 13 | 15 | 14 | 18 |
| Cr | 140 | 130 | 150 | 150 | 220 |
| Ni | 63 | 71 | 59 | 54 | 67 |
| Se | 9.1 | 6.9 | 7 | 7 | 9.4 |

Table 13. Concentrations of main HTEs in the feed and the carbon fractions during the flotation process

According to the results from Table 13, the concentrations of zinc, barium, cadmium, chrome and selenium in the carbon fraction were increased with time. This indicates that a longer flotation time may reduce the HTEs concentrations in the carbonate fraction.

9.2.4 Flotation of Calcite

The concentrations of HTEs were relatively high in the carbonate fraction, thus a second flotation step is needed to remove these harmful elements. The aim of Experiment 5 was to recover calcite by direct flotation, while leaving the HTEs and magnesium in the tailings i.e. waste fraction.

The formation of the calcite froth started immediately as the air valve was opened. The formed froth was light and difficult to control, thus the entrainment and entrapment of undesired particles were likely to occur. Tall oil is a very easily foaming agent, thus the 1 ml/l addition was probably too high for this purpose. In the experiment, 70% of the solids were recovered in the float fraction, leaving approx. 30% of the solids in the waste fraction. The main elements and their concentrations in the calcite and the waste fractions are shown in Figure 18a and the formed calcite froth can be seen in Figure 18b.





Figure 18b. Formed calcite froth

Figure 18a. Concentrations of main elements in the calcite and waste fractions

The results from the experiment are not completely accurate due to the uncontrollable and unstable froth formation. According to the results, calcium, carbon and sodium were recovered in the calcite fraction, while sulphur and potassium are concentrated in the tailings. The selectivity of was relatively poor, thus the chemical composition of the calcite fraction did not significantly differ from the one of the waste fraction. The concentrations of HTEs in the flotation fractions are shown in Table 14.

| Element | Calcite fraction | Waste fraction | |
|---------|------------------|----------------|--|
| | mg/kg | mg/kg | |
| Zn | 2500 | 2500 | |
| Ва | 590 | 550 | |
| Cd | 14 | 14 | |
| Cr | 140 | 140 | |
| Ni | 140 | 63 | |
| Se | 21 | 9.1 | |

Table 14. Concentrations of main HTEs in the calcite and waste fractions

According to the results in Table 14, zinc, chrome and cadmium were equally distributed in the float and waste fractions, while barium, nickel and selenium were concentrated in the float fraction.

9.3 Error Sources in the Flotation Experiments

During the laboratory flotation experiments, many possible error sources were recognized. In this thesis the error sources are divided into flotation process and sample handling errors.

Flotation process

The main error sources in the laboratory flotation tests were related to the collection of the samples. The quality of the concentrate was highly affected by the intensity and depth of the scraping, since a too deep and intense scraping causes recovery of the slurry in the concentrate container. The concentrate was manually scraped in the laboratory experiments, which may have caused minor errors in the results due to recovery of slurry or water. The samples of the tailings were collected from the bottom of the cell, thus the amount of coarse settled calcite particles had a great impact on the concentration of calcium in the studied samples. During the flotation process, a varied amount of make-up water was added to the cell in order to retain the slurry level. The addition of water decreases the density and reagent concentrations in the slurry, which both affect the flotation performance. Additionally, measurements errors in dosing of reagents may have had occurred. Especially, dosing of tall oil was complicated due to its high viscosity.

Sample handling

Approx. 80% of the substances in the unfiltered GLD were water soluble, thus the added water in the flotation process and the actual filtration had significant impacts on the final results. The filtration was affected by the quantity, density and temperature of the GLD slurry. The unfiltered GLD and its flotation fractions were difficult to filtrate with the laboratory filtration equipment. Especially, the fractions containing calcium, including the untreated GLD (feed), were difficult to filtrate due to pore clogging of the filter paper caused by the fine calcite particles. The volume of the samples varied between 200 ml to 500 ml, which affected the filtration process significantly, since the bigger samples caused pore clogging of the filter paper resulting in a cleaner filtrate.

10. PILOT-SCALE EXPERIMENTS

The pilot-scale experiments were carried out during two months at the causticising plant at the Imatra Mills with a 1 m³ pilot-scale Outotec TankCell[®] flotation cell. The flotation experiments were conducted according to the one- and two-step methods described in Chapter 8, of which the two-step method was studied as the first option due to the better utilization potential of the produced calcite fraction compared to carbon-calcite fraction from the one-step method. Furthermore, the results from the laboratory experiments indicated that most of the harmful elements present in the GLD are possible to be floated to the carbon fraction by using hexadecane as collector and DF250 as frother, hence the produced tailings i.e., carbonate fraction could be suitable for utilization without a second flotation step. The aim of the pilot-scale experiments was to evaluate the scale-up potential of the flotation process developed in the laboratory. The main objects were to study the impacts of the quality variations of the GLD on the flotation performance and to optimize the best process variables for a flotation process with a continuous feed. Since the Outotec TankCell[®] pilot cell uses the same technology as the industrial scale TankCells[®] units, the results from the pilot-scale tests gives a good insight about the scale-up potential of the flotation process.

10.1 Pilot Flotation Cell

The experiments were carried out with a 1 m³ pilot-scale version of Outotec TankCell[®] equipped with the newest FloatForce[®] mixing mechanism, which corresponds according to its flotation performance the industrial scale TankCell[®] described in Appendix 5. The pilot cell had an active volume of 1 m³ and it was equipped with an adjustable froth cone and external launders. The air flow rate, rotor speed, and the slurry level were controlled with CellStation[™]. Figure 19 shows the pilot cell.



Figure 19. Outotec TankCell[®] pilot. The green arrow shows the route of the feed and the red and blue arrows shows the outlets of the concentrate and the tailings

10.2 Process Description of the Batch Tests

The aim of the batch tests was to determine the optimal reagent doses and slurry density for flotation of unburned carbon and calcite. Additionally, the machine variables, including slurry level, mixing speed and air flow rate were determined visually in accordance with the findings from the laboratory experiments. According to the results from the laboratory experiments, the selectivity of the flotation process could be improved by using higher impeller speed and lower air flow rate.

Flotation of unburned carbon from unfiltered GLD (Trials 1-7)

The cell was filled with unfiltered GLD and water to a slurry level of 14 cm. The slurry was first mixed at tip speed 4.2 m/s for 2 minutes, after which 0.5 -1 dl Hexadecane was added to the slurry and the slurry was conditioned for 3 minutes. 2-4 dl of DF250 was then added and the slurry was conditioned for an additional 5 minutes time. The tip speed was increased to 4.7 m/s accompanied by air addition of 0.95-1 m³/min. Samples of the concentrate was collected during the first five minutes of the experiment, while the samples of the tailings were collected after 20 minutes of the flotation. Figure 20a shows the view on the formed carbon froth from the cell and Figure 20b the tailings, i.e., carbonate fraction from the flotation process.



Figure 20a. View of the froth carbon froth



Figure 20b. View of the outflow of the tailings

Flotation of calcite from unfiltered GLD (Trial 15)

The Trial was started with flotation of unburned carbon, where 0.5 dl Hexadecane and 2 dl DF250 were used as reagents. After this flotation step, the mixing speed was reduced to 4.1 m/s and 10 ml of tall oil, which serves as both collector and frother, was added to the carbonate slurry in order to start the flotation of calcite. Samples of the concentrate were collected during 5 minutes of the flotation in one container, while the sample of the tailings was collected after the flotation process.

Flotation of calcite from pre-coat filtered GLD (Trial 16)

120 kg of fresh pre-coat filtered GLD was collected from the GLD container after the pre-coat filter. To improve the mixing of the pre-coat filtered GLD in the water, the cell was filled with water and the addition of the GLD was accompanied by rapid mixing. However, due to the clayish and dense nature of the pre-coat filtered GLD, most of the GLD was not dissolved in the water and had to be removed from the process, causing a decrease in the density of the slurry.

The experiment was started with flotation of unburned carbon. The prepared slurry was mixed at tip speed of 4.2 m/s for 2 min, after which 1 dl Hexadecane was added to the slurry. The slurry was conditioned for 3 minutes, after which 2 dl of DF250 was added and the slurry was conditioned for an additional 5 minutes of time. After the 10 minutes of conditioning, the tip speed was increased to 4.7m/s accompanied by air addition of 0.95-1m³/min. The flotation of the unburned carbon was continued for 10 minutes. The aim of this flotation step was to reduce the carbon content of the slurry in order to get a cleaner carbonate fraction for the next flotation step. In the next flotation

step, 10 ml of tall oil was added to the carbonate rich slurry in order to separate the calcite from it. The slurry was conditioned for 10 minutes at tip speed 4.1 m/s, followed by air addition of 0.85 m^3 /min. Samples of the concentrate were collected during 5 minutes of the flotation in one container, while samples of the tailings were collected after the flotation process. Figure 21a shows the view of the calcite froth in the cell and Figure 21b a mixture of the carbon and calcite froths collected from the concentrate outlet.



Figure 21a. View of the calcite froth from the flotation of calcite from pre-coat filtered GLD



Figure 21b. formed carbon and calcite froth

10.3 Process Description of the Continuous Tests

Continuous tests were carried out in order to study the effect of a continuous feed on the selectivity of the flotation process. In the continuous tests, diluted and conditioned unfiltered GLD slurry was pumped from a mixing tank to the cell according to the process scheme presented in Figure 22.



Figure 22. Process scheme of the continuous test

The unfiltered GLD was led through a hose from a sampling point after the dregs clarifier to the mixing tank (1 m³). The flow rate of the unfiltered GLD from the hose was measured to be approx. 30 l/min and the temperature 90 °C. Due to the temperature restrictions of the pump, cool water was used for the dilution of the slurry. The flow rate of the water to the mixing tank was adjusted by using a rotameter to 15 l/min to attain a GLD:water ratio of 2:1 and a slurry temperature of 65 °C. The reagents (Hexadecane, DF250) were added to the mixing tank by using adjustable laboratory dosing pumps. The conditioned slurry was pumped from the mixing tank to the cell with a submersible pump at flow rate 33 l/min, which was the maximum what the pump was able to provide.

Flotation of unburned carbon from unfiltered GLD (Trials 11-14)

The continuous tests were carried out according to the best process variables, slurry density and reagent doses determined in the batch tests. The froth bed was fixed to 13 cm and the slurry feed rate was about 33 l/min, giving the slurry a residence time of 30 minutes in the cell. The tailings outflow was 22-28 l/min, resulting in a concentrate outflow of 5-9 l/min. The airflow rate was 0.96 m³/min and the tip speed of the rotor was 4.7 m/s. The trials were carried out in 3-5 hours periods and samples of the concentrate and the tailings were collected hourly during the flotation process.

The flotation of carbon-calcite from the unfiltered GLD was studied in Trials 13-14. The flotation of carbon-calcite was conducted according to the one-step method, where all reagents (0.5 ml/l

hexadecane, 2 ml/l DF250 and 0.01 ml/l tall oil) were added simultaneously to the slurry in the mixing tank. The froth bed was fixed to 15 cm and the slurry feed rate was about 33 l/min, giving the slurry a residence time of 30 minutes in the cell. The tailings outflow was 5-10 l/min, resulting in a concentrate outflow of 23-28 l/min. The tip speed in the trials was 4.1 m/s and the air flow rate 0.85 m³/min. The trials were carried out in 3-5 hours periods and samples of the concentrate and tailings were collected hourly during the flotation process.

10.4 Results and Discussion

The flotation of unburned carbon i.e., non-carbonated carbon, from the GLD was examined according to the concentrations of total carbon in the feed and the flotation fractions. According to the analysis in Chapter 7, only 8% of the total carbon present in the unfiltered GLD was in non-carbonic form, which complicates the determination of the results. In the examination of the results, it is assumed that the concentration of unburned carbon is in proportion to the concentration of total carbon.

In the flotation of calcite or carbon-calcite the valuable particles are floated to the float fraction, hence the success of the flotation process was determined according to the recovery of calcium and the rate of entrainment of undesired particles to the float fraction.

10.4.1 Operating Conditions and Feed Characteristics

The composition of the GLD has a great influence on the flotation performance. According to the results from the laboratory experiments, the dry solids contents together with the concentrations of total carbon and calcium in the GLD had great impacts on the selectivity of the flotation process. Due to these observations, the dry solids content and the suspended solids concentrations were measured regularly during the two months experiment period, the results from the analysis are presented in Table 15.

| Date | Dry solids | Suspended solids | |
|------|------------|---------------------|--|
| | % | g/l | |
| 13.1 | 22.3 | | |
| 16.1 | 21.0 | | |
| 22.1 | 20.5 | | |
| 5.2 | 21.3 | 36.1 | |
| 12.2 | 22.1 | 42.1 | |
| 19.2 | 22.9 | 61.5 | |
| 20.2 | 22.2 | | |
| 25.2 | 21.5 | | |
| 26.2 | 21.4 | 45.2 | |
| 27.2 | 22.8 | | |
| 3.3 | 21.1 | | |
| 4.3 | 21.1 | | |
| 5.3 | 21.3 | 30.1 | |
| 11.3 | 22.8 | | |

Table 15. Concentrations of dry solids and suspended solids in the unfiltered GDL

Approximately 80% of the compounds in the unfiltered GLD were water soluble, which explains the high dry solids content compared to the suspended solids concentration. The main water soluble compounds were sodium and potassium carbonates, while the calcium and magnesium carbonates were the prominent compounds in the water insoluble fraction. As can be seen from Table 15, the dry solids contents of the GLD did not significantly change during the two months experiment period, while the concentration suspended solids varied daily.

The formation and the quality of the froth in flotation of unburned carbon and carbon-calcite depend highly on the concentrations of both carbon and calcium in the GLD. The concentrations of total carbon and calcium in the unfiltered GLD during the experiment period are shown in Table 16.

| Date | Trial | С | a | С | | |
|-------|-------|--------|------|--------|-------|--|
| | | mg/kg | % | mg/kg | % | |
| 27.1 | 1-4 | 88700 | 8.87 | 133791 | 13.38 | |
| 3.2 | 5-7 | 254000 | 25.4 | 92758 | 9.28 | |
| 3.2 | 5-7 | 204000 | 20.4 | 82741 | 8.27 | |
| 13.2* | 11 | 140000 | 14 | 78008 | 7.8 | |
| 17.2* | 12 | 142000 | 14.2 | | | |
| 25.2 | 13 | 191000 | 19.1 | 85303 | 8.53 | |
| 3.3 | 14 | 124000 | 12.4 | 74409 | 7.44 | |
| 5.3 | 15 | 95500 | 9.55 | 67628 | 6.76 | |

Table 16. Concentrations of calcium and total carbon in unfiltered GLD

According to Table 16, the concentration of total carbon was considerably decreased after the first weeks of the experiment period. The concentrations of total carbon and calcium in the unfiltered GLD were easy to determine from the formed froth. During the first weeks of the experiment period (Trials 1-4), the froth formed in the flotation of unburned carbon was thick and carbon rich, resembling the carbon froth from the laboratory experiments. The quality of the froth was considerably changed after two weeks of the experiment period. By combining the visual observations with the analysis results it can be assumed that the flotation performance is highly affected by the concentrations of total carbon in the GLD. During the experiment period, it was also observed that a significantly higher mixing speed was required for slurries with low carbon contents.

10.4.2 Batch Tests

The aim of the batch tests was to optimize the flotation variables for the continuous tests and study the influence of the feed variations on the flotation performance. The samples of the concentrates were collected only during the first five minutes of the flotation process, thus the samples of the concentrate do not represent the overall quality of the concentrate.

Flotation of unburned carbon from unfiltered GLD

The aim of Trials 1-7 was to determine the optimal reagent doses and slurry density for flotation of unburned carbon from unfiltered GLD, the process data and the analysis results from the Trials 1-7 are presented in Table 17.

| Trial | GLD in slurry | Hexadecane | DF 250 | NaHCO ₃ | slurry level |
|-------|---------------|------------|--------|--------------------|--------------|
| | % | ml/l | ml/l | g/l | cm |
| 1 | approx. 35 | 0.05 | 0.2 | - | 16 |
| 2 | approx. 35 | 0.05 | 0.2 | - | 16 |
| 3 | approx. 35 | 0.1 | 0.4 | - | 16 |
| 4 | approx. 35 | 0.1 | 0.4 | 2.3 | 16 |
| 5 | approx. 35 | 0.05 | 0.2 | 2.3 | 16 |
| 6 | approx. 50 | 0.1 | 0.4 | 2.3 | 14 |
| 7 | approx. 50 | 0.1 | 0.4 | 2.3 | 14 |

Table 17. Process data and reagent doses in Trials 1-7

Figure 23 shows the concentrations of total carbon in the feed and the different flotation fractions.



Figure 23. Concentrations of total carbon in the feed and the flotation fractions in Trials 1-7

According to the results, the quantity of the reagents and density of the slurry had minor effects on the flotation performance. As can be seen from Figure 23, the flotation of unburned carbon depended highly on the concentration of total carbon in the feed. Since the samples of the concentrate only represents the first five minutes of the flotation process, the success of the flotation process was determined according to the residual total carbon in the carbonate fractions. The concentrations of total carbon in the carbonate fractions were reduced approx. 20-30% in Trials 1-4, where the concentration of total carbon in the feed was 17-19%. While in Trials 5-7, where the concentrations of total carbon in the feed were below 10%, the reduction of total carbon in the carbonate fraction was only 0-3%. The high concentrations of total carbon in the feed and the high recoveries of total carbon in Trials 1-4 indicate that the concentration of unburned carbon in the GLD was exceptionally high during the experiment day. The effect of the concentrations of total carbon in the feed on recovery of calcium is shown in Figure 24.



Figure 24. Concentrations of calcium in the feed and the flotation fractions in Trials 1-7

As can be seen from Figure 24, the concentration of total carbon had a great influence on the recovery of calcium. In Trials 1-4, where the concentration of total carbon in the feed was above 17%, the recovery of calcium was negligible, while in Trials 5-7, where the concentration of total carbon in the feed was below 10%, almost as much calcium as total carbon was recovered in the carbon fraction. The high recovery of calcium is due to the absence of unburned carbon particles in the feed, which decreases both the recovery and the selectivity of the flotation.

Flotation of calcite from unfiltered GLD

The flotation of calcite from unfiltered GLD was studied in Trial 15. The main elements in the feed and the flotation fractions are shown in Figure 25 and Table 18.



Figure 25. Concentrations of main elements in the feed and the flotation fractions in Trial 15

| Element | Feed | Calcite fraction | Waste fraction |
|---------|--------|------------------|----------------|
| | mg/kg | mg/kg | mg/kg |
| Ca | 137000 | 161000 | 109000 |
| С | 73498 | 91727 | 68088 |
| Mg | 61600 | 53900 | 60700 |
| S | 63000 | 50000 | 58000 |
| Na | 117000 | 87500 | 120000 |
| Fe | 6700 | 6200 | 6800 |
| AI | 7300 | 6600 | 7300 |
| Р | 830 | 930 | 710 |
| Zn | 4700 | 4100 | 4600 |
| Ва | 1100 | 1700 | 1100 |
| К | 17900 | 12900 | 17900 |
| Cr | 240 | 220 | 280 |
| Ni | 140 | 140 | 160 |
| Se | 18 | 18 | 22 |
| Cd | 15 | 14 | 18 |

Table 18. Concentrations of main elements in the feed and the flotation fractions in Trial 15

The formed calcite froth was very light and almost transparent, which indicates that the recovery of water was high. According to the results in Figure 25 and Table 18, calcium, carbon, phosphorus and barium were recovered in the calcite fraction, while magnesium, sulphur, iron, aluminium,

zinc, potassium, chrome and cadmium are concentrated in the waste fraction. The selectivity of the flotation process was however rather poor; the differences in the concentrations between the fractions and the feed were small, thus the utilization potential of the GLD was not much improved. The results from the experiment indicate that entrainment of undesired particles is even greater in flotation of calcite from unfiltered GLD than in the flotation of unburned carbon. According to the results from the laboratory experiments, the entrainment of the undesired particles could be reduced by decreasing the recovery rate and shorten the flotation time.

Flotation of calcite from the pre-coat filtered GLD

The flotation experiments with pre-coat filtered GLD were carried out during the last weeks of the experiment period. The results from the previous pilot-scale experiments indicated that most of the harmful substances, including HTEs, are concentrated in the tailings, thus flotation of calcite according to the two-step method was studied as a separation technique for the pre-coat filtered GLD. The performed batch test is illustrated in Figure 26 and the concentrations of the main elements in the feed and the flotation fractions are presented in Table 19.



Figure 26. Schematic illustration of the flotation of calcite from pre-coat filtered GLD.

Table 19. Concentrations of main elements in the feed and the flotation fractions in the flotation of calcite from the pre-coat filtered GLD

| Element | Feed | Calcite fraction | Waste fraction |
|---------|--------|------------------|----------------|
| | mg/kg | mg/kg | mg/kg |
| Са | 248000 | 317000 | 273000 |
| С | 91937 | 110198 | 87962 |
| Mg | 44800 | 20800 | 52800 |
| S | 18000 | 15000 | 22000 |
| Na | 6600 | 6500 | 4600 |
| Fe | 5300 | 2500 | 6400 |
| AI | 5000 | 4200 | 6000 |
| Р | 4100 | 3800 | 4100 |
| Zn | 3800 | 1700 | 4500 |
| Ва | 1200 | 1700 | 1100 |
| К | 440 | 410 | 300 |
| Cr | 200 | 79 | 210 |
| Ni | 120 | 50 | 120 |
| Se | 16 | 5 | 18 |
| Cd | 15 | 6 | 16 |

The flotation of calcite from pre-coat filtered GLD gave promising results. According to the results from the batch test, the concentration of calcium in the calcite fraction increased with 22% to a concentration of 31.7%, while the concentrations of the HTEs reduced to approx. a third from their initial concentration. However, the results from the batch test are not completely accurate due to technical problems during the preparation of the slurry. Due to the clayish and dense nature of the filtered GLD, most of the GLD was not dissolved in the water and had to be removed from the process, causing a decrease in the slurry density. The dry solids content of the feed was only 23.4 g/l (2.4%), which may have improved the selectivity of the flotation process.

10.4.3 Continuous Tests

The effect of the continuous feed on the qualities of the flotation fractions in flotation of unburned carbon and carbon-calcite from unfiltered GLD was studied in Trials 11-14. The process data and the results from the flotation tests are presented in Table 20.

Table 20. Process data from Trials 11-15

| Trial | Flotation method | GLD in the feed % | Hexadecane ml/l | DF 250 ml/l | Tall oil ml/l | C in feed % | Ca in feed % |
|-------|------------------|----------------------|--------------------|----------------|------------------|----------------|-----------------|
| 11 | carbon | 50-70 | 0.05 | 0.2 | - | 14 | 7.2 |
| 13 | carbon-calcite | 50-70 | 0.1 | 0.4 | 0.01 | 19.1 | 8.53 |
| 14 | carbon-calcite | 50-70 | 0.1 | 0.4 | 0.01 | 12.4 | 7.44 |
| 15 | carbon-calcite | 50-70 | 0.1 | 0.4 | 0.01 | 9.55 | 6.76 |

Flotation of unburned carbon from unfiltered GLD

The effects of the continuous feed on flotation of unburned carbon from unfiltered GLD were studied in Trial 11. The trial was carried out during 5 hours and samples from the feed, concentrate and the tailings were collected hourly during the flotation process. The average concentrations of the main elements in the feed and the flotation fractions are presented in Figure 27 and Table 20.



Figure 27. Average concentrations of the main elements in the feed and the flotation fractions in Trial 11

| Element | Feed (100 m-%) | Calcite fraction (80-90 m-%) | Waste fraction (10-20 m-%) |
|---------|-------------------|---------------------------------|-------------------------------|
| | mg/kg | mg/kg | mg/kg |
| Zn | 6050 | 6725 | 3775 |
| Cr | 273 | 303 | 170 |
| Ni | 135 | 147.5 | 100 |
| Se | 20 | 22.25 | 13.5 |
| Cd | 25.75 | 28.5 | 15.75 |

Table 21. Average concentrations of the HTEs in the feed and the flotation fractions in Trial 11

The results from Trial 11 indicate that the recovery of calcium is high in proportion to the recovery of carbon when the concentration of the total carbon in the feed is low. Contrary to the results from the laboratory experiments, in which sulphur and HTEs were floated to the carbon fraction in flotation of unburned carbon, most of the HTEs and sulphur were concentrated in the carbonate fraction. The differences in the results may be due to the high turbulence in the laboratory cell, which may have lifted up light HTEs particles to the float fraction. The specific air flow rate in the laboratory cell was 0.625 I/min, while the one in the pilot cell was 0.016 I/min. The lower concentrations of calcium in the samples of the tailings from the pilot-scale experiments can also be explained by the fact that most of the coarse calcium particles were trapped in the cell due to sanding. In the laboratory experiments, thus the coarse calcium particles influenced the results. According to the results from Trial 11, the flotation time should be decreased to maximize the recovery of unburned carbon and the selectivity of the flotation process. The effects of the variations in the feed and the stability of the continuous flotation test are studied in Figure 28.



Figure 28 Concentrations of total carbon in the feed and the flotation fractions in Trial 11 during different time intervals

According to the results from Trial 11, the concentration of total carbon in the feed was almost constant during the whole trial, while the concentration of calcium increased slightly in the end of the flotation test. The variations in the feed properties during the trial did not affect considerably the overall quality of the carbonate fraction. The effects of the flotation process on the recovery of other elements present in the GLD are studied in Figure 29.



Figure 29. Concentrations of the main elements in the carbon fraction in Trial 11 during different time intervals

The results from both the batch and continuous pilot-scale experiments indicate that both carbon and calcium are recovered in the float fraction in the flotation of unburned carbon, while HTEs, sulphur and magnesium are concentrated in the tailings. According to these findings, it is recommendable to float the from utilization perspective valuable calcites to the float fraction.
Since the studied unfiltered GLD contained less than 1% of floatable non-carbonated carbon, the flotation of carbon-calcite is suggested for the flotation method.

Flotation of carbon-calcite from unfiltered GLD

The flotation of carbon-calcite from unfiltered GLD was studied in Trials 13 and 14. The results from the trials are shown in Appendix 7. Trial 13 was started with flotation of carbon in aim to study the effects of the addition of tall oil. The collection of the concentrate was started one hour after the formation of the carbon-calcite froth to assure that the slurry from the carbon flotation step had left the process. Consequently, four fractions including, carbon, carbonate, carbon-calcite and the waste fraction were produced during the experiments. The results from Trial 13 are shown in Figure 30 and Table 22.



Figure 30. Concentrations of the main elements in the feed and the flotation fractions in Trial 13

| Element | Feed mg/kg | Carbon fraction mg/kg | Carbonate fraction mg/kg | Carbon-calcite fraction mg/kg | Waste fraction mg/kg |
|---------|---------------|-----------------------------|--------------------------------|-------------------------------------|----------------------------|
| Zn | 3900 | 3700 | 4300 | 4150 | 4450 |
| Ва | 900 | 1100 | 850 | 1100 | 800 |
| Cr | 150 | 140 | 170 | 145 | 180 |
| Ni | 110 | 110 | 120 | 110 | 130 |
| Se | 11 | 9.7 | 11 | 10 | 12 |
| Cd | 21 | 18 | 22 | 20 | 24 |

Table 22. Concentrations of the main HTEs in the flotation fractions in Trial 13

The selectivity of the flotation of carbon-calcite from unfiltered GLD was even poorer in the continuous tests compared to the batch tests. According to the results from Trial 13, the carbon-calcite fraction had almost the same chemical composition as the feed. The poor selectivity was due to the low concentrations of unburned carbon combined with the high concentrations of water soluble compounds in the feed. Additionally, the flotation process was affected by problems in the controlling of the slurry level. In order to maximize the recovery of calcium to the carbon-calcite fraction and minimize the loss of calcium to the waste fraction, the tailings outflow was kept between 5-10 l/min, corresponding 15-30% of the feed inflow. Due to the low tailings outflow rate, the tailings outflow pipe was continuously clogged by settled coarse particles, causing overflow of the slurry to the concentrate container thus decreasing selectivity of the carbon-calcite fraction.

The elemental compositions of the filtrates of the flotation fractions were studied in order to determine whether the flotation process will affect the filtration of the dregs and the quality of the weak liquor, thus the chemical recovery. The effects of the flotation process on the filterability were examined by comparing the filtrates from the unfiltered GLD to the filtrates of the flotation fractions. The main elements of the filtrates from the flotation fractions from Trial 13 and the unfiltered GLD are presented in Table 23.

| Element | Unfiltered GLD mg/kg | Feed mg/kg | Carbonate fraction mg/kg | Carbon-calcite fraction mg/kg | Waste fraction mg/kg |
|---------|----------------------------|---------------|--------------------------------|-------------------------------------|----------------------------|
| Na | 54000 | 44600 | 45700 | 47800 | 48500 |
| S | 22000 | 17000 | 17000 | 16000 | 16000 |
| К | 9600 | 7500 | 7700 | 7950 | 8100 |
| Са | 3.6 | 2 | 1.7 | 1.75 | 1.7 |
| Mg | 0.81 | 0.4 | 0.74 | 0.315 | 0.7 |
| Ва | 1.2 | 0.63 | 0.65 | 1.155 | 1.8 |
| Zn | 0.056 | 0.0043 | 0.071 | 0.0405 | 0.074 |
| Cr | 0 | 0 | 0 | 0 | 0 |
| Ni | 0 | 0.016 | 0.015 | 0.0225 | 0.016 |
| Se | 0 | 0 | 0 | 0 | 0 |
| Cd | 0 | 0 | 0 | 0 | 0 |

Table 23. Concentrations of the main elements in the filtrates of the flotation fractions in Trial 13

Due to the water addition in the flotation process, the concentrations of the different elements were significantly lower in the filtrates of the flotation fractions than in the filtrate of the untreated unfiltered GLD. Generally, the filtrate of the waste fraction had higher elemental concentrations than the filtrate of the carbon-calcite fraction, which may be due to the lower water content combined with the higher concentrations of certain elements in the waste fraction. In some cases the flotation of carbon-calcite may improve the quality of the produced weak liquor, since harmful elements including, zinc and magnesium are leaving the chemical cycle with the waste fraction. However, also sodium is lost in the waste fraction, which affects the chemical recovery negatively.

10.5 Error Sources in the Flotation Tests

The error sources in the batch and the continuous tests are discussed independently. The error sources from the sample handling are discussed in chapter 9.3.

Performance of Outotec TankCell®

The Outotec TankCell[®] pilot cell performed well in the batch tests, in which the concentrations of total carbon were above 10%. The formation of the carbon or carbon-calcite froth started with

relatively low tip speed (4.2 m/s) and air flow rates (0.94 m³/min), which proves that the FloatForce[®]- mechanism is effective in creating bubble-particle attachments.

The design of the pilot cell was not suitable for the planned continuous tests, in which the slurry residence time was optimized to be 30 min. The slurry feed rate was 33 l/min, while the tailings outflow rate varied between 5 and 25 l/min depending on the flotation method. The pilot, which slurry level is controlled through adjustment of the tailings outlet valve, was clearly design for higher slurry feeds. To achieve a tailings outflow rate below 20 l/min the tailings outflow valve was opened with only a few percent. During the continuous tests coarse particles were settled at the bottom of the cell blocking the tailings outlet pipe, thus causing overflow of the slurry to the concentrate container. The overflow of the slurry was prevented by opening the tailings outflow valve every five minutes with a tenth of a percentage during the flotation experiment.

Batch tests

The test results were most affected by errors caused by the sampling. Depending on the flotation method, 150-600 litre of concentrate was produced during the 20 minutes of the flotation. Due to the high production of concentrate, samples were collected only during a short period of time at the beginning of the flotation tests. Since the recovery and grade of the concentrate changes significantly during the flotation process in semi-batch tests, the concentrate samples do not represent the overall quality of the concentrate. The samples of the tailings were collected after 20 minutes of flotation, hence the tailings were expected to be free from floatable particles. On the other hand, most of the calcium rich coarse particles in the slurry were settled on the cell floor, thus not recovered with the tailings. The absence of the coarse particles in the samples of the tailings may also explain the low concentrations of calcium in the flotation fractions compared to the feed. Measurements errors and errors caused by the addition of make-up water may have influenced the test results. The unfiltered GLD was measured and diluted directly into the cell, thus the exact amount of the unfiltered GLD was difficult to determine. The addition of water decreases the dry solids content and the concentrations of reagents in the slurry, which both have significant impacts on the flotation performance. Additionally, the temperature of the slurry varied among the trials due to the varied amount of water used in the trials.

Continuous tests

The main error in the continuous tests was caused by the problems in the control of the slurry level. During the continuous tests, slurry was overflowed to the concentrate container, thus causing a decrease in the grade of the concentrate. Like in the batch tests, coarse calcium particles were not recovered in the tailings.

10.6 Utilization Potential of the Flotation Fractions

The utilization of the carbon, carbon-calcite and calcite fractions depends on their chemical compositions and behaviour in different conditions and environments. In this thesis the GLD and the flotation fractions were analysed only for their total concentrations of the main elements present in the GLD, thus the improvements in the utilization potential of the different fractions are examined according to the decrease of harmful substances in them. In order to determine the real utilization potential of the flotation fractions analysis of the total concentrations of soluble HTEs are required. Additionally, the flotation fractions should be analysed for their physical properties. Legislation governing the utilization of by-products and waste are discussed in Chapter 5.

10.6.1 Pre-coat Filtered GLD from the Imatra Mills

The elemental composition of the pre-coat filtered GLD from the Imatra Mills are presented in Chapter 7. The pre-coat filtered GLD from the Imatra Mills contain many elements that are beneficial for fertilizers. The GLD are highly alkaline and have high neutralizing capacity with high concentration of calcium (24.2%), thus GLD could be utilized e.g. as a soil improver or pH buffer for acidic soils. Additionally, the GLD contain small amounts of nutrients originated from the wood including phosphorous (0.23%). However, also HTEs are concentrated in the GLD, of which cadmium and zinc may exceed the limit values according to their total concentrations set for fertilizer products in the Decree (24/11).

10.6.2 Carbon Fraction from the Flotation of Unfiltered GLD

The volume of the carbon fraction depends on the concentrations of unburned carbon in the GLD. The concentration of unburned carbon in unfiltered GLD from the Imatra Mills was determined to be less than 1%. To avoid the recovery of calcite to the carbon fraction, the volume of the concentrate was optimized to be approx. 5% of the volume of the feed. The concentrations of the main elements in the carbon fractions from the continuous tests 11 are presented in Figure 27 and Table 21 in Chapter 10.4.3. According to the results from the continuous pilot-scale tests, the

concentrations of total carbon increases approx.40-50% from its initial concentration, while the concentrations of HTEs are significantly reduced. The concentrations of secondary nutrients (Ca, Mg, S and K) in the carbon fractions are above the requirements for nutrients for inorganic by-products (1A6) set in Decree 24/11. However, the minimum requirements for primary nutrients (P + K >2 %) are not reached in the carbon fraction, thus phosphorous or potassium need to be added to the fraction. Additionally, in order to determine the utilization potential of the carbon fraction, analyses of the concentrations of soluble HTEs are required.

Another option is to burn the washed and dried carbon fraction in the bark boiler, which will reduce the total quantity of waste needing landfill disposal. In the combustion process, the unburned carbon in the carbon fraction is combusted while the carbonates are decomposed to metal oxides.

10.6.3 Carbon-calcite Fraction from the Flotation of Unfiltered GLD

To assure that most of the calcites are recovered in the float fraction, the volume of the carboncalcite fraction was optimized to be 60-70% of the volume of the feed. In the ideal situation, the concentrate contains only unburned carbon and calcite. The pilot-scale continuous tests were not successful, thus the separated carbon-calcite fraction had almost the same elemental composition as the feed. As recognized in the laboratory and the pilot-scale experiments, the selectivity increases with higher concentrations of total carbon, thus better results could be achieved with unfiltered GLD from another mill. The produced carbon-calcite fraction could be filtered with the existing pre-coat filter at the mill, which also increases the concentrations of calcite and reduces the concentrations of sodium, potassium and hazardous trace metals. In the flotation of carboncalcite, it can be presumed that all unburned carbon present in the GLD is floated with carboncalcites to the concentrate. Unburned carbon may limit the utilization potential of the material, thus combustion of the material in aims to remove the unburned carbon may be advantageous in some cases. Carefully washed and pre-coat filtered material could be possible to burn in the lime kiln. Combustion involves several risks, and especially sodium, potassium and magnesium compounds may cause problems in the combustion. Additionally, some of the HTEs (Cd, Pb, Zn) present in the carbon-calcite material may vaporize in the high temperatures in the lime kiln. After the combustion, the remaining material constitutes of calcium oxide and oxides of other metals. The combusted material is dry enough for e.g. production of asphalt. Due to the low

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concentrations of unburned carbon in the studied unfiltered GLD, the concentration of total carbon was not significantly increased in the carbon-calcite fraction, thus combustion of the fraction might not have been necessary. A washed and filtered carbon-calcite material could be suitable for production of cement and bricks on condition that the limit values set for certain metal elements and chlorine are not exceeded.

10.6.4 Calcite Fraction from the Flotation of Pre-coat Filtered GLD

The flotation of pre-coat filtered GLD was carried out only in one semi-batch pilot-scale test, thus the mass balance of the process is not completely accurate. The samples of the concentrate were collected during 5-10 minutes of the flotation process, while the samples of the tailings were collected after 20 minutes of the flotation. The volume of the calcite fraction was determined to be above 50% of the volume of the feed. The results from the test are presented in Table 24.

| | Unfiltered | Food | Calcite | |
|---------|------------|--------|----------|--|
| Element | GLD | reeu | fraction | |
| | mg/kg | mg/kg | mg/kg | |
| Са | 242000 | 248000 | 317000 | |
| С | 94600 | 91937 | 110198 | |
| Mg | 58400 | 44800 | 20800 | |
| S | 27000 | 18000 | 15000 | |
| Na | 13700 | 6600 | 6500 | |
| Fe | 7400 | 5300 | 2500 | |
| AI | 6300 | 5000 | 4200 | |
| Р | 2300 | 4100 | 3800 | |
| Zn | 5500 | 3800 | 1700 | |
| Ва | 1080 | 1200 | 1700 | |
| К | 1800 | 440 | 410 | |
| Cr | 350 | 200 | 79 | |
| Ni | 140 | 120 | 50 | |
| Se | 15 | 16 | 5 | |
| Cd | 25 | 15 | 6 | |

Table 24. Concentrations of the main elements in original GLD from the pre-coat filter, feed and the calcite fraction

According to the results, the concentration of calcium in the calcite fraction is increased with 22% to a concentration of 31.7%. Additionally, the concentrations of the HTEs are reduced to approx. a third from their initial concentration. The calcite fraction could be suitable for raw material for production of cement, plaster, bricks and asphalt. However, the material must fulfil certain

technical and environmental criterion set by the legislation and the application. Important technical criterions include the particle size and particle size distribution, variations in the quality and the degree of moisture of the material. The importance of the CE-marking for construction materials is growing, which could complicate the utilization of the calcium fraction, since a CE-marked product must fulfil the requirements set by the hENs or ETA. The legislative requirements for construction products are discussed in Chapter 5.2.

The flotation process works also as an additional dregs washer, since great amounts of water is added to the filtered GLD in order to obtain a slurry density of 50-60 g/l. The concentrations of the water soluble elements (Na, K and S) in the calcite fraction were 2-5 times lower than those in the original GLD. Due to the lower concentrations of sodium, potassium, magnesium and HTEs in the calcite fraction, the combustion of the calcite fraction in the lime kiln is safer than the combustion of the original GLD. The combusted calcite fraction could be pure enough to be recycled back in the lime cycle. The calcite fraction could be used as a liming agent or soil improver. The concentrations of the secondary nutrients in the calcite fraction are above the minimum requirements for inorganic by-products used as fertilizers. However, the minimum requirements for primary nutrients were not reached, thus phosphorous or potassium would be needed to be added to obtain the required concentrations. Additionally, the market and demand for liming agents are limited, while many industries produce similar calcium containing by-products.

10.7 Scale-up Potential of the Flotation Process

According to the results from the pilot-scale flotation experiments, the froth flotation technique developed in the VISA project is not suitable for treatment of the studied unfiltered GLD. The most promising results were achieved from the batch experiment, where calcites were separated from pre-coat filtered GLD from the Imatra Mills according to the two-step method. In the performed batch test, the concentration of calcium was increased with 22%, while the concentrations of HTEs were concentrated in the waste fraction. The pre-coat filtered GLD differ significantly from the unfiltered GLD according to its chemical composition. Contrary to the unfiltered GLD, the pre-coat filtered GLD consist mainly of water insoluble calcium and magnesium carbonates, while the concentration of unburned carbon is approx. 12% of the total carbon. According to these findings,

carbon and calcite could be separated from pre-coat filtered GLD by using the studied flotation methods.

The results from the batch test performed with pre-coat filtered GLD are however not completely accurate due to technical problems during the preparation of the slurry. The clayish GLD was not completely dissolved in the water, thus the dry solids content of the slurry was only 23.4 g/l. From a scale-up perspective, slurry densities this low are not economically sustainable due to the high water and energy consumptions. According to the results from the continuous tests performed with unfiltered GLD, the selectivity decreases with a continuous feed. In order to determine the scale-up potential of the flotation process, continuous experiments with higher slurry density are required.

The flotation of unburned carbon and calcite from pre-coat filtered GLD is technically challenging. Firstly, fresh pre-coat GLD need to be dissolved in water in order to obtain a dry solid content of approx. 50-60 g/l, which is basically the same dry solid content as the GLD has before the pre-coat filtration. Secondly, depending on the flotation conditions, including flotation residence time, feed rates and slurry density, 3-4 flotation cells are needed in order to avoid short circuiting. Thirdly, the produced flotation fractions require 2-3 filters for removal of water.

11. CONCLUSION

A froth flotation procedure developed in the VISA project, where unburned carbon and hazardous trace elements (HTEs) are separated from GLD, was studied with laboratory and pilot-scale experiments. The flotation experiments were conducted according to two methods, referred as the one-step method and the two-step method, in which the unburned carbon was separated alone or together with calcite to a froth fraction, leaving the from utilization perspective harmful substances in the tailings.

The pilot-scale experiments were carried out with a 1 m³ Outotec TankCell pilot cell at the causticising plant at Stora Enso Imatra Mills using the unfiltered GLD from the dregs clarifier and pre-coat filtered GLD. Since the Outotec TankCell[®] pilot cell uses the same technology as the industrial scale TankCells[®] units, the results from the pilot-scale tests gives a good insight about the scale-up potential of the flotation process.

The flotation of unburned carbon and carbon-calcite was greatly affected by the composition of the GLD. The results from the pilot-scale flotation experiments indicate that carbon and calcite can be efficiently separated from pre-coat filtered GLD that contains primarily water insoluble compounds and has relatively high total carbon content. According to these results, froth flotation could be used for separation of carbon and calcite from GLD with similar chemical composition. However, the daily variations in the composition of the GLD may complicate the optimization of the flotation process, since the machine variables and the reagent doses are determined according to the slurry properties. Consequently, the qualities of the flotation fractions vary according to the elemental composition of the GLD, which complicates the utilization of these fractions.

The flotation of unburned carbon and calcite from unfiltered GLD was studied as a first option, following was observed during the laboratory and pilot-scale experiments:

 Sufficient concentrations of unburned carbon in the unfiltered GLD are required for formation of carbon and carbon-calcite froth. Better selectivity and recoveries were achieved with unfiltered GLD slurries with high concentrations of total carbon

- In flotation of unburned carbon from unfiltered GLD, the reduction of total carbon was between 0 and 30%, depending on the concentrations of total carbon in the feed. Since the concentration of unburned carbon in the studied unfiltered GLD was only approx. 8% of the total carbon, it can be assumed that most of the unburned carbon was recovered in the carbon fraction.
- The selectivity of the flotation of unburned carbon and carbon-calcite from the unfiltered GLD was poor due to the low concentrations of unburned carbon combined with the high concentrations of water soluble compounds in the unfiltered GLD. The poor selectivity in the continuous tests might have been partly due to problems in controlling the slurry level, which caused overflows of the slurry to the concentrate container.

The flotation of calcite from the pre-coat filtered GLD gave the most promising results as the concentrations of calcium was increased with 22% to a concentration of 32%, while the concentrations of HTEs and NPEs were decreased to less than a third from their initial concentrations. The results from the experiment are not completely accurate due to technical problems in the preparation of the slurry. Additionally, the experiment was carried out according to the batch principle, thus continuous tests are required in order to determine the scale-up potential of the flotation process.

In this thesis the flotation fractions were analysed only for their total concentrations of the main elements present in the GLD, thus the improvements in the utilization potential of the different fractions were examined according to the decrease of harmful substances in them. In order to determine the real utilization potential of the flotation fractions, analyses of the total concentrations of soluble HTEs are required. From the formed flotation fractions, the calcite fraction from the pre-coat filtered GLD had the greatest utilization potential. The calcite fraction could be possible combusted in the lime kiln and recycled back into the lime cycle. The calcite fraction could also be suitable for production of construction products, such as bricks and cement. However, the growing importance of the CE-marking for construction materials may complicate the utilization.

12. SUGGESTIONS FOR FURTHER STUDIES

According to the results from the pilot-scale experiments, froth flotation is most suitable for treatment of pre-coat filtered GLD, which contains primarily water insoluble compounds and has relatively high carbon content. According to these findings, flotation of unburned carbon and calcite should be studied for GLD with similar elemental compositions.

The flotation of unburned carbon and calcite from the pre-coat filtered GLD is challenging due to the clayish nature of the GLD. In this thesis the flotation of calcite from pre-coat filtered GLD was studied only in one batch test in which the slurry density was too low for industrial application. In order to determine the scale-up potential of the flotation process, continuous experiments with higher slurry density should be performed.

The flotation of carbon and calcite from pre-coat filtered GLD requires in addition to the flotation machine(s), a mixing tank for the preparation of the slurry and 2-3 filters for water removal from the flotation fractions. The investment and operational cost of the flotation procedure should be investigated and compared with the current GLD handling.

The waste quantities requiring landfill disposal should be minimized primarily by preventing the production of the waste. By using a filter press instead of the conventional pre-coat filter for filtration of GLD, the waste production can be reduced down to a half of the current amount. However, the operational costs of the filter presses are relatively high due to the poor filterability of the GLD.

Additionally, the utilization potential of the untreated GLD should be investigated by analysing the concentrations of the soluble HTEs. Due to the complicated legislation and directives governing the utilization of waste and by-products it may be difficult to find a user for the treated GLD. The market and demand for inorganic calcium containing products should be surveyed.

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Appendix 1 Kaukopää causticizing plant

Appendix 2 Analysis methods used in the laboratory analysis of the GLD samples

The pHs for the GLD samples were determined according to European standard SFS 3021:1979. The dry solids contents were determined according to European standard SCAN-N 22:77. The elemental analyses for the GLD samples and their soluble and insoluble fractions were conducted by Thermo Scientific IRIS intrepid II XDL inductively coupled plasma-atomic emission spectrometer (ICP-AES) after microwave assisted acidic wet digestion (H₂O₂ and HNO₃) from the original composite samples and the filtrates and the residues of thoroughly washed and filtered (S&S black ribbon filter) composite samples. The sulphides were determined according to European standard SCAN-N 31:94. The water soluble CO₃²⁻ were determined according to European standard SCAN-N 32:1998. The concentrations of organic elements were determined with Thermo Flash 2000 CHNS-analyser of oven dried powdered composite samples. The non-CO₃²⁻-C were determined with the Thermo Flash 2000 CHNS-analyser to dried composite samples, which were acidified with hydrochloric acid and subsequently dried (105 °C). Additionally, the mineralogical composition of the oven dried powdered unfiltered GLD sample was analysed with with a Philips X'Pert MPD X-ray diffractometer and the powder method.



Appendix 3 X-ray diffraction of unfiltered GLD from Stora Enso Imatra Mills

| EXPERIMENT 1 Pulp concistency 52,5 g/l | | | | | | | | | | |
|--|--------|---------------|-----------|---------|-----------|---------|-----------|--|--|--|
| Sampla | Zero | Carbon | Carbonate | Carbon | Carbonate | Carbon | Carbonate | | | |
| Sample | sample | 1 | 1 | 2 | 2 | 3 | 3 | | | |
| Hexadecane/DF250 | 0 | 0,1/0,4 | 0,1/0,4 | 0,1/0,4 | 0,1/0,4 | 0,2/0,8 | 0,2/0,8 | | | |
| NaHCO3 g/l | 2,2 | 2,2 | 2,2 | 2,2 | 2,2 | 2,2 | 2,2 | | | |
| C % | 11,7 | 22,9 | 10,4 | 25,2 | 10,5 | 20,0 | 10,5 | | | |
| S % | 2,30 | 3 <i>,</i> 30 | 2,20 | 5,30 | 2,30 | 4,10 | 2,00 | | | |
| Ca % | 23,4 | 17,3 | 22,2 | 14,9 | 24,8 | 17,4 | 23,5 | | | |
| К % | 0,54 | 0,91 | 0,65 | 1,69 | 0,59 | 1,33 | 0,56 | | | |
| Mg % | 3,93 | 4,55 | 3,29 | 4,48 | 3,39 | 4,21 | 3,03 | | | |
| Na % | 3,85 | 5 <i>,</i> 66 | 4,72 | 10,50 | 4,37 | 8,59 | 4,12 | | | |
| Zn % | 0,27 | 0,31 | 0,22 | 0,33 | 0,23 | 0,29 | 0,20 | | | |
| Ba mg/kg | 470 | 410 | 470 | 360 | 490 | 400 | 500 | | | |
| Cd mg/kg | 12 | 14 | 11 | 14 | 10 | 13 | 9,7 | | | |
| Cr mg/kg | 120 | 140 | 110 | 140 | 100 | 130 | 98 | | | |
| Ni mg/kg | 45 | 66 | 40 | 71 | 36 | 60 | 38 | | | |
| Se mg/kg | 5,3 | 6,5 | 4,8 | 1,2 | 4,2 | 6,2 | 4,1 | | | |
| Al mg/kg | 2600 | 2900 | 2900 | 2400 | 2400 | 2200 | 2200 | | | |
| As mg/kg | <0,75 | <0,75 | <0,75 | <0,75 | <0,75 | <0,75 | <0,75 | | | |
| Cu mg/kg | 220 | 250 | 250 | 230 | 190 | 180 | 170 | | | |
| Fe mg/kg | 3300 | 3700 | 3600 | 3500 | 3000 | 2900 | 2700 | | | |
| Mn mg/kg | 16100 | 18900 | 25500 | 22000 | 18500 | 19100 | 15700 | | | |
| Mo mg/kg | 0,83 | 1,3 | 1,8 | 1,6 | 0,95 | 0,85 | 0,86 | | | |
| Sb mg/kg | 1,1 | 1,4 | 1,6 | 1,4 | 1,1 | <1,0 | 1 | | | |
| Si mg/kg | 200 | 290 | 460 | 270 | 150 | 150 | 150 | | | |
| P mg/kg | 2300 | 1200 | 1100 | 1800 | 1500 | 2200 | 2300 | | | |

Appendix 4 Laboratory experiments: flotation of unburned carbon from unfiltered GLD

| | EXPERIMENT 2 Pulp concistency 60 g/l | | | | | | | | | | | | | |
|--------------|--------------------------------------|------|----------|----------|----------|---------|--------|-------|---------|----|---------|---------------|----------|----------|
| | | Zer | o | Carbo | n | Carbona | at Car | bon | Carbona | at | Carbon | Carbona | Carbon | Carbonat |
| Sample | | sami | ple | 4 | | e 4 | | 5 | e 5 | | 6 | e 6 | 7 | e 7 |
| Hexadecane/D | F250 | 0 | | 0,1/0 | 4 | 0,1/0,4 | 0,1 | /0,4 | 0,1/0,4 | ŀ. | 0.2/0.8 | 0.2/0.8 | 0.2/0.8 | 0.2/0.8 |
| NaHCO3 g | / | 2,2 | 2 | 2,2 | | 2,2 | 2 | 2,2 | 2,2 | | 2,2 | 2,2 | 3.2 | 3.2 |
| C % | - | 10. | .8 | 16.8 | | 9.9 | 14 | 4.3 | 9.8 | | 20.2 | 10.2 | 18.1 | 10.4 |
| S % | | 3,8 | 0 | 4,70 | 1 | 3,30 | 4 | ,60 | 3,70 | | 4,70 | 2,90 | 4,60 | 2,00 |
| Ca % | | 19, | 9 | 19,2 | | 26,7 | 1 | 8,4 | 24,4 | | 16,0 | 23,9 | 16,7 | 26,8 |
| К % | | 1,2 | 1 | 1,47 | | 1,04 | 1, | ,59 | 1,19 | | 1,66 | 0,86 | 1,63 | 0,43 |
| Mg % | | 3,1 | 7 | 4,76 | | 3,25 | 4 | ,30 | 3,07 | | 4,27 | 3,33 | 4,50 | 3,52 |
| Na % | | 7,9 | 4 | 9,30 | 1 | 7,61 | 10 | ,30 | 8,30 | | 10,10 | 6,00 | 10,10 | 3,35 |
| Zn % | | 0,1 | 8 | 0,27 | | 0,19 | 0, | ,24 | 0,18 | | 0,25 | 0,19 | 0,26 | 0,21 |
| Ba mg/kg | | 39 | 0 | 490 | | 480 | 4 | 50 | 580 | | 420 | 480 | 430 | 520 |
| Cd mg/kg | | 8,1 | 1 | 12 | | 7,7 | 1 | 11 | 7,6 | | 11 | 8,5 | 11 | 9,5 |
| Cr mg/kg | | 10 | 0 | 150 | | 95 | 1 | 30 | 94 | | 130 | 110 | 140 | 120 |
| Ni mg/kg | | 30 |) | 47 | | 28 | 3 | 39 | 27 | | 45 | 32 | 46 | 33 |
| Se mg/kg | | 4,1 | 1 | 5,9 | | 3,9 | | 5 | 3,5 | | 5,3 | 4,6 | 5,2 | 4,7 |
| | EXPERIMENT 3 Pulp concistency 55 g/l | | | | | | | | | | | | | |
| | | z | ero | Carb | on | Carbon | at Ca | rbon | Carbon | at | Carbon | Carbona | Carbon | Carbonat |
| Sample | • | sai | mple | 8 | | e 8 | | 9 | e 9 | | 10 | e 10 | 11 | e 11 |
| Hexadecane/I | DF250 | | 0 | 0,1/ | 0,4 | 0,1/0, | 4 0,: | 2/0,8 | 0,2/0,8 | 8 | 0,1/0,4 | 0,1/0,4 | 0,2/0,8 | 0,2/0,8 |
| NaHCO3 g | g/I | 1 | 2,2 | 2, | 2 | 2,2 | | 2,2 | 2,2 | | 3,2 | 3,2 | 3,2 | 3,2 |
| C % | | 1 | 1,6 | 20, | 50 | 10,32 | 2 | 4,42 | 9,85 | | 18,12 | 10,15 | 21,82 | 9,85 |
| S % | | 3 | 8,10 | 4,9 | 0 | 2,50 | 3 | 3,10 | 3,10 | | 3,50 | 2,90 | 4,10 | 2,90 |
| Ca % | | 2 | 25,8 | 21 | ,3 | 25,9 | 1 | 19,2 | 25,2 | | 20,2 | 23 <i>,</i> 6 | 15,5 | 24,4 |
| K % | | C |),75 | 0,7 | 3 | 0,65 | 0 | 0,61 | 0,49 | | 0,85 | 0,76 | 1,17 | 0,67 |
| Mg % | | 4 | ,49 | 4,9 | 1 | 3,96 | 4 | 1,83 | 3,94 | | 4,81 | 3,97 | 5,26 | 4,72 |
| Na % | | 5 | 5,59 | 4,8 | 2 | 4,32 | 3 | 3,82 | 5,30 | | 5,01 | 5,14 | 6,98 | 4,54 |
| Zn % | | 0 |),25 | 0,2 | 29 | 0,25 | |),29 | 0,25 | | 0,28 | 0,28 | 0,35 | 0,30 |
| Ba mg/k | g ~ | 5 | 14 | 53 | 0 | 600 | | 12 | 550 | | 520 | 560 | 460 | 550 |
| | 8 7 | 1 | 14 | 16 | <u>^</u> | 9,7 | | 13 | 130 | | 140 | 140 | 14 | 12 |
| Ni mg/kg | 5 J | 1 | 40 | 8 | 7 | 31 | | 62 | 32 | | 86 | 39 | 65 | 39 |
| Se mg/kg | <u> </u> | - | 21 | 6. | 3 | 5.8 | | 7 | 5.6 | | 6.5 | 6.8 | 7.2 | 8.5 |
| | | | | <u> </u> | | EX | PERIME | NT 4 | 1 | | | | Experi | ment 5 |
| Component | Zer | o | | | Car | bonate | Carbor | n | Carbon | | Carbon | Carbon | Float | Tailing |
| | sam | ple | Carbo | n tot. | | tot | (5 min |) (| 10 min) | (| 15 min) | (20 min) | fraction | (waste) |
| C % | 11, | ,4 | 20 |),1 | | 9,9 | 30,1 | | 20,7 | | 15,3 | 13,2 | 11,7 | 9,0 |
| S % | 3,8 | 8 | 4, | 6 | | 3,4 | 14 | | 2,5 | | 3,4 | 3,8 | 3,1 | 3,8 |
| Ca % | 22, | ,7 | 16 | i,2 | | 23,3 | 18,5 | | 23,7 | | 21,2 | 25,5 | 25,8 | 22,7 |
| К % | 1,1 | 8 | 1,2 | 26 | (| 0,94 | 0,86 | | 0,49 | | 0,94 | 0,82 | 0,75 | 1,18 |
| Mg % | 4,2 | 27 | 4,5 | 53 | | 4,1 | 4,69 | | 5,75 | | 5,19 | 6,49 | 4,49 | 4,27 |
| Na % | 7,4 | 4 | 8,5 | 58 | (| 6,54 | 4,55 | | 2,82 | | 5,78 | 5,63 | 5,59 | 0,74 |
| Ni mg/kg | 63 | 3 | 5 | 0 | | 39 | 71 | | 59 | | 54 | 67 | 140 | 63 |
| Se mg/kg | 9,3 | 1 | 5, | 6 | | 7,2 | 6,9 | | 7 | | 7 | 9,4 | 21 | 9,1 |
| Zn mg/kg | 250 | 00 | 26 | 00 | 2 | 2700 | 3200 | | 3200 | | 3100 | 4300 | 2500 | 2500 |
| Ba mg/kg | 55 | 0 | 37 | 70 | | 530 | 410 | | 500 | | 460 | 650 | 590 | 550 |
| Cd mg/kg | 14 | 1 | 1 | 2 | | 11 | 13 | | 15 | | 14 | 18 | 14 | 14 |
| Cr mg/kg | 14 | 0 | 12 | 20 | | 140 | 130 | | 150 | I | 150 | 220 | 140 | 140 |

Appendix 5 Outotec TankCell®

Outotec TankCell[®] is a symmetrical tank formed flotation cell, optimized for flotation of both fines and coarse particles. TankCell[®] units are used worldwide in the mining industry for separating valuable minerals from gangue minerals. The TankCell[®] units are available in a wide size range, the smallest cells on market having an active volume of 5 m³ and the largest 500 m³.

Outotec TankCell[®] is a bottom stirred forced-air flotation cell. The cell can be divided into two sections considered as the contact zone and froth zone. The bottom part of the cell is considered as the contact zone, which functions are to keep the solids in suspension and to provide turbulence conditions for particle-bubble collisions. The air is introduced through a hollow shaft, i.e., impeller to the rotor, which disperse the air stream into small bubbles. Hydrophobic particles are captured by the bubbles forming aggregates in the contact zone, and the particle-bubble aggregates rise by buoyancy towards the froth zone forming a froth phase. The froth phase acts as a cleaning zone, which rejects undesired solids and water, thus improving the grade. The formed froth flows over the concentrate lip into the collection launder. The tailings are flown through the tailings outlet at the bottom of the cell tank.(Malhotra, Taylor et al. 2009) The conceptual operation of the Outotec TankCell[®] is shown in pictures below.





Prototype of Outotec TankCell® (modified from Outotec 2014)

The TankCell[®] units are equipped with the newest FloatForce [®] rotor-stator mechanism which operates according to the forced air principle. The main advantage in the FloatForce[®] mixing mechanism compared to mixing mechanisms used in other flotation cells is the way air is introduced in the slurry. The FloatForce[®] rotor introduces the air to a dedicated area of the impeller, thus the core of the rotor is used only for pumping of the slurry without disturbing mixing efficiency as air is added. By maintaining a high slurry flow through the impeller large amounts of air can be evenly dispersed into the slurry. Additionally, high slurry flow also prevents sanding of the cell bottom. The tank cell design and the rotor design minimise short-circuiting, as the slurry flow is towards the bottom of the cell and the new feed entering is directed towards the mechanism due to the suction action of the rotor. (Malhotra, Taylor et al. 2009; Gronstrand and Kuwaja 2009)

| Appendix 6 Pilot-scale batch experiments: flotation of unburned |
|---|
| carbon from unfiltered GLD |

| Batch experiments, flotation of unburned carbon from unfiltrated GLD trials 1-7 | | | | | | | | |
|--|-----------|--------|--------|---------|---------|--|--|--|
| Trial | Fraction | Carbon | Carbon | Calcium | Calcium | | | |
| mar | ridetion | mg/kg | % | mg/kg | % | | | |
| | Feed | 169388 | 16,9 | 142000 | 14,2 | | | |
| 1 | Carbon | 626167 | 62,6 | 5200 | 0,5 | | | |
| | Carbonate | 115534 | 11,6 | 281000 | 28,1 | | | |
| n | Carbon | 550693 | 55,1 | 5300 | 0,5 | | | |
| Z | Carbonate | 136288 | 13,6 | 165000 | 16,5 | | | |
| | Feed | 196574 | 19,7 | 171000 | 17,1 | | | |
| 3 | Carbon | 281881 | 28,2 | 7400 | 0,7 | | | |
| | Carbonate | 132208 | 13,2 | 215000 | 21,5 | | | |
| 4 | Carbon | 524843 | 52,5 | 5600 | 0,6 | | | |
| | Carbonate | 137369 | 13,7 | 154000 | 15,4 | | | |
| | Feed | 83231 | 8,3 | 175000 | 17,5 | | | |
| 5 | Carbon | 155044 | 15,5 | 125000 | 12,5 | | | |
| | Carbonate | 84606 | 8,5 | 247000 | 24,7 | | | |
| | Feed | 84047 | 8,4 | 162000 | 16,2 | | | |
| 6 | Carbon | 193605 | 19,4 | 117000 | 11,7 | | | |
| | Carbonate | 81888 | 8,2 | 189000 | 18,9 | | | |
| | Feed | 88835 | 8,9 | 199000 | 19,9 | | | |
| 7 | Carbon | 157449 | 15,7 | 175000 | 17,5 | | | |
| | Carbonate | 87975 | 8,8 | 221000 | 22,1 | | | |

| Trial 11, feed | | | | | | | | | |
|---------------------------|---------------------------|---------------|---------|---------|--|--|--|--|--|
| Measured element mg/kg | 60 min | 120 min | 180 min | 240 min | | | | | |
| Ca | 140000 | 135000 | 149000 | 154000 | | | | | |
| С | 78008 | 75013 | 79276 | 77966 | | | | | |
| S | 66000 | 67000 | 65000 | 63000 | | | | | |
| Na | 116000 | 116000 | 113000 | 102000 | | | | | |
| Zn | 6100 | 6100 | 5700 | 6300 | | | | | |
| Ba | 980 | 990 | 960 | 1000 | | | | | |
| К | 18100 | 18400 | 18400 | 11700 | | | | | |
| Cr | 270 | 280 | 260 | 280 | | | | | |
| Ni | 130 | 140 | 130 | 140 | | | | | |
| Se | 21 | 20 | 19 | 20 | | | | | |
| Cd | 26 | 26 | 24 | 27 | | | | | |
| | Trial 11, carbon fraction | | | | | | | | |
| Measured element mg/kg | 60 min | 120 min | 180 min | 240 min | | | | | |
| Ca | 135000 | 146000 | 157000 | 193000 | | | | | |
| С | 205427 | 168576 | 175148 | 109881 | | | | | |
| S | 60000 | 62000 | 55000 | 50000 | | | | | |
| Na | 126000 | 120000 | 104000 | 88400 | | | | | |
| Zn | 2900 | 4100 | 3700 | 4400 | | | | | |
| Ba | 1000 | 1200 | 1200 | 1400 | | | | | |
| К | 22400 | 20800 | 18600 | 14400 | | | | | |
| Cr | 130 | 180 | 170 | 200 | | | | | |
| Ni | 90 | 110 | 100 | 100 | | | | | |
| Se | 11 | 13 | 14 | 16 | | | | | |
| Cd | 12 | 17 | 16 | 18 | | | | | |
| | Trial 11, carb | onate fractio | n | | | | | | |
| Measured element mg/kg | 60 min | 120 min | 180 min | 240 min | | | | | |
| Ca | 146000 | 134000 | 135000 | 146000 | | | | | |
| С | 70638 | 66465 | 69641 | 69791 | | | | | |
| S | 67000 | 74000 | 71000 | 68000 | | | | | |
| Na | 105000 | 116000 | 120000 | 108000 | | | | | |
| Zn | 6900 | 7100 | 6400 | 6500 | | | | | |
| Ва | 970 | 960 | 940 | 990 | | | | | |
| К | 16300 | 18800 | 19700 | 17900 | | | | | |
| Cr | 310 | 310 | 290 | 300 | | | | | |
| Ni | 150 | 150 | 140 | 150 | | | | | |
| Se | 22 | 23 | 23 | 21 | | | | | |
| Cd | 29 | 30 | 27 | 28 | | | | | |

Appendix 7 Pilot-scale continuous experiments: flotation of unburned carbon from unfiltered GLD

| Trial 13, continious test-flotation of calcite | | | | | | | | | | |
|--|--------|--------|-----------|--------------------|----------------|----------------|----------------|--|--|--|
| Fractions, solids | | | | | | | | | | |
| Measured element mg/kg | Feed | Carbon | Carbonate | Carbon-calcite | Carbon-calcite | Waste fraction | Waste fraction | | | |
| Са | 182000 | 164000 | 156000 | 189000 | 172000 | 149000 | 139000 | | | |
| С | 81744 | 132787 | 71985 | 90731 | 71399 | 87155 | 67991 | | | |
| Mg | 56600 | 50400 | 60700 | 50900 | 54100 | 61300 | 65300 | | | |
| S | 54000 | 53000 | 60000 | 50000 | 51000 | 60000 | 63000 | | | |
| Na | 92400 | 88400 | 99700 | 84400 | 87600 | 103000 | 93700 | | | |
| Zn | 3900 | 3700 | 4300 | 3800 | 4500 | 4300 | 4600 | | | |
| Ва | 900 | 1100 | 850 | 1100 | 1100 | 820 | 780 | | | |
| К | 14300 | 14300 | 15100 | 13100 | 13600 | 16100 | 16500 | | | |
| Cr | 150 | 140 | 170 | 140 | 150 | 170 | 190 | | | |
| Ni | 110 | 110 | 120 | 110 | 110 | 120 | 140 | | | |
| Se | 11 | 9,7 | 11 | 9,5 | 10 | 11 | 13 | | | |
| Cd | 21 | 18 | 22 | 19 | 20 | 23 | 25 | | | |
| | | | Fr | actions, filtrates | | | | | | |
| Measured element Unfiltrated | | Food | Carbon | Carbonata | Carbon calcita | Carbon calcita | Wasto fraction | | | |
| mg/kg | GLD | reeu | Carbon | Carbonate | Carbon-calcite | Carbon-calcite | waste fraction | | | |
| Na | 54000 | 44600 | 44300 | 45700 | 50600 | 45000 | 48500 | | | |
| S | 22000 | 17000 | 16000 | 17000 | 17000 | 15000 | 16000 | | | |
| К | 9600 | 7500 | 7500 | 7700 | 8400 | 7500 | 8100 | | | |
| Ca | 3,6 | 2,0 | 1,9 | 1,7 | 1,8 | 1,7 | 1,7 | | | |
| Mg | 0,81 | 0,40 | 0,39 | 0,74 | 0,26 | 0,37 | 0,70 | | | |
| Ва | 1,2 | 0,63 | 0,68 | 0,65 | 0,71 | 1,6 | 1,8 | | | |
| Zn | 0,056 | 0,0043 | 0,038 | 0,071 | 0,045 | 0,036 | 0,074 | | | |
| Cr | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | | |
| Ni | 0 | 0,016 | 0,021 | 0,015 | 0,028 | 0,017 | 0,016 | | | |
| Se | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | | |
| Cd | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | | |