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# LITERATURE STUDY OF PRESENT AND NEW METHODS FOR REDUCING NON-PROCESS ELEMENTS IN THE LIME CIRCULATION OF A KRAFT PULP MILL

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 12 August, 2013.

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## Abstract

Kraft pulping has for long relied on its chemical recovery system in regenerating cooking liquors. One important process part in this chemical recovery system is the lime cycle, where lime plays an important role. Lime is slaked with green liquor during causticization reaction and converted to calcium carbonate during the process. The overall efficiency of lime in the chemical recovery system is strongly dependant on the amount of different impurities or non-process elements that are present. These non-process elements are chemical elements or compounds originating from various sources, for example from the wood raw-material, used make-up lime or from the internal process sources such as piping corrosion and they do not participate in the main process in any beneficial way, hence are producing inert dead-load to the circulation, which harmfully effects the whole operation performance of the system. The aim of this literature study is to present some of the current solutions for removing non-process elements and to also consider new possibilities for reducing impurities from the lime cycle.

Conventional way of reducing these non-process elements is to simply purge some amount of spent lime mud from the process from selected purge points within the lime cycle and by doing so also reduce the amount of circulating impurities. However, where being relatively in-expensive method, the purging of lime mud and treating it as a waste looses all the potential of the spent lime mud. Tightening environmental regulations for plant waste generation are also driving the need of finding alternative ways for doing the recycling of these solid plant wastes such as lime mud. Based on the conducted brief economical analysis, depending on the selected method, if proven to be suitable for process environments, the economical impact can be significant. In the end the spent lime mud can generate positive, negative or zero price depending on its end-of-life use.

There exist several possibilities for recycling the spent lime mud either back to process viable raw-material or to potential product used in alternative places. Most of these methods, presented in this thesis are already widely researched in the past, where some are introduced as new ideas that would potentially require further studies with possible detailed experimental setups. In this thesis, the methods were presented as singular process steps and due to the theoretical approach their practical functionality wasn't evaluated. Based on the results some of the presented methods might only prove to be functional and effective when used as combination of each other.

**Keywords** NPE, Lime mud, Chemical recovery, lime cycle, PCC

**Tekijä** Niko Mehtonen

**Työn nimi** Kirjallisuustutkimus nykyisistä ja uusista metodeista epäpuhtauksien poistamiseksi sellutehtaan kalkkikierrosta

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## Tiivistelmä

Nykyaikaisen sellutuotannon taloudellisuus on pitkään perustunut kemikaalien talteenottojärjestelmään, jonka avulla kierrätetään käytettyä keittolipeää. Kemikaalien talteenottojärjestelmässä tärkeässä osassa on kalkkikierto, jossa kalkilla on erityisen tärkeä rooli. Poltettu kalkki reagoi kaustisoinnissa viherlipeän kanssa muodostaen lopulta kalsium karbonaattia. Kemikaalien talteenottojärjestelmällä saavutettava kalkin kokonaishyötysuhde riippuu voimakkaasti eri kierrossa mukana olevien epäpuhtauksien määrästä. Näillä epäpuhtauksilla tarkoitetaan alku- tai muita aineita, jotka ovat peräisin eri lähteistä, esimerkiksi puuraaka-aineesta, käytetystä make-up kalkista tai sisäistä prosessilähteistä kuten putkistojen korroosiosta ja ne eivät osallistu prosessiin millään hyödyttävällä tavalla, jonka seurauksena ne tuottavat inerttiä kuormaa kiertoon, mikä haitallisesti vaikututtaa koko kalkkikierron suorituskykyyn. Tämän kirjallisuustyön tavoitteena on luoda katsaus olemassa oleviin ratkaisuihin epäpuhtauksien poistamiseksi kalkki kierrosta sekä pohtia myös uusia mahdollisuuksia epäpuhtauksien poistoon.

Perinteinen tapa vähentää näitä epäpuhtauksia on yksinkertaisesti poistaa jonkin verran käytettyä meesaa prosessista valituista poistokohdista ja näin myös vähentää kiertävien epäpuhtauksien määrää. Meesan poisto ja sen käsitteleminen jätteenä on suhteellisen edullinen menetelmä. Näin kuitenkin menetetään käytetyn meesan kaikki mahdollinen potentiaalinen arvo uudelleen käytössä. Lisäksi alati tiukentuvat ympäristömääräykset tehtaalla tuotettavien jätteiden määrässä ajavat tarvetta löytää vaihtoehtoisia tapoja kierrätykselle. Lopulta, riippuen valitusta puhdistus metodista, mikäli nämä osoittautuvat tehdasolosuhteisin soveltuvaksi, voi tuotantolaitoksen näkemä taloudellinen hyöty olla merkittävä, sillä arvioitaessa käytetyn meesan vaikutusta kustannuksiin muodostaa se laitokselle lopulta positiivisen, negatiivisen tai nolla hinnan riippuen käytetystä loppukäsittelymallista.

Prosessissa syntyvälle meesalle on olemassa useita mahdollisuuksia kierrätyksen suhteen, joiden avulla meesa voitaisiin mahdollisesti käsitellä takaisin raaka-aineeksi kelpaavaan puhtauteen tai vaihtoehtoisesti muualla käytettäväksi tuotteeksi. Useimpia tässä työssä esitellyistä menetelmistä on jo laajalti tutkittu aiemmin kirjallisuudessa sekä osa perustuu uusiin työssä esiteltyihin ideoihin, jotka mahdollisesti vaativat yksityiskohtaisempaa teoreettista ja kokeellista tutkimusta. Työssä menetelmien toimivuutta ei arvioitu kokonaisuutena, vaan metodit esiteltiin yksittäisinä prosesseina. Useammat työssä esitellyistä menetelmistä todennäköisesti olisivat kuitenkin vasta toistensa yhdistelmänä tehokkaasti toimivia.

**Avainsanat** Epäpuhtaudet, meesa, kemikaalien talteenotto, kalkkikierto, PCC

## Foreword

This master's thesis was carried out at the Department of Materials Science and Engineering, in the Research group of mechanical processing and recycling, Aalto University during February 2013 – August 2013 for Andritz Oy. The work is part of Carbon Capture and Storage Program, Task 5.2, $CO_2$ Fixation by Mineral Matter.

The supervisor of this thesis was Prof. Kari Heiskanen from Aalto University. MSc. Juhani Vehmaan-Kreula from Andritz, was operating as an instructor for the thesis.

I want to thank my instructor, Juhani Vehmaan-Kreula for the interesting and challenging subject, guidance throughout the whole thesis and providing valuable information and details to my questions during the course of this thesis. I also want to thank my supervisor Prof. Kari Heiskanen for the valuable advices during thesis and for providing teaching in various interesting courses during my whole studying time. I also want to show my gratitude to Mika Kottila from Andritz Oy for providing co-assistance during my thesis together with my instructor. I'd like to thank Eero Haimi from Aalto University for providing assistance and conducting the SEM analysis included for this work, Sirpa Vapaavuori from VTT Expert Services Oy for the conducted XRF and XRD analyses and Toni Orava from UPM kymmene - Kymi for introducing Kraft pulp mill and its chemical recovery system in practise. I would also like to thank Prof. Jaakko Puhakka from Tampere University of Technology for assistance in my microbiology related inquiries and Prof. Olli Dahl from Aalto University for feedback from my ideas in this thesis. Finally I would like to thank my friends, family and especially my wife Janni and my daughter Siiri for giving me motivation during my thesis and the whole study time.

Espoossa 12.8.2013

Niko Mehtonen

## List of abbreviations

| | |
|---|---|
| AOX | Adsorbable organic halide |
| ATP | Adenosine triphosphate, the principal energy carrier of the cell |
| BAT | Best available technology |
| COD | Chemical Oxygen Demand |
| NPE | Non-process element |
| PCC | Precipitated calcium carbonate |
| SEM | Scanning electron microscopy |
| SRB | Sulphate reducing bacteria |
| TOC | Total organic carbon |
| XRD | X-ray diffraction |
| XRF | X-ray fluorescent |

# 1 Introduction

Non-process elements or NPEs are elements that are not active components in the specific process of a pulp mill. What are classified as NPEs hence vary depending on what process part they are looked at, for example calcium is major process element in the lime cycle but it is considered as NPE in other parts of the pulping processes. These non-process elements are causing, when allowed to precipitate in the lime cycle above given limitations, increase in dead load, efficiency declinations and material losses in the cycle. These effects are all ultimately causing rise in the operating costs and in some cases these issues caused by NPEs, may eventually lead into production halts and cause costly repairs to equipment by for example formation of lime kiln rings.

The current way to reduce the amount of NPEs in circulation is to simply purge away some amount of the lime mud from the lime cycle and by doing so, reduce the amount of circulating impurities. Where being inexpensive method, the changes in for example the EU legislation, attempts to improve resource-efficiency and the overall shift towards eco-awareness are driving the need to find alternative ways to reduce the amounts of waste generated by the pulping industry, while still maintaining the cost-efficiency of production.

The motivation of this thesis comes from the need to find effective ways for doing the cleaning of lime mud waste. Another very attractive target is to clean the lime in the lime cycle to a level where it could be directly purged as a raw material for precipitated calcium carbonate manufacture. This thesis is done by literature survey of the research done in past among the topic and also extending the survey to indentify possibilities from other fields of industry in order to find fresh ideas, which could ultimately lead into adaptation of new recycling methods for lime mud recycling. Based on the literature survey the objective of this thesis is to draw conclusions about the current possibilities for removing non-process elements from the lime cycle by implementing new process methods. Finally from the results of the thesis, viable suggestions are constructed as recommendations to guide further research and possible experimental setups.

# 2 Literature review

In the following chapter relative literature for the topic of this thesis is presented. Starting from the definitions and theories related to lime and its role in the pulp mill processes, followed by the formation method of lime mud and the input sources of non-process elements into the lime cycle, in addition to which of them are considered as most harmful towards the lime cycle of a pulp mill are introduced.

## 2.1 Limestone and lime

Limestone is found in many parts of the world and it is essential component in various diverse industries such as chemical, building, agriculture and papermaking industry. Studies done by various researches in the past have given estimates for the calcium content in earth's crust being from 3 to 4 percent depending on the determination method.[1] Partly due to this abundant availability it can be classified as one of the oldest materials used by mankind. The earliest recorded usages of limestone date back to the Egyptian pyramids, where limestone was used as huge building blocks and lime for component in mortar and plaster.[2] Lime that can be considered as burned or calcined form of limestone is produced by thermal decomposition of limestone. In the presence of heat, limestone dissolves into calcium oxide and carbon dioxide is produced during the process. This reversible reaction makes calcium oxide so versatile in use and because of this reversible nature it can be widely used in various fields of industry.[2]

The limestone found in the Earth's crust consists mainly of calcium oxide with various included impurities such as silica and alumina.[2] Chemical compositions of different commercially available limestone are presented in the table 1.

**Table 1. Chemical composition of different commercially available limestone by mass percent.[2,3]**

| Limestone | CaO | MgO | $CO_2$ | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $SO_3$ | $P_2O_5$ | $Na_2O$ | $K_2O$ | $H_2O$ | Other |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **A** | 55,28 | 0,46 | 43,73 | 0,42 | 0,13 | 0,05 | 0,01 | - | - | - | - | 0,08 |
| **B** | 54,54 | 0,59 | 42,90 | 0,7 | 0,68 | 0,08 | 0,31 | - | 0,16 | - | - | - |
| **C** | 55,0 | 0,4 | 44,2 | 0,2 | 0,1 | 0,05 | -- | 0,001 | 0,01 | 0,03 | - | 0,015 |

The presented limestones, in the table 1 originate from the following locations:

A – Virginia high calcium stone
B – Indiana high calcium stone
C – Norwegian limestone, Tromsdalen

As can be seen from the table 1, the chemical composition, included impurities and also their amounts vary by the type and location of the used limestone. It has to be noted that what is considered as included impurities in different limestone, vary between the fields of use where some chemical elements may be considered as beneficial towards the processes instead of impurities that need to be removed.[2,3]

Limestone can also be bought directly in its calcined form as calcium oxide, which also has some effect on the chemical composition of the product as can be seen from the following table 2, where analysis on commercial grade calcium oxide produced from Finnish and Norwegian limestone by Nordkalk is presented.[3]

**Table 2. Analysis of commercial grade calcium oxide provided by Nordkalk.[3]**

| Product | CaO | MgO | $CO_2$ | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | S | P | $Cl^-$ | $K_2O$ | $Na_2O$ | Other |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Nordkalk QL 0-8LV | 90,4 | 1,9 | 1,9 | 4,7 | 0,3 | 0,2 | 0,01 | 0,02 | < 0,01 | 0,05 | 0,1 | 0,41 |
| Nordkalk QL 0-15VT Silva | 95,8 | 0,6 | 1,3 | 0,5 | 0,2 | 0,1 | 0,07 | 0,01 | < 0,01 | 0,03 | 0,02 | 1,36 |

In the table 2 the other elements consist of, for example manganese, fluoride and different trace elements such as cobalt, chromium, and zinc. Amount of these trace elements are however usually on the scale of ppm. The Nordkalk QL 0-15 seen in the table 2 is produced from the Norwegian limestone presented earlier in the table 1 and as can be seen from the chemical composition when compared the burned lime to the raw material, there are some minor changes in composition during the burning process.

## 2.2 Lime and its role in the chemical recovery system

Chemical pulping industry has high requisite to be as environmentally friendly as possible, yet it still needs maintain its economical feasibility. To achieve this, energy and also chemicals used in the pulping process are recycled with aim to reach as high recycling efficiency as possible within the pulping plant. Here the chemical recovery system plays an important role and the modern Kraft pulp mill is often self-sufficient in energy by energy produced in its recovery processes.[4]

The history of chemical pulping dates back to the late 19th century, where the first chemical pulping plants with recovery and regeneration systems for the cooking chemicals were introduced in the USA. These inventions in pulping were greatly influenced by the need of using also other materials, such as wood fibres as raw material in papermaking. Improvements ultimately led to the sulphate process, where sodium sulphate replaced the sodium carbonate used in the recovery system. This new pulping process produced much darker, harder to beat and bleach pulp when compared to the pulp produced by the soda process. This defined the process as Kraft pulping, originating from the German and Swedish word for strength. From environmental standpoint, the vast use of chemicals in this type of pulping also required the recycling of used cooking chemicals; here the chemical recovery systems played an important role. The chemical recovery systems have been available for long, but not until 1930s and 1940s their use became more common and also more efficient, when modern, continuously operable regeneration systems of spent liquor were introduced. These modern chemical recovery systems of pulping chemicals involve recycling spent black, green and white liquors and renewing used lime that enters the lime cycle in form of lime mud. In the figure 1 is presented flow sheet from an overall recovery cycle that can be found in a Kraft pulp mill. It has to be noted that the modernization has resulted in integration of some process parts into a single process step, for example slaking and causticizing or lime mud filtering and washing. [5,6,7]

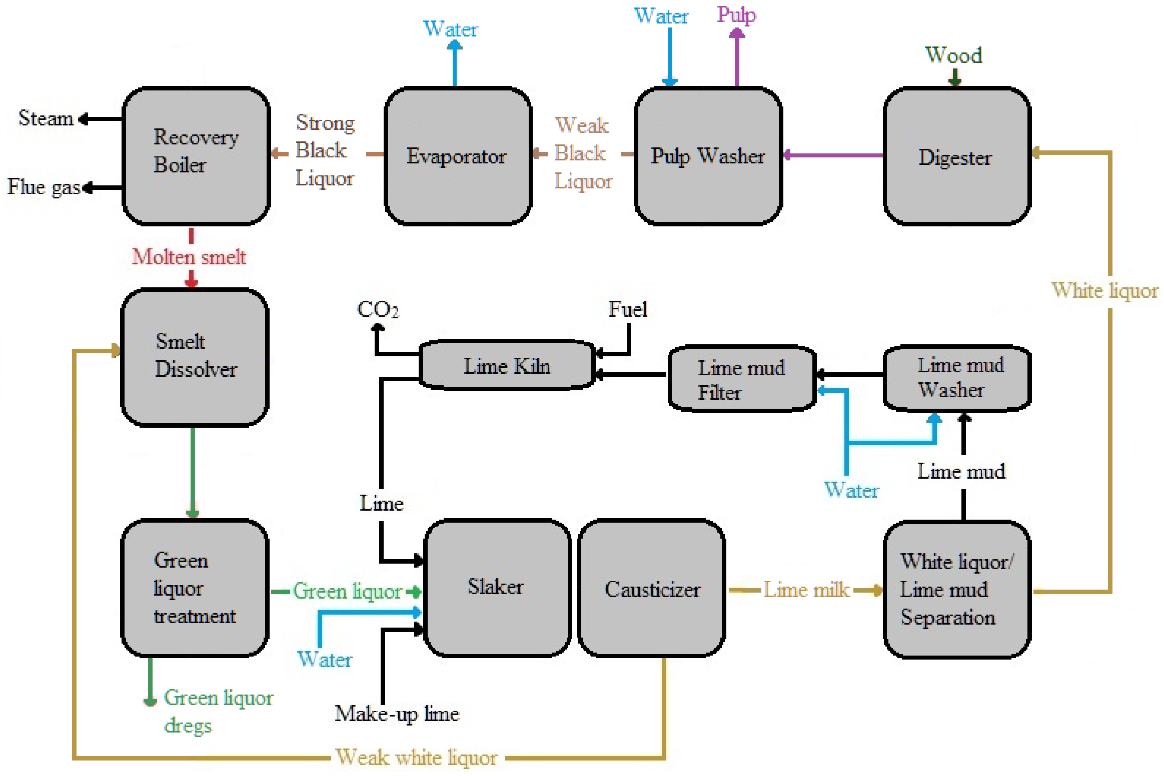


**Figure 1. Flow sheet of a typical recovery cycle in Kraft pulp mill.[8]**

The recovery of chemicals begins with processing spent cooking liquor, weak black liquor that is condensed in the evaporators. The resulting strong black liquor is the main feed of the recovery boiler. The black liquor consists of organic and inorganic components, where the organic components originate from the wood raw material and inorganic components are mostly residues from the cooking chemicals that come from the delignification phases.[4] Since the first recovery boilers there have been various improvements, most affecting the operating efficiency such as increase in capacity or improvements in the energy efficiency of the boiler.[5] In the figure 2 is presented two-drum recovery boiler on the left and on the right is for comparison a typical single-drum design.

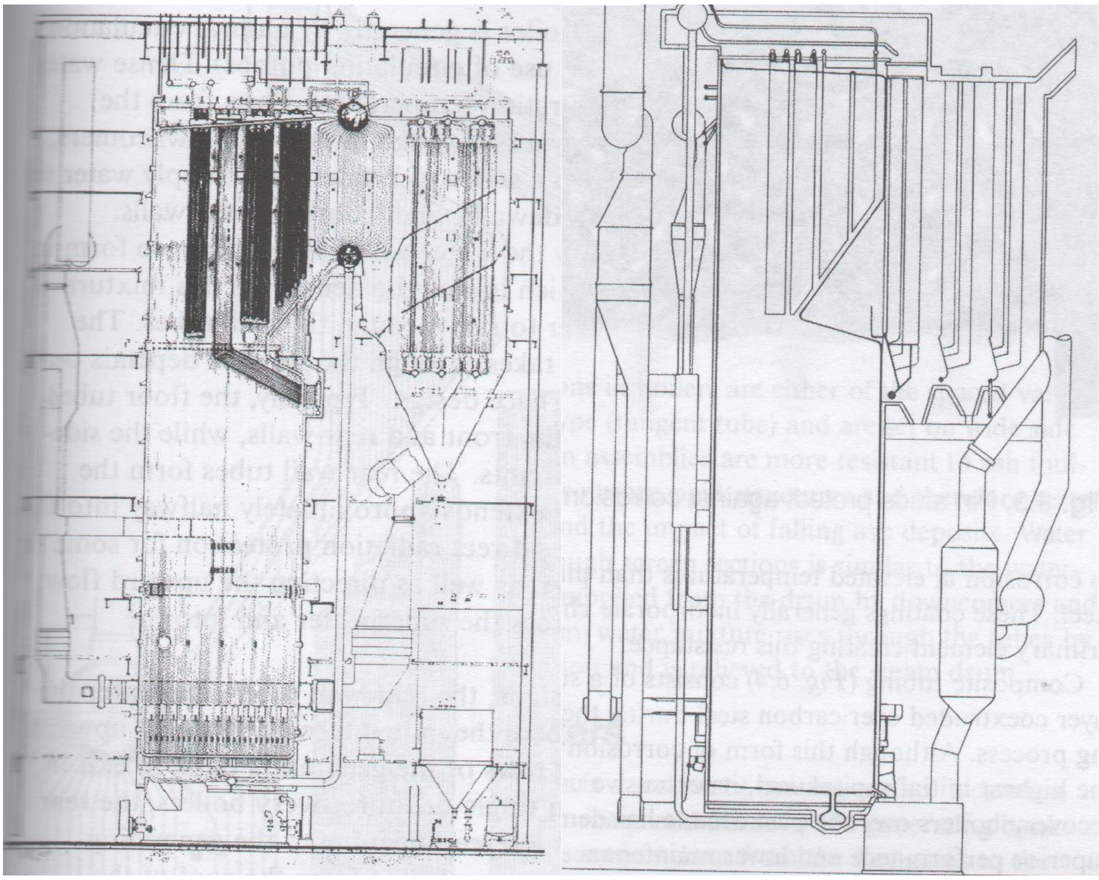


**Figure 2. Schematic of a two-drum and a typical single drum recovery boilers.[7]**

When compared the modern recovery boiler to those been in use in the past, the biggest change is the implementation of a single drum design. This single drum construction provides increased operation safety as they can withstand elevated pressures and thus have better operating efficiency. Reaction-wise the operating mechanism of these two boiler types is relatively similar. The major occurring reaction in the recovery boiler is the reduction of sodium sulphate into sodium sulphide, that occurs together with other important reactions such being the formation of sodium carbonate from the various available sodium compounds and carbon dioxide. Organic materials contained in the black liquor combust and during the process molten mixture of chemicals runs out from the furnace to the smelt dissolver. This molten mixture is then dissolved with weak wash coming from the mud washer to produce green liquor, which is then used in the recausticizing.[4,5,7,8]

### 2.2.1 Recausticizing

The consecutive combination of two chemical reactions, slaking and causticizing is called recausticizing and its main purpose is to produce impurity free white liquor for the cooking processes and also to prepare as clean lime mud as possible to be processed in the lime cycle. Causticizing plays an important role in controlling the overall efficiency of the recovery cycle, as low causticizing efficiency easily results in the increase of circulating inert dead-load. Inert components in the recovery cycle increase the need of caustic make-up and the consumption of white liquor at the digester.[5,9,10]

Lime in form of quicklime (CaO) participates in the chemical recovery process in converting green liquor to white liquor which is then reused in the cooking process. Before lime is introduced into causticizing it is dissolved in green liquor to produce slaked lime, $Ca(OH)_2$ in the following reaction 1,

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

The slaking is fast and exothermic reaction that is performed usually at around 100 °C in a mixing vessel that keeps the particles suspended in liquid, this increases the reaction rate. Immediately after the slaking of lime has begun the causticizing reaction also begins. In causticizing, slaked lime produced in the slaking reaction reacts with the green liquor. In the reaction, green liquor containing sodium carbonate reacts with solid calcium hydroxide resulting in formation of sodium hydroxide and calcium carbonate in the following slightly exothermic reaction 2,

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

The forming sodium hydroxide from the reaction 2 is an active alkali in the white liquor, which is then used in the pulping process. The forming calcium carbonate from the reaction 2 is filtrated out as lime mud and fed into the lime cycle.[5,9,11,12]

Equilibrium conditions of the presented reaction 2 are determined by solution properties such as temperature of the liquor.[12] As the reaction progresses, causticizing becomes progressively slower. This slowing occurs because the overall rate of the reaction is limited by diffusion of the moving ions to and from the reaction interfaces. Because the diffusion limitation exists within the solid particles, the retention time in the vessels is of great importance when physical properties for the produced lime mud are determined.[11,12] The physical properties of the produced lime mud vary greatly depending on the mixing conditions in the causticizing, inert non-process elements can also change the physical properties of the lime mud. Qualities such as filtration resistance of the lime mud are in straight correlation with the residence time in the causticizer.[5,12]

Because the causticizing reaction is reversible, 100 % causticity cannot be achieved. The equilibrium that can be achieved with causticizing is a function of total titratable alkali at different sulfidity levels.[5,13] The efficiency of causticizing can be enhanced by increasing the retention time of the solution and due to this causticizing is usually done in series of several mixing vessels that can be either single stage or multi-compartment causticizers. In the figure 3 is presented example of a system used for slaking and causticizing.[10]

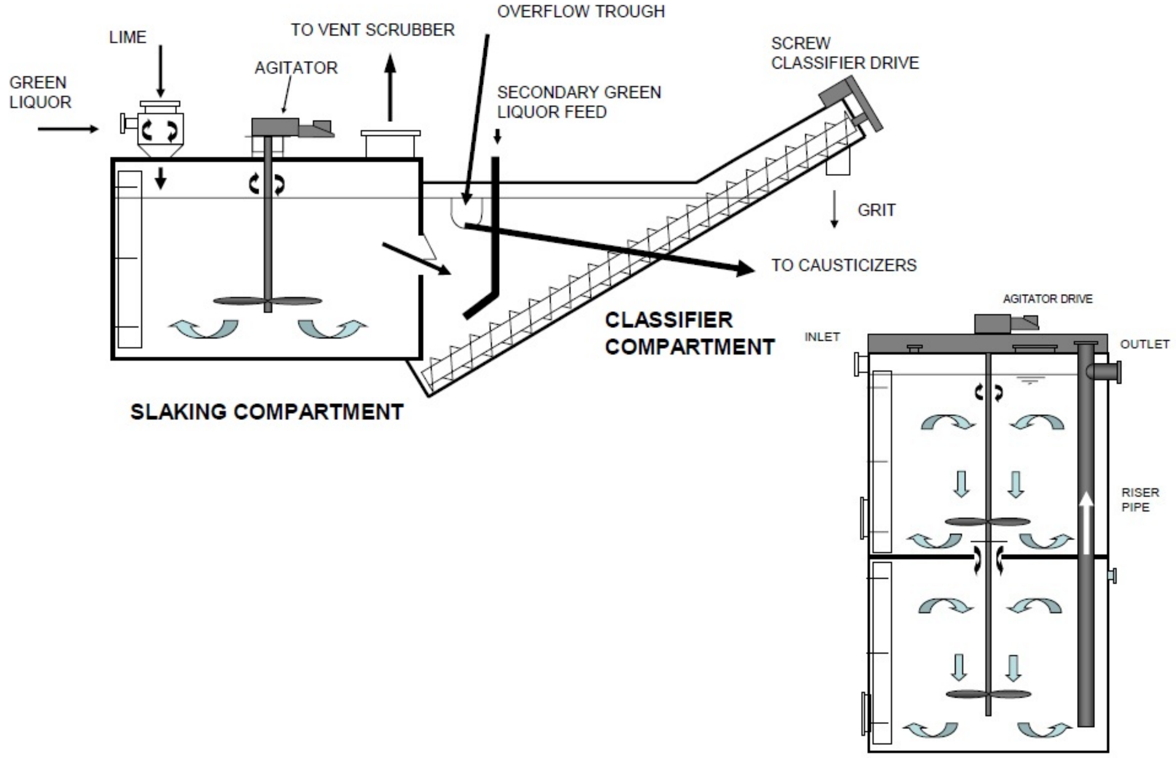


**Figure 3. Schematic of a slaker and multi-compartment causticizer.[10]**

From the figure 3 can be seen that slaking and causticizing is carried out in a series of reaction-wise connected vessels, where the causticizing reactions begin already at the slaker and continue until the equilibrium is reached in the causticizer vessels that can be either single-stage or multi-compartment vessels. Differences between these two vessel types comes from the obvious volume capacity, as the increase in number of mixing compartment also raises the mixing and retention efficiency in the causticizers. Benefit gain in the retention efficiency, from the increase in number of active mixing vessels hinders after six units due to overall retention time being the greatest factor to be met in causticizing at that point.[10]

## 2.3 Lime cycle in the pulp mill

Lime cycle in the pulp mill begins when recycled lime from the lime kiln and purchased make-up lime is introduced into the recausticizing process. One of the most important functions of the lime cycle is to maintain the lime circulation as pure from impurities as possible and by doing so reduce the required amount of added make-up lime into the process. The lime cycle exists in the pulp mill within the chemical recovery system as can be seen from the figure 4, where the lime cycle found in modern pulp mill is highlighted from the overall recovery system.[7,8]

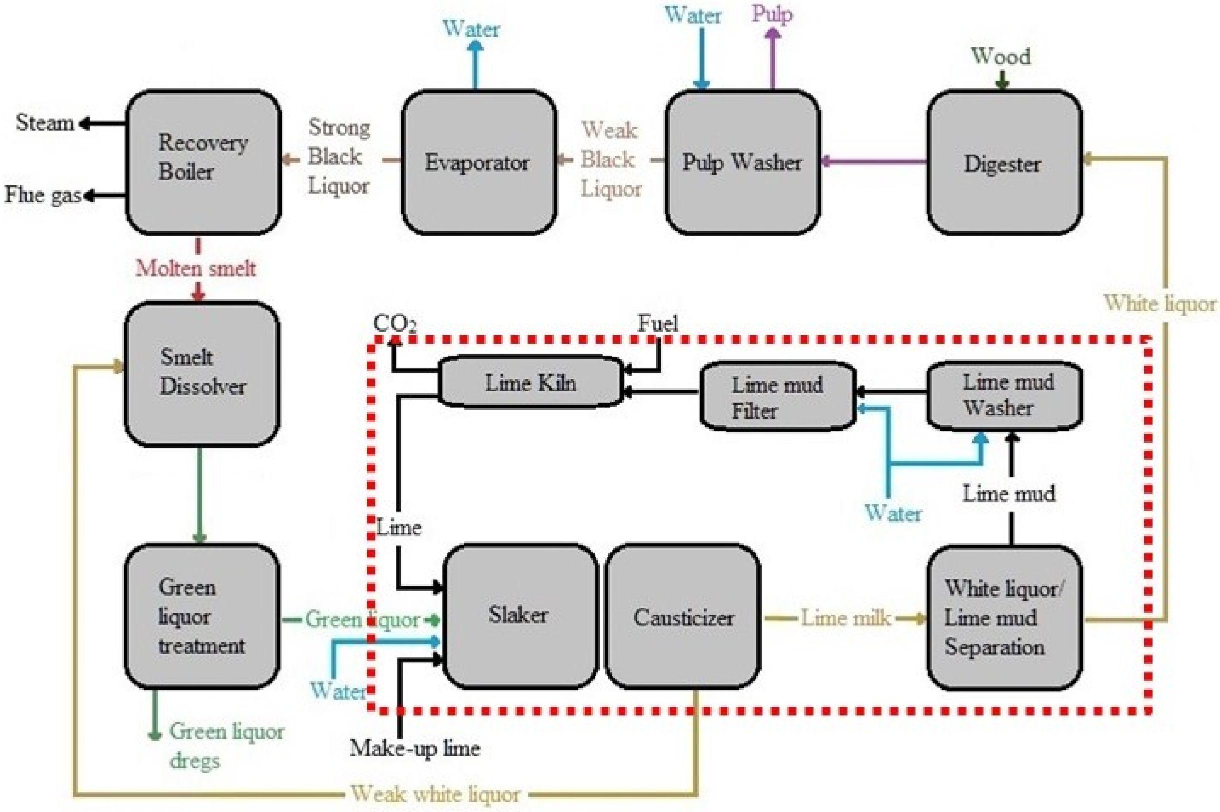


**Figure 4. Lime cycle inside the overall kraft recovery cycle.[7,8]**

As seen from the highlighted section in the figure 4, the lime cycle usually consists of components that are slaking, causticizing, white liquor and lime mud separation, lime mud washing and filtering and finally the lime kiln.

As the lime cycle clearly flows in parallel within the white liquor preparation parts of the recovery cycle, as seen from the figure 4, a simplified view of these two parallel cycles can also be used. This simplified schematic of these two parallel flows is presented in the following figure 5 showing the main functions of the liquor and lime cycle together with the material flows.

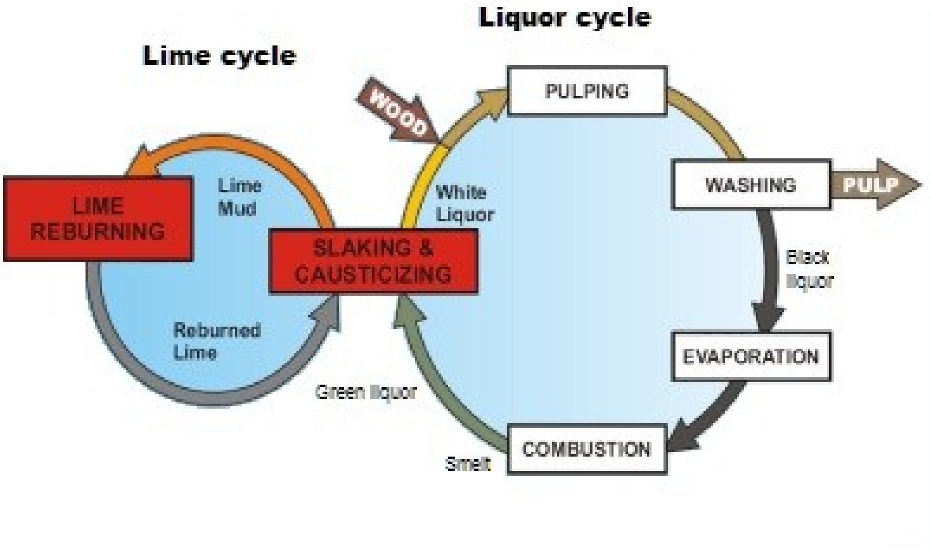


**Figure 5. Simplified figure from parallel lime- and alkali cycle.[14]**

The actual recycling of the used lime begins when lime mud is separated out from the white liquor solution, which is usually called as the lime milk at this point, and transported into the mud cleaning processes. This separation of lime mud from the white liquor can be done in various ways, for example clarification by settling is commonly used method. In the clarifier lime mud settles to the bottom of the vessel, where it can be collected as the white liquor remains on top of the lime mud. After the separation is done, the separated lime mud is first washed and filtered to reduce the amount of alkali that has been carried over to the lime mud. This wash product usually contains some amount of water soluble alkali, which can be used in the weak wash liquor elsewhere. After the filtration the water soluble alkali content should be under 0.1 % to avoid issues.[5,14]

The closure requirements for the mill water balance have led to the integration of white liquor separation and lime mud washing into one process. Pressurized disc filtration or CD-filter is more often used in the washing and filtering of the lime mud. Pressurized disc filter consists of disc shaped filter elements that are placed on to rotating shaft in a pressurized vessel, where the lime milk remains in the bottom of the vessel. Part of the filter elements passes through the lime milk layer and pressure differences force the lime mud to remain in the filter cloth surface while the white liquor flows through the filter elements into a pressurized vessel, where it is separated from the gas. White liquor filtrate is pumped to storage and the gas is compressed back to the filter. Lime mud cake forming on to the surface of the filter elements is washed with water and the top layer of the cake is removed by scraping elements before the disk rotates again into the lime milk solution. The resulting lime mud from the filtration is then dewatered to reduce the moisture in the lime mud. Dry solids content of the mud usually has to be over or close to 75 % in order to still maintain sufficient operating efficiency in the lime kiln.[5,14]

Lime kiln is the final process step in the lime cycle and its purpose is to convert the calcium carbonate produced in the causticizing into calcium oxide to be reused in slaking. This conversion is done by burning the partially moist lime mud entering the kiln, where the primary reaction is the dissociation of calcium carbonate by heat into lime and carbon dioxide. This reburning of lime mud is usually done in a rotating kiln, which makes it a continuous process, where constant flow of lime mud is entering the lime kiln from the cold end of the kiln and from the hot end, reburned or calcined lime is removed. In the following figure 6 is presented a typical rotary lime kiln.[5,8,15]

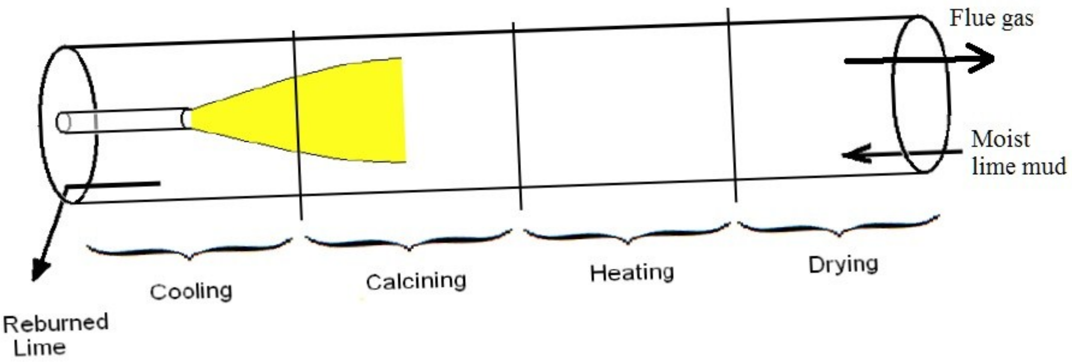


**Figure 6. Schematic of a typical rotary lime kiln.[15]**

From the figure 6 can be seen that the lime kiln consists of different temperature zones, which the entering lime mud flows through. The partially moist lime mud coming from the dewatering typically has a solid content of 75 % or higher. This moist lime mud dries when it enters the kiln by heat radiation; the heating efficiency is further increased by internal heat transfer elements, which increase the heat transfer efficiency to the lime mud. These elements can be for example chain systems, dams, tumblers, lifters or bars that lime mud flows through. After the first drying zone, the lime mud solids content raises up to 95 %. In modern kilns the role of drying zone has however greatly diminished by the introduction of pre-drying systems, such as flash driers that are utilized for nearly completely drying the lime mud prior to the kiln feed. The flowing lime mud that is continuously heated enters the third zone, where the endothermic calcination reaction occurs. The temperature needed for calcination depends on the partial pressure of carbon dioxide, where higher partial pressure results in higher temperature requirement for the reaction. Under normal operation conditions calcination occurs above 800 °C at atmosphere containing 20 % of carbon dioxide. Temperatures above 1150 °C will result in over burning of the lime mud and also causing damage to the refractory walls of the lime kiln. Flue gases produced in the kiln are processed in the flue gas handling systems, which usually consists of wet scrubbers, electrostatic precipitators and cyclone separators or combination of these.[5,7,8,14,15]

The resulting lime from the lime kiln can be divided roughly into two categories based on the burn conditions present in the kiln, these categories are soft- or hard burned lime. Soft burned lime is produced when the conditions in the kiln are mild, which mean that the sintering of the lime has been little and as a result smaller agglomerate sizes are produced. Hard burned lime refers to conditions, where the temperature in the kiln is higher compared to the conditions with formation of soft burned lime. These two lime types have different physical properties, which cause different performance of the produced lime in the chemical recovery system, as can be seen from the following figure 7, where the effects of the different burned lime are presented.[8]

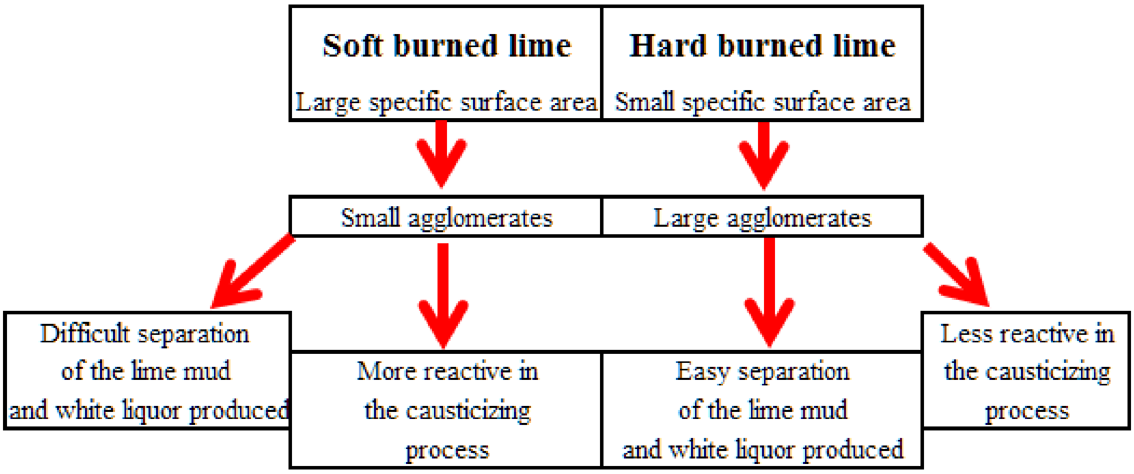


**Figure 7. Differences in physical properties of soft and hard burned lime.[8]**

It can be seen from the figure 7 that the both burned lime types have beneficial factors resulting from the size of the agglomerates. Small agglomerates give good response in causticizing but they are more difficult to separate from the lime milk, where the larger agglomerates result in less reactive performance in causticizing and can cause problems with over liming, but are easier to separate from the lime milk. Therefore careful optimization of the lime kiln is in great importance regarding the performance of the whole lime cycle and the overall chemical recovery system.[5,8,14,15]

As has been seen, the lime cycle requires careful optimization to be operated with sufficient efficiency. Major threat to this sufficient operating efficiency is caused by the impurities constantly entering and already present in the circulation. In the following chapter will be looked at which of these impurities are considered as most harmful inside the lime cycle. Also the problems resulting from these harmful impurities, as reported in the found literature cases are presented.

## 2.4 Harmful non-process elements in the lime mud

Non-process elements are considered as elements that do not participate in any beneficial ways in the main reactions of the pulping processes; due to this they are only producing increasing amounts of circulating dead-load. The build-up of this inert dead-load in the lime cycle is mainly due to the limited solubility, volatility and reactivity of a given element in that part of the chemical recovery system. This inert dead-load in the circulation not only lowers the efficiency of the recovery cycle by being extra load, but in the lime cycle it participates in reactions with calcium, lowering its availability by binding it to insoluble mineral forms. NPEs in the lime circulation can also harmfully affect the particle size of the lime mud. By these harmful effects on the particle size, they also have effect on the filtering properties of the lime mud and hence lower the dry solids content and decrease the reactivity of lime. These effects combined, result in increased demand of lime, increased production costs and they cause extra load to the lime kiln, which causes lime re-burning to require more energy.[14,16]

In efforts to reduce the emissions and also the use of chemicals in the pulping process, the aim is to keep the chemical recovery system relatively closed, however this eventually causes the build-up of inert weight into the recovery system and therefore it is often needed to keep the cycle partially open at some purge point. Due to this there has to be number of potential purge points for the NPEs. The chemical recovery system offers some purge points, where the amount of circulating non-process elements can be reduced together with some natural exit points for the impurities, where usually some trace amounts of NPEs are exiting the system. These natural exit points are, for example through the white liquor and further in the system, through the produced pulp. The conventional purge points can be seen from the figure 8, where they are highlighted. [14,16]

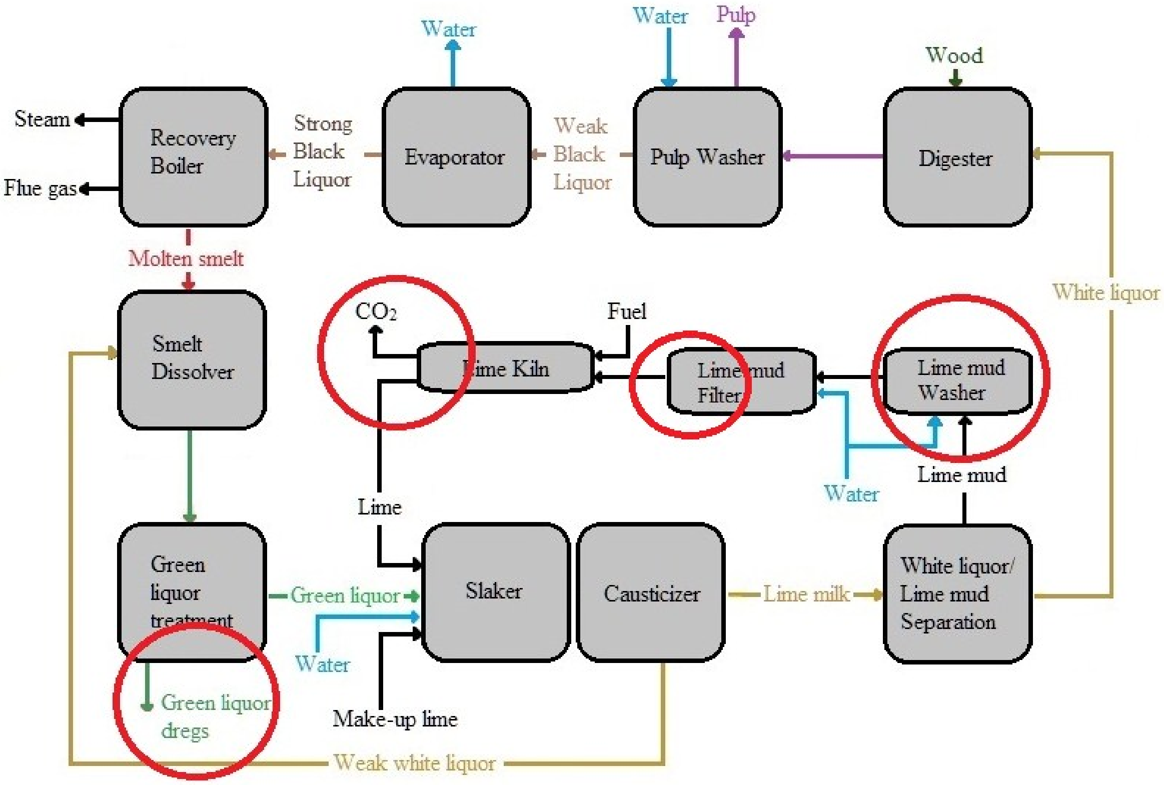


**Figure 8. Possible purge points for NPEs within the chemical recovery system.[8]**

As can be seen from the figure 8, purge points can exist in different locations at the chemical recovery system and it is highly dependent on plant design what impurity removal is prioritized and which purge point or points are chosen as active.

The amount of non-process elements in different raw materials varies greatly. In wood raw material NPEs consists generally from the inorganic mass of the raw material. Different climate conditions or environmental aspects have an impact on the inorganic material balance within the raw material; this can alter the normal chemical composition of the raw material. In woods that are growing in temperate zones, the inorganic elements make-up between 0.1 to 0.5 % of the dry solids in the wood, whereas the tropical and subtropical regions cause the wood to contain close to 5 % inorganic elements. The total amount of wood inorganics can be measured from the ash forming from the combustion of the organic wood sample. In the following table 3, can be seen approximate concentration of various elements in the dry softwood and hardwood raw materials.[17]

**Table 3. Approximate concentration of various elements in different wood raw materials.[17]**

| Range in ppm | Elements | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 400-1000 | K | Ca | | | | | | | | |
| 100-400 | Mg | P | | | | | | | | |
| 10-100 | F | Na | Si | S | Mn | Fe | Zn | Ba | | |
| 1-10 | B | Al | Ti | Cu | Ge | Se | Rb | Sr | Y | Nb |
| | Ru | Pd | Cd | Te | Pt | | | | | |
| 0,1-1 | Cr | Ni | Br | Rh | Ag | Sn | Cs | Ta | Os | |
| < 0,1 | Li | Sc | V | Co | Ga | As | Zr | Mo | In | Sb |
| | I | Hf | W | Re | Ir | Au | Hg | Pb | Bi | |

It has to be noted that some of these inorganic elements seen in the table 3, are essential for the growth of the wood and some of the elements are beneficial inside the chemical recovery cycle. These elements in wood raw material can be further classified by their solubility to different liquors in the chemical recovery system, as some are more soluble in, for example green liquor than in white liquor. This classification according to Ulmgren can be seen from the following table 4, where the different elements are sorted into three groups by their solubility to white and green liquor.[18]

**Table 4. Different elements divided into three groups based on their solubility in green liquor and white liquor.[18]**

| **Group I**<br>Soluble in WL and GL, Accumulate into liquor cycle | **Group II**<br>Insoluble or sparingly soluble in WL and GL, Purged with GL Dregs | **Group III**<br>Insoluble or sparingly soluble in WL and GL, Accumulate into lime cycle |
|---|---|---|
| **Al** | **Ca** | **P** |
| **Si** | **Mg** | **Mg** |
| **K** | **Mn** | **Al** |
| **Cl** | **Fe** | **Si** |
| **Ba** | **Cu** | **(Mn, Fe)** |
| | **Pb** | |

Some of the elements seen in the table 4 are considered to be more harmful towards the lime cycle than others. These elements are especially those accumulating into the lime cycle, for example phosphorus, silicon, magnesium and aluminium. In the following chapters will be presented most of the impurities seen in the table 4, which can be considered as most harmful, when considering the lime cycle of the chemical recovery system.[19]

### 2.4.1 Phosphorus

Phosphorus can be considered as one of the most harmful NPE in the lime cycle because of its solubility difference in white liquor when compared to green liquor. Ulmgren & Rådeström[20] have shown the concentration of phosphorus as phosphate ions in green liquor to been from three to five times higher than in white liquor. When entering the lime cycle in form of phosphate ions this solubility difference causes phosphate ions to bind available calcium, which results into the formation of calcium phosphates that occurs in the lime mud, according to several studies in complex mineral forms such as apatite or calcium hydroxyapatite and taking after the lime kiln forms such as tricalcium phosphate. However the tricalcium phosphate form is assumed to re-convert back to hydroxyapatite in causticizing process, as hydroxyapatite is the dominant phosphate form found in the lime mud before the lime kiln. The apatite crystals can also contain amounts of sodium or carbonate ions in addition to calcium and phosphate ions.[20,21] These phosphate based mineral forms are one of the hardest impurities to remove because of their nature to change the solubility during recausticizing.[5] Because of this increasing inert dead-load, the amount of available calcium oxide reduces. It has been investigated by Ulmgren & Rådeström that one weight percent of phosphorus reduced the amount of active calcium oxide in lime by 5 weight percents.[20,22]

The main source of phosphorus into the Kraft pulp mill is from the wood raw material; hence the used raw material type mainly defines the intake of phosphorus. Biosludge used as an added element to power the recovery boiler is also a significant source of phosphorus; also the make-up lime can contain some trace amounts of phosphorus. Studies are also showing that lime kiln fuel, when wood based biofuels are used, for example gas produced from the gasification of wood, could be one additional source of phosphorus into the lime cycle. From the main source of phosphorus, the wood raw material to the chemical recovery system phosphorus enters through the black liquor phase due to prevailing liquid conditions in the smelt.[3,19,20,23]

Phosphorus removal methods are limited due to its solubility in the white liquor. However in the lime cycle phosphorus can be controlled by the filter dregs and by purging lime mud from the circulation. It has also been studied that some amount of phosphorus is accumulated from the lime kiln into the electric precipitators, however the exact mechanism of this is somewhat unknown.[19,20]

### 2.4.2 Silicon

Silicon is also a problematic impurity in the lime cycle because like phosphorus it is more soluble in green liquor than it is in white liquor. Silicon can exist in multiple different forms that are soluble, colloidal and suspended form. In addition to these three forms silicon also has polymeric and crystalline form that both have an effect on its reactivity. However the most dominant form for silica in lime mud is its amorphous form. When silicon concentration in white liquor is elevated, it reacts with calcium oxide forming calcium silicates, $(1\text{-}2)CaO \cdot SiO_2$ and calcium silicate hydrates, $xCaO \cdot ySiO_2 \cdot zH_2O$, that have a gel-like structure and accumulate to the lime mud. This results into a reduction of available amount of free calcium in lime mud, as can be seen from the chemical compositions this reduction is approximately 6 mass-percent per each mass-percent of silicon present in the lime mud. Silicon also participates in the formation of various other impurities such as sodium aluminosilicates.[21,22,24,25,26]

Sources of silicon into the pulping processes are mainly through the used raw material together with make-up chemicals, process waters, burning of biosludge and usage of biofuels in the lime kiln. Silicon can also enter the chemical recovery cycle from the refractory bricks used in the lime kiln if they contain aluminosilicates. The amount of silicon entering the chemical recovery cycle varies depending on the used raw material type. Typical silicon content in wood raw material is relatively low when compared to, for example plants and especially plants that are growing in water such as rice, where the main part of the plants inner core is composed of silicon resulting in silicon concentration up to 10 %. The elevated accumulation and difficulty in reduction of silicon concentration practically rules out the use of these types of plants as pulping raw-material.[21,22,23,25,27]

As silicon remains relatively unchanged during the phases in white liquor production its main purge point is at the pulp production. Some amount of silicon can also be reduced by disposal of dregs from the green liquor clarifier, through the discharge of lime mud and via precipitator dust.[22,28,29]

### 2.4.3 Aluminium & Magnesium

Aluminium and magnesium are presented under the same category within the non-process elements of lime cycle due to their similar effects on each other. Aluminium participates in formation of aluminosilicates, but it can also form hydrotalcite together with magnesium. Problems caused by aluminium in the chemical recovery system are mainly with the increase of circulating dead load and the formation of aluminosilicate scales that can cause plugging in the filters and efficiency declinations in heat transfer surfaces. Magnesium can also cause problems with filter plugging, which can easily result into decreased solids content in the lime mud before the lime kiln, resulting in increase of the energy demand of the lime kiln.[23,29,30]

Main source of aluminium and also magnesium to the chemical recovery system is from the wood raw material together with the used limestone or make-up lime. Process waters and burning of biosludge in the recovery boiler are also suspected to increase aluminium and magnesium content in the chemical recovery system.[29,30]

Magnesium and aluminium share an important reducing mechanism towards each other. Addition of magnesium salts i.e. magnesium sulphate to the chemical recovery have been studied to result in formation of insoluble double salt, hydrotalcite that can be removed by filtration. This results into reduction of free aluminium in the lime mud.[29,30]

### 2.4.4 Sulphur

Sulphur is presented here as a non-process element mostly due to the potential problems it can cause in the lime cycle if its concentration is high and partly due to the possible issues it may result into as an impurity element if the lime mud is used as a raw-material in, for example PCC manufacturing where the high raw-material purity is required. Within the lime cycle possible issues caused by high sulphur concentration are, for example the formation of lime kiln rings, especially in close proximity to the burner end of the lime kiln. This formation of hot-end rings occurs if the calcium sulphate formation takes place near the burner end of the lime kiln. Under normal operating conditions sulphur is not problematic element due to the definition of non-process elements being that they constantly increase the circulating inert mass within the chemical recovery cycle. Sulphur only binds calcium for a short period of time, as under normal operating conditions heat in the lime kiln will release the bound calcium from the sulphur resulting in majority of the sulphur present in lime mud to exit through flue gases.[22,28,31]

The source of sulphur into chemical recovery system is closely linked to the fuel used in powering the lime kiln. Due to this, operation problems caused by sulphur are mainly related to fuel-sources containing high amounts of sulphur such as petroleum coke, which is used especially in the United States. The amount of sulphur entering the system has however greatly reduced with the implementation of cleaner energy sources and therefore sulphur isn't considered that harmful towards the lime cycle anymore with the current reduced input concentrations. For example in a typical Finnish Kraft pulp mill the concentration of sulphur in the lime mud is in the region of 100-200 ppm.[28,32]

### 2.4.5 Others

There are also several other elements circulating in the lime cycle and from these other elements only some have raised interest and been subject to studies. This is mostly because many of these elements have so small concentrations in the lime cycle that it is complicated to pinpoint their exact input sources or mineralogical form and behaviour. Some of the most relevant among these other elements are elements such as iron, potassium and copper. These elements are mainly causing dusting in the lime kiln, and aren't considered as problematic when compared to other NPEs. These elements typically originate from various sources into the lime cycle, for example iron and copper can come from the wood raw material as seen from the table 3, but their quantities in wood are relatively low, especially for copper. It is more likely that, for example majority of iron and in some extent also copper comes from the metal surfaces that are in-contact to corrosive liquids in the chemical recovery system. Some of the possible problems caused by iron include, for example difficulties in separation of lime mud from the white liquor, which results into higher water content in lime mud. These other elements can also participate in the formation of lime kiln rings, for example high concentration of potassium is found to been causing ring formation in the lime kiln due to low melting point of potassium carbonate.[29]

# 3 Methods for non-process element removal

It was noticed during the literature survey that the research done in past years hasn't yet come up with a certain, all-inclusive solution for the removal of non-process elements that would be in the same time efficient enough to remove sufficient amount of NPEs and still be cost-efficient method to be used in typical process environments. Therefore the focus was turned also to other fields of industry having similar conditions or problems that are underlined within this thesis in finding methods that could be possibly introduced as new possibilities for the recycling of lime mud.

When discussing the non-process elements in the lime cycle, the complexity of removing these impurities comes from the nature of calcium to easily form insoluble compounds together with impurities present in the lime mud, also as these impurities present in the lime mud are very dependent on process conditions, for example of the used raw material type, makes it harder to compare the literature cases to each other as there are so many possible factors affecting the impurity balance in the lime mud. Therefore it was evident that there was need to compare the found literature cases of non-process element composition in lime mud to new analysis data of lime mud from conditions present in selected Finnish Kraft pulp mill. This was done in order to better understand the forming non-process element compounds in the lime mud and to especially investigate in what form they commonly exists in conditions at typical Finnish pulp mill, whether the results are well in-line with the literature cases. Total of four samples originating from the selected mills were analyzed using X-ray fluorescence (XRF) and also by X-ray diffraction (XRD). From these results it is possible to compare, for example the effect of raw materials from different locations on the build up of NPEs.

In the following table 5 is presented the results from the semi-quantitative XRF analysis.

**Table 5. The results from semi-quantitative XRF analysis in percentages.[32]**

| Element | 1. Lime mud | 2. Esp Dust | 3. Lime mud | 4. Esp Dust | 5. Lime mud |
|---|---|---|---|---|---|
| **Sodium, Na** | 0,57 | 0,54 | 0,47 | 0,81 | 0,57 |
| **Magnesium, Mg** | 0,29 | 0,20 | 0,20 | 0,43 | 0,41 |
| **Aluminium, Al** | 0,02 | 0,05 | 0,02 | 0,02 | 0,02 |
| **Silicon, Si** | 0,07 | 0,30 | 0,26 | 0,06 | 0,05 |
| **Phosphorus, P** | 0,45 | 0,27 | 0,20 | 0,53 | 0,35 |
| **Sulphur, S** | 0,02 | 0,08 | 0,02 | 0,03 | 0,02 |
| **Potassium, K** | 0,01 | - | - | 0,02 | 0,01 |
| **Calcium, Ca** | 39 | 39 | 39 | 39 | 39 |
| **Manganese, Mn** | - | - | 0,02 | 0,03 | 0,02 |
| **Iron, Fe** | 0,01 | 0,05 | 0,02 | 0,02 | 0,02 |
| **Strontium, Sr** | 0,08 | 0,19 | 0,17 | 0,03 | 0,02 |
| **Barium, Ba** | 0,03 | - | - | - | - |

Concentrations in the table 5 presented as “-“ were under the detection limit of 0.01%. From the results can be seen that the problematic impurities in these cases would be phosphorus, partly magnesium, aluminium and silicon. Because it was also relevant to be able to verify the chemical composition of different elements present in the lime mud, an XRD-analysis was performed. This should give information of what chemical compositions are present in the lime mud. The result of XRD-analysis from lime mud sample 1 is presented in the following figure 9 and the results of other conducted analyses are presented in the appendices 1-4.

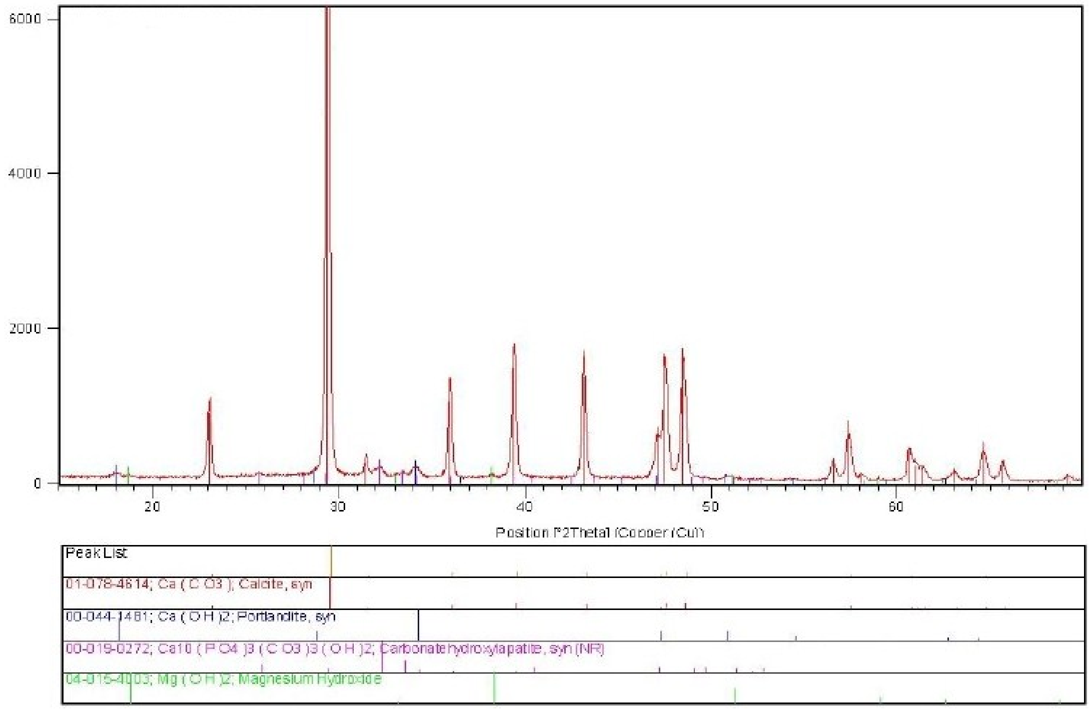


**Figure 9. XRD analysis from the lime mud sample 1.[32]**

As can be seen from the XRD-analysis in the figure 9, the most dominant chemical composition present in the lime mud is calcite and of the circulating impurities the most concerned one, phosphorus seems to be present mainly as carbonatehydroxyapatite. These results appear to be well in-line with the comparable analysis found in the literature, where the suggested form for phosphorus is usually hydroxyapatite. From the appendices 1 to 4 can be seen that there is also some variance between the different lime muds, for example the lime mud sample 3 would seem to have some amount of carbonate apatite, instead of carbonatehydroxyapatite.

Because there was also interest in being able to verify what mineral forms exist in the lime mud, the samples were further analyzed using SEM. In the figures 10 and 11 can be seen SEM-images of the lime mud sample 1.

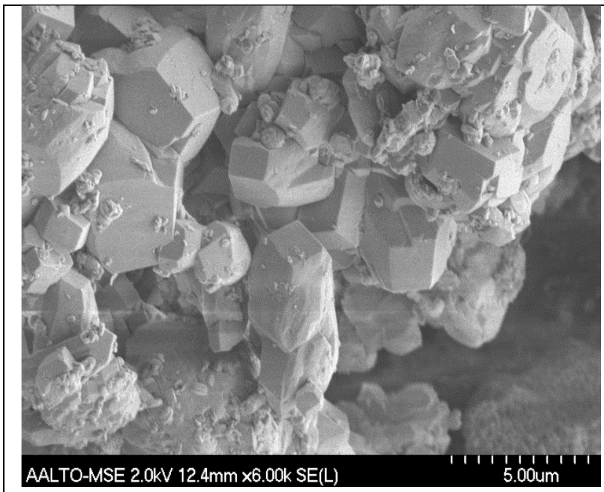


**Figure 10. 6000x enhanced SEM-image of lime mud sample 1.[33]**

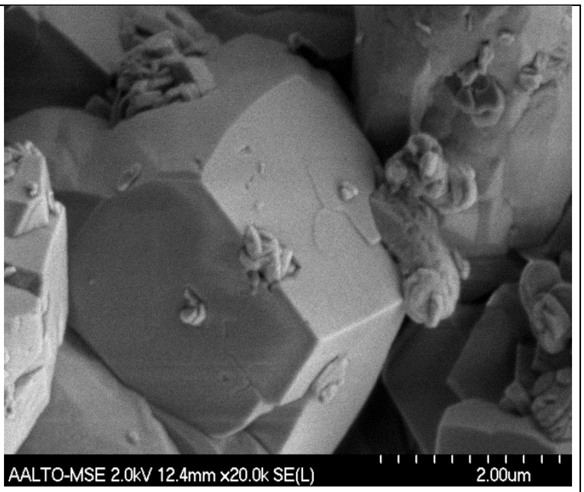


**Figure 11. 20000x enhanced SEM-image of lime mud sample 1.[33]**

From the figures 10 and 11 can be seen that the calcite crystals, determined as the main calcium containing fraction in the lime mud by XRD-analysis, are relatively uniform in size and shape, but it can be seen from the figures 10 and 11 that there are already particles on the surfaces of the crystals that are assumed to be impurity fractions or alternatively smaller agglomerates of calcite crystals. The chemical composition of these smaller particles remained unknown as the SEM-equipment used for the analysis wasn't equipped with an analyzer capable of detecting different elements. Also what remains unknown from the conducted SEM-analysis is the internal purity of these calcite crystals. It could well be possible that there is contamination by other elements inside the calcite structure. Figure 11 has an example where the calcite structure would appear to be fractured and having growing particles from inside. As was noticed, these calcite crystals presented in the figures 10 and 11 are relatively pure and smooth surfaced, hence another set of SEM-images were taken from a lime mud sample originating from a pulp mill located in Asia, where the lime mud seemed to have a gel-like structure. It was presented earlier in the chapter 2.4.2 that calcium silicates may cause this gel-like composition to the lime mud. In the figures 12 and 13 is presented SEM-figures of such lime mud type.

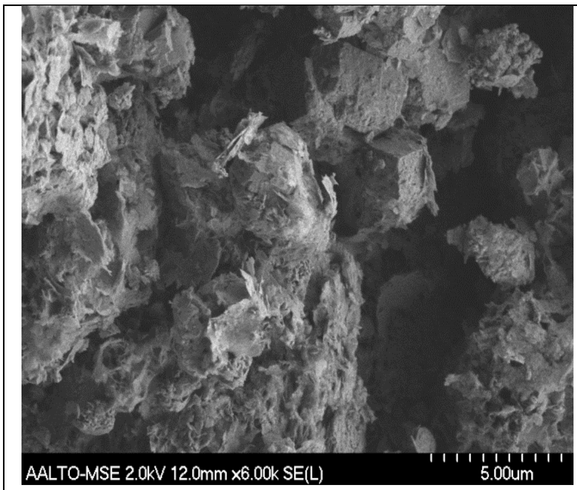


**Figure 12. 6000x enhanced SEM-image of lime mud sample from Asia.[33]**

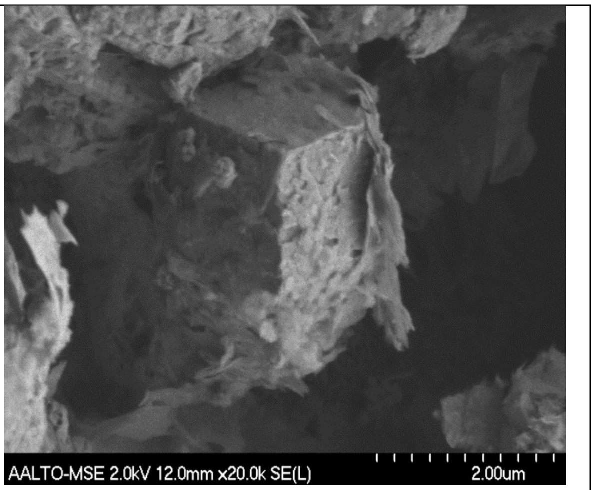


**Figure 13. 20000x enhanced SEM-image of lime mud sample from Asia.[33]**

It can be clearly seen from the figures 12 and 13 that the calcite crystals are completely covered by a layer of some substance that is assumed to be caused by the formation of calcium silicates or alternatively by process chemicals. As was seen from the SEM images of the lime mud presented in the figures 10-13, the scale of the calcite crystals is in the range of few micrometers or even smaller for some particles and the assumed impurity fractions on the surface of these crystals can be even smaller. This arguably makes the range of methods, possibly usable for cleaning the spent lime mud limited, for example mechanical cleaning methods are virtually impossible to be used.

In the following chapter, methods that were considered as viable ways to confront the non-process elements build-up in the lime cycle are introduced. It has to be noted that as the nature of this thesis was strictly based on literature survey there were no experimental part performed relating to the presented solutions. Therefore these presented solutions serve more as an idea and suggestions what could be done in order to achieve non-process element reduction from the lime mud in chemical recovery system.

## 3.1 Selective reduction inside the lime cycle

Solubility differences between the green- and white liquor makes removal of some non-process elements relatively complicated or near impossible from the lime cycle. In-order to be able to reduce non-process elements such as silicon, aluminium or for example phosphorus from the lime cycle, it is needed to alter their solubility. But because one of the key parameters in the lime cycle is also to maintain the quality of circulating lime, the lime has to be unaffected from the methods used in attempting to reduce the circulating impurities. Because of this requirement, the method can be described as selective reduction that only attempts to remove pre-determined impurities from the circulation. As the fundamental idea behind selective reduction is to reduce specific impurity concentration it can be only done by very limited methods. These can be, for example altering the solution properties in order to change solubility, attempting to reduce the impurity concentration by addition of compound that will cause binding of the selected element that could enable, for example filtering to remove the formed compound or alternatively enhance the reduction of targeted impurity via various chemical interactions enhancing possible precipitation. In the following sub-chapters is presented the different ways to achieve selective reduction.[29,30,34]

### 3.1.1 Altering solution properties such as pH or temperature for reduction of silicon

When estimating the different methods to reduce silicon concentration in lime mud, it has to be noticed that silicon usually participates in formation of compounds containing silicon together with different elements present in lime mud, as was described before in the chapter 2.4. Because silicon rarely exists in the solution as pure element, the methods have to take into account the most dominant form of silicon present in lime mud. Based on the literature, this form is amorphous silica. It has been studied that the solubility of amorphous silica in water is primarily dependant of the temperature, liquor composition and the presence of cations. The solubility of amorphous silica, for example increases with increasing temperature and with increasing pH when it's above 9. However presence of calcium and addition of aluminium has reducing effect on the solubility of silicon due to formation of other mineral compounds such as sodium aluminosilicates and calcium silicates. The effect of temperature on solubility of amorphous silica in pure water has been studied by various researchers and the results presented in the figure 14, were compiled by Gunnarsson and Arnórsson.[29,34]

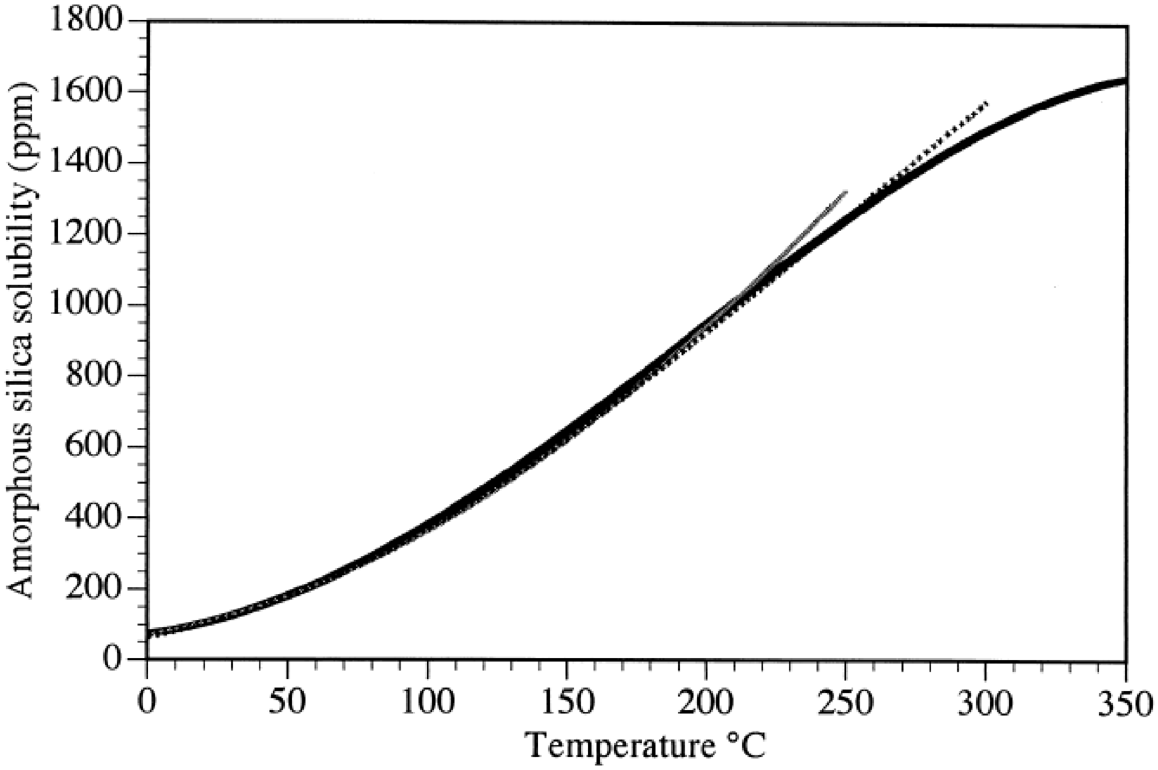


**Figure 14. Data for the solubility of amorphous silica in pure water at $P_{sat}$.[34]**

Different lines in the figure 14 represents the data compiled from other researches. As can be seen from the figure 14, the solubility of amorphous silica is relatively low in the region below 100 degrees Celsius, having only limited increase in the temperature region up to 200 degrees Celsius. Based on this data it could be possible to achieve slight reduction in concentration of amorphous silica by changing the solution temperature. However as these results are from a system consisting of pure water and relatively neutral solution environment, they should be further compared to data from more similar environments present in the recovery system. Assumption is that the impact of alkaline environment on the solubility behaviour of amorphous silica is relatively similar when compared to the case of pure water; there should be seen change in the absolute solubility values.[31]

### 3.1.2 Removal of aluminium and silicon by promoting formation of aluminosilicates within the recovery cycle.

Fundamental reason behind promoting aluminosilicates is to achieve controlled formation of this kind of impurity. From promoting the formation of impurities, arose the idea of introducing controlled surfaces within the cycle, which could be easily enough removed and cleaned. These surfaces should be heated in order to achieve the needed, localized change in the solution properties that will result into formation of aluminosilicate scales onto these surfaces. The heating of the surface could be done by using steam produced in the plant or alternatively by conductive plates, heated by electric current.[29,30]

The main problem with aluminosilicate formation is that they form glossy scales that cause efficiency declinations and ultimately breakage of equipment by being very difficult to remove. These aluminosilicate scales can be found in the chemical recovery system at locations, where there are hot surfaces, for example at the heat exchangers. The precipitation will take place in the region of heated surface because of decrease in the solubility of sodium aluminosilicate due to increase in local temperature and concentration of aluminium and silicon. Increased concentrations of aluminium and silicon result, within precipitating conditions in formation of aluminosilicates that are usually in form of sodalite, $Na_4Al_3Si_3O_{12}Cl$. However it is not entirely certain whether the formation of aluminosilicates is caused by purely increase of temperature or concentration. More likely it is consequence of them both, as local increase in temperature is likely to also locally increase the concentration. Other affecting factors in formation are, for example the concentration of hydroxide ions in the solution, which partially determines the formation location of the precipitate. This can be seen from the following figure 15, where the effect of different hydroxide ion concentrations on the precipitate formation location is presented.[18,24,29]

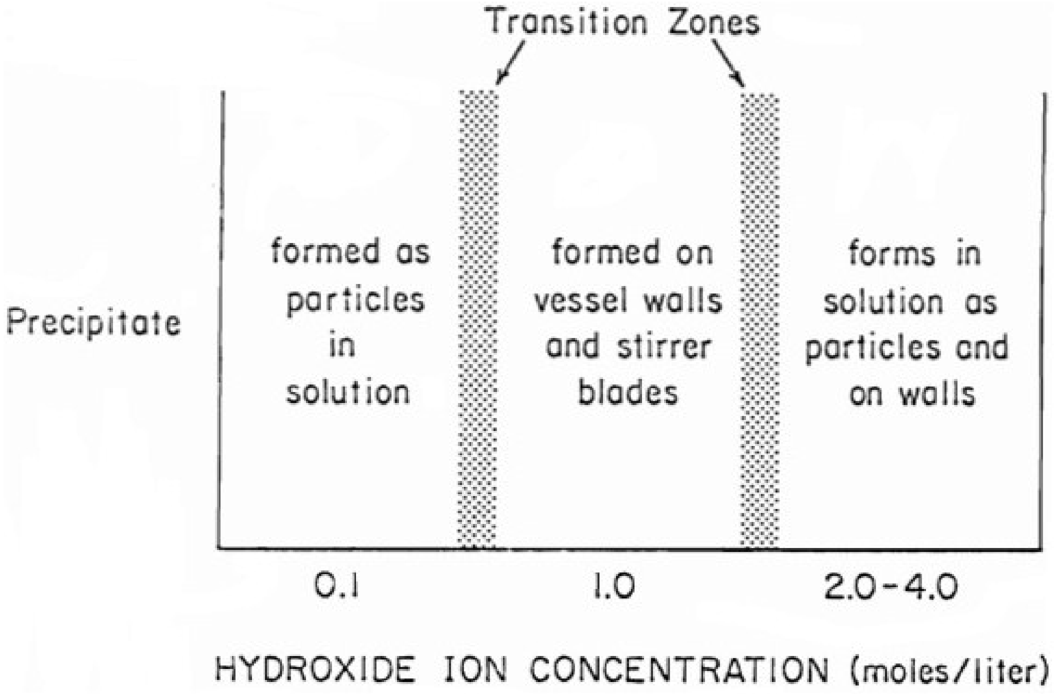


**Figure 15. The effect of hydroxide ion concentration to formation of precipitates.[29]**

Based on the information seen in the figure 15, it could be said that the desired formation location of aluminosilicate scales, when using this method would be on the planted surfaces within the container and therefore the hydroxide ion concentration should be in the region of 1.0 mole per litre. In the literature, Gasteiger et al. have conducted experiments for the solubility of aluminosilicates in alkaline solutions and constructed thermodynamic equilibrium model. Graphical representation of this solubility model of aluminium and silicon as a function of ionic strength and pH is presented in the figure 16.[29,35]

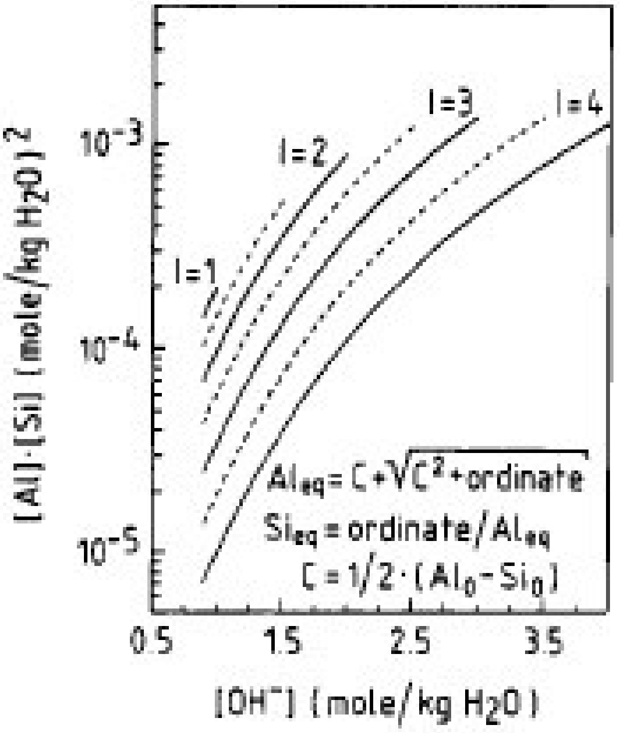


**Figure 16. Graphical representation of [Al][Si] as a function of ionic strength and pH.[35]**

According to the figure 16, when ionic strength and the hydroxide molality are known, the solubility of Al and Si compound can be estimated. According to Gasteiger this model, in the figure 16 should provide reasonable accurate approximation for sodalite solubility also in technical liquors. Based on the results by Ulmgren for aluminium and silicon concentration in technical liquor the error between the figure 16 and the results measured by Ulmgren was approximately 3 orders of magnitude. By using the presented information it should be possible to construct general formation parameters for this reduction method when combined to sufficient practical data.[35]

Based on the experience gained from Finnish Kraft pulp mill the safe aluminium concentration in green liquor would seem to be around 40-100 mg/l and after 100 mg/l the risk of alumininosilicate formation grows rapidly. Based on these concentration values it is possible to estimate some general formation parameters for aluminosilicate scales that are compiled in the following table 6. Assumedly these values would be relatively similar for also white liquor with slight alterations.[36,37]

**Table 6. General estimates for conditions required by the aluminosilicate-formation-surface, compiled from literature and plant experience.[36,38]**

| Parameter | Value |
|---|---|
| Local surface temperature [°C] | > 95- |
| Hydroxide ion concentration [moles / litre] | 1.0-2.0 |
| Aluminium concentration [mg/l] | > 100 |
| Silicon concentration [mg/l] | > 100 |

As can be seen from the estimates in the table 6, the needed temperature would most likely require that there is sufficient methods to remove this excess heat energy from the processed liquor, as it can result in further issues in the other parts of the lime cycle.

### 3.1.3 Removal of aluminium or magnesium by promoting the precipitation of hydrotalcite

As was presented before in the chapter 2.4.3, the removal of aluminium can be closely linked to magnesium and vice versa, the removal of magnesium closely to aluminium. This is possible because aluminium and magnesium are known to produce insoluble compound of hydrotalcite under alkaline conditions. Hydrotalcite, according to Ulmgren has the following chemical composition $Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \cdot nH_2O(s)$, where x is in the region of $(0.1 < x < 0.34)$. In the formation reaction of hydrotalcite some part of magnesium ions in magnesium hydroxide are replaced by aluminium ions and carbonate ions are entering the structure as balancing elements to achieve electrochemical neutrality. This overall reaction can be presented as following in the reaction 3

$$(1-x)Mg(OH)_2(s) + \ xAl(OH)_4 + \frac{x}{2CO_3^{2-}} + mH_2O \leftrightarrow Mg_{1-x}Alx(OH)_2(CO_3)_{x/2} \cdot nH_2O(s) + 2xOH^-. \qquad (3)$$

Because the product hydrotalcite has a larger particle size compared to magnesium hydroxide it is possible to remove the formed product from the solution via, for example sedimentation or filtration and hence reduce the current magnesium and aluminium concentration in the circulation.[16,30]

When beginning to estimate the amount of non-process elements, possible to reduce by this presented method the following factors are to be considered. Under alkaline conditions the solubility of aluminate ions is affected by three factors that are the hydroxyl - and magnesium ion concentration together with the temperature of the solution. Also the silicate - and hydrogen ions have some effect on the solubility. Therefore the removal of aluminate ions is the combined function of reduced hydroxyl ion concentration, decreased temperature and increased concentration of magnesium ions in the solution. In the figure 17 is presented graphical representation of the total concentration of aluminate ions in solution as a function of reaction temperature in green (G) and white (W) liquors at different ratios of Mg/Al (mol/mol).[16]

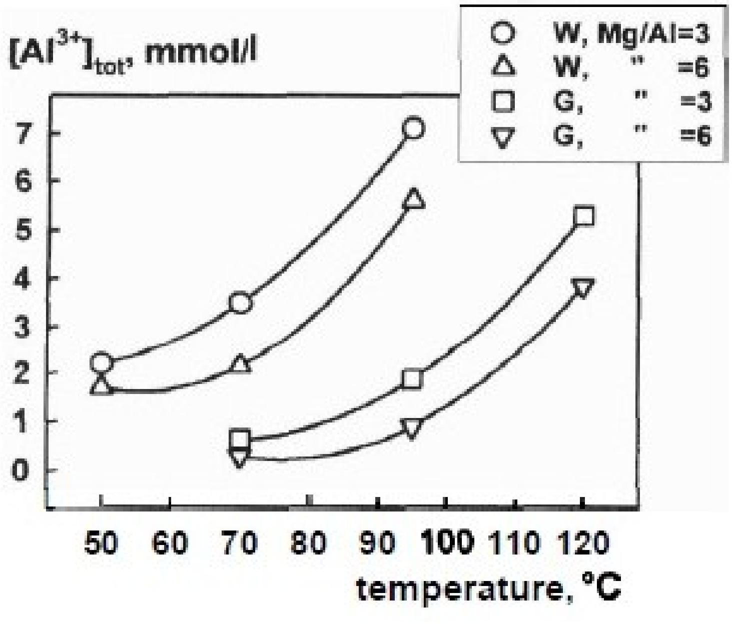


**Figure 17. The removal of aluminate ions from alkaline liquors by addition of magnesium sulphate.[16]**

As can be seen from the figure 17 the concentration of aluminium was at its lowest value when the ratio of Mg/Al was at its highest value and the temperature being in its lowest value. From the figure 17, can also be seen that the effect of aluminium on the reduction of magnesium is strongest in the green liquor, but it also has effect in the white liquor. As a removal method the addition of magnesium can approximately precipitate aluminium in a ratio of 4 g of magnesium per 1 g of aluminium. As an example, during a practical mill trial conducted in a Swedish Kraft mill by Ulmgren, reduction of 125 kg aluminium in two days by the addition of 360 kg magnesium sulphate per hour, which equals 2 kg of magnesium sulphate per $m^3$ of green liquor or Mg/Al ratio of 8, was observed.[16,18,30]

Based on the presented formation mechanism of hydrotalcite, the main purpose with this method is arguable within the reduction of aluminium from the recovery system. However as hydrotalcite is composed of magnesium and aluminium it should also be possible to remove excess magnesium from the solution by addition of aluminium when high magnesium concentrations are the problem.[16,18]

## 3.2 Biological treatment for reducing non-process element concentration in the lime mud

Biological treatment is a widely used technology and also, according to European Commission accounted as one of the best available technology(BAT) in recycling of used process waters or waste streams from, for example Kraft pulping. The main function of biological treatment is to reduce or completely remove organic matter from the input stream by living micro-organisms causing biological degradation or decomposition. This biological degradation can be achieved by various ways of which the most common are anaerobic, aerobic or combinations of these methods. The fundamental idea behind biological treatment is in using micro-organisms, which are essentially beneficial bacterial colonies, to process these waste streams and their contained impurities resulting into substantially cleaner product to be used again in the processes. Biological treatment methods based on micro-organisms are well suited into processing waste streams from Kraft pulping, because as an essential criterion to be functioning correctly they always requires some basic components from the environment. Such components include organic matter together with major nutrients for example nitrogen, carbon, phosphorus, sulphur, potassium, magnesium and calcium. In Kraft pulping waste streams, organic matter is usually already present, or the addition of it shouldn’t compromise the functionality of other parts of the processes. Nutrients in these Kraft waste streams are usually present as compounds, combined into the other particles.[39,40,41]

As biological treatment is conventionally used for the cleaning of waste streams, it also has the potential and could possibly be adaptable for the recycling of lime mud. Based on the conducted XRF analysis from the lime mud samples they already contain some of the major nutrients required by the micro-organism as seen from the table 5. For micro-organisms perspective most of these contained elements are necessary in order to maintain growth and some only act as a, for example stabilizing agent providing protection to the bacteria's cell from hostile environmental conditions present outside of the cell. The rest of the required nutrients are typically those present in organic matter, which however is harmful and highly un-wanted substance in the lime cycle; but introducing it to the lime mud would be necessary for biological treatment to be possible. This addition of organic matter should be carefully executed by separation or additional process step if the recycling of lime mud is to take place as an internal part of the process. The removal of the organic matter assumedly could be possible by taking advantage of the different densities of organic matter and lime mud, which would possibly enable separation by sedimentation. Alternative option for recycling the lime mud could be using the microbial activity for the already removed lime mud and returning the processed product back to the lime cycle.[42]

Micro-organisms interact with their environment in various ways, of which the most important ones, in the case of processing wastes or recycling lime mud are the methods related to consumption of elements that are considered harmful for the end-product. For example, in the case of carbonate precipitation the way bacteria interact between its micro- and macro-environments can be described by the passive and active interactions between the bacteria and its local environment as seen from the figure 18.[42,43]

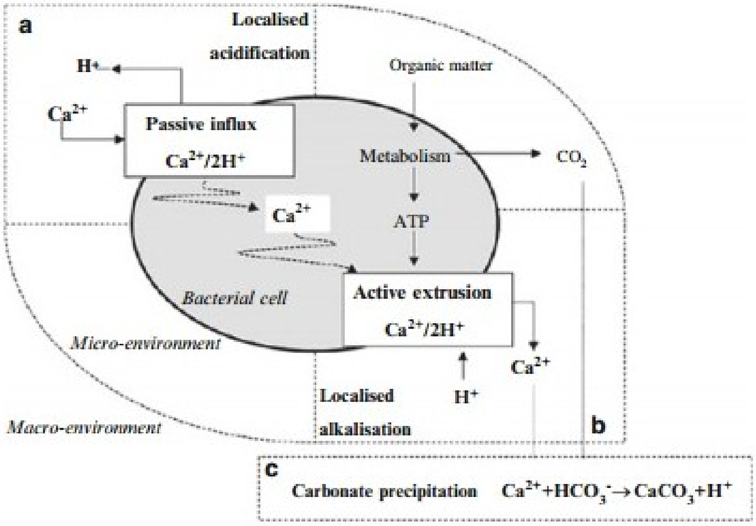


**Figure 18. Bacterial calcium metabolism and subsequent $CaCO_3$ precipitation under high-pH and high-$Ca^{2+}$ conditions.[43]**

In the figure 18, bacteria process the organic matter to produce adenosine triphosphate (ATP), which is the cell's major energy currency. This ATP produced in the metabolic system of the cell, can be used in various ways to drive the needed endergonic reactions, for example in the presented case of carbonate precipitation, the active extrusion of calcium ions back into the micro-environment. This extrusion can be the case, where the combination of extracellular alkaline pH and calcium ions will lead into intercellular build-up and excess of calcium ions. Hence the ATP is required for active extrusion of these excess intercellular calcium ions, resulting in further increase of localized pH that will eventually produce ideal conditions for localized precipitation of $CaCO_3$.[42,43]

Because removal of impurities by bacterial activity is likely to require co-operation of multiple different bacterial strains, only some of the considered pathways are presented in this thesis and in the following chapters 3.2.1 and 3.2.2 two detailed cases of consuming elements from the lime mud are presented. It has to be also noted that it might be well possible that these cases could co-exist rather than being separate events as presented in this thesis, as micro-organisms usually produce larger colonies functioning in co-operation.

### 3.2.1 Non-process element consumption through biological reduction of sulphur

The ideology with biological sulphur reduction is to have the bacteria consume available sulphur and in the same time have them also reduce the impurity amount from the lime mud. As a prerequisite the biological treatment based on sulphur requires excess of sulphur in the solution; this can be achieved by acidic effluents, which when in-contact with the lime mud produce gypsum slurry to be processed by bacteria. The bacterial interactions consume the sulphur present in gypsum and produce calcium carbonate during the process that should be once again usable in lime cycle when separated from the organic mass. This method relies on the passive production of gypsum from the lime mud by addition of acidic effluents and bacterial activity. This means that no added chemicals should be required to assist the process hence enhancing its cost-efficiency.

As a starting requirement biological sulphur reduction requires sulphur rich environment i.e. in the case of lime mud recycling, to achieve this one possible way would be to convert majority of the lime mud to calcium sulphate. Because the lime mud is primarily composed of calcium carbonate, as was determined before in the conducted XRF-analysis shown in the table 5, it can be converted to gypsum by using acidic effluents originating from Kraft pulping. For example, typically acidic effluents consist of sulphuric acid, sodium hydroxide and various chloride compounds, where the contained sulphuric acid in the effluent will cause the following reaction,

$$H_2SO_4 + CaCO_3 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2. \quad (4)$$

This reaction 4 is likely to result into gypsum based slurry that will serve as a starting point for the sulphate reducing bacteria (SRB) that will begin to consume it. Possible strains capable of consuming gypsum are, for example *Desulfuvibrio.* This strain of bacteria belongs to group of complete oxidizers, which means that they possess the ability to fully oxidize organic compounds into carbon dioxide. High degree consumption of the organic matter from the stream is ultimately beneficial for the considered process, because it potentially enables the product to be reused when the added organic matter is consumed.

These sulphate reductive bacteria are micro-organisms that consume available sulphur and produce hydrogen sulphide and carbon dioxide in their metabolic system. The formation of calcium carbonate occurs when calcium ions, separated by the bacteria from the gypsum react with carbon dioxide resulting in the following overall reaction 5,

$$6CaSO_4 + 4H_2O + 6CO_2 \rightarrow 6CaCO_3 + 4H_2S + 2S + 11O_2. \qquad (5)$$

The forming calcium carbonate is in its crystalline form and formed outside of the bacterial cell; this means it could be possible to reversibly produce calcium carbonate from the gypsum slurry, consuming impurities during the process.[41,43,44,45,46]

General requirements for the calcium carbonate precipitation by sulphur reducing bacteria are anoxic environment that is also rich in organic matter, calcium and sulphate. These bacteria can function in a wide range of pH; however the optimum growing conditions require that the environmental pH is in the region of 5 to 9. Values outside this range will result in reduced activity of the bacteria. The optimum temperature range of growing conditions for *Sulfuvibrio* has been reported to be in the range of 25 to 40 degrees Celsius. These conditions could be achieved by methods described further in the chapter 3.3.[43,44,46,47]

Because the use of sulphate reducing bacteria produces hydrogen sulphide as a product in their cell reactions, there has to be readiness to remove this due to it is considered as highly unwanted emission, having serious health effects already in small concentrations. When considering the possible methods for removing $H_2S$ from the solution, care has to be taken in maintaining the conditions required for the optimal function of SRB. For example, potentially enabling more aerobic conditions would reduce the generated amount of hydrogen sulphide, however aerobic conditions can eventually seize the activity of SRB by inducing operation of alternative micro-organisms. Finally when aim is to attempt the regeneration of lime mud to a process viable state it is needed to include separation of the bacteria containing organic mass from the produced calcium carbonate before it is possible to be considered in actual process. This separation could be achieved by, for example sedimentation or separating the microbial mass by membranes.[47]

### 3.2.2 Biological consumption of phosphorus

The ideology with biological consumption of phosphorus is very similar to the case of biological consumption of sulphur. The exceptions come from the differences in reaction mechanics as it is considered that the biological consumption of phosphates, straight from the present mineral forms of phosphorus in lime mud is not likely to be possible. In lime mud phosphorus is usually bound in the mineralogical form of hydroxyapatite and before it is possible to biologically consume phosphorus, the phosphates have to be released from their mineral “host” into the liquid. This can be done in similar ways that were presented in the chapter 3.2.1, by the use of acidic effluents. Sulphuric acid is presumed to cause breakage of hydroxyapatite resulting in release of phosphoric acid to the solution in the following reaction 6,

$$Ca_5(PO_4)_3OH + 5H_2SO_4 + 9H_2O \rightarrow 3H_3PO_4 + 5CaSO_4 \cdot 2H_2O. \quad (6)$$

This phosphoric acid is assumed to be in a suitable form for bacterial consumption having numerous possible strains capable of consuming it, depending on the desired operation conditions. In general, the biological phosphorus removal requires the use of anaerobic or anoxic stage before introducing the organic mass to aerobic conditions, where the “luxury” up-take of phosphorus occurs. In absence of oxygen, at anaerobic conditions the bacteria begin consuming short chain fatty acids available in the solution as their energy source during which intercellular phosphates are released into the liquor. When subjected to aerobic conditions the stored energy from short chain fatty acids is metabolised, providing energy to the cell for uptake of all available phosphates.[44,45,48]

The combination of Kraft acidic effluent and lime mud should provide the sufficient amount of nutrients to meet the bacterial requirements in order to achieve the described "luxury" uptake of phosphates. General solution parameters needed to achieve the optimal conditions for biological phosphorus removal are usually that the pH of the solution needs to be above 7, with the temperature ranging from 20 to 40 degrees Celsius. Due to the pH requirement, in process perspective the phosphorus removal might only be functional after the acidic effluent is neutralized enough to achieve the optimal process conditions. The resulting waste product, organic mass could potentially be used as raw-material for fertilizers because it contains majority of the phosphorus present in the solution, bound within the bacterial cells. Absence of harmful impurity elements needs to be verified as these harmful element concentrations in fertilizers are highly regulated and the values can be seen later in the chapter 3.5.1 table 10.[48]

## 3.3 Neutralization of acidic effluent with lime mud

In the previous chapter 3.2, was presented the potential use of acidic effluents in the pre-stages for biological treatment of lime mud. In addition to the desired recycling of lime mud, acidic effluents could have additional potential in recycling within Kraft pulping. Such potential could be, for example focusing in producing also purified water rather than just purified calcium carbonate to be reused in the chemical recovery. Water is becoming more and more important resource and especially in locations, where the sources of water are scarce. Therefore achieving potential savings in water consumption are in great value within Kraft pulping and potential new methods, which would enable higher efficiency in water use, are very valuable.

One potential method for recycling the used plant water could be, for example through the combinative use of lime mud and acidic effluent. With this method the spent lime mud is used in raising the pH of the acidic effluent. As described earlier, the addition of acidic effluent to lime mud produces mostly gypsum based slurry that should be first separated to clarifier. Here the probable reaction would be the transformation of gypsum into calcium carbonate and sodium sulphate that could be reused in the chemical cycle. Inclination in pH of the already partially cleaned water is continued by the addition of lime, this addition of lime will likely result in formation of a slurry substance, which should now be mainly calcium carbonate. If the produced calcium carbonate is pure enough it could be used as lime mud, if not it needs to be clarified again to result into cleaned water. [31,49]

Before acidic effluent water can be reused, complicated fractions such as lignin needs to be removed. This problematic lignin should be prioritized for removal in order to fully enable the potential reuse of the water. The way lignin and calcium interacts with each other has been studied by Torre et al. who found that calcium ions posses great influence on available lignin. Assuming the key factor in lignin binding are the interactions between lignin and calcium ions it could be possible to achieve conditions, where the lignin in solution acts as a core for the forming gypsum particles encasing the lignin. Hence the presented example should produce partially cleaned water, where the troublesome lignin could potentially act as an anchor for forming gypsum. Based on the studies done by Torre et al. lignin becomes saturated of calcium in the ratio of 100 milligrams of fibre to 0.5 milligram of calcium and at higher pH the capabilities of lignin to bind calcium ions are moderately higher. The resulting waste fraction from this process, the gypsum-bound lignin could have some possible uses instead of being simply treated as a waste, for example as a raw-material in the bacterial treatment processes.[31,49,50]

Estimations for the required degree of purity for process waters can be based on various limits depending on what purpose the water is ultimately used for. Therefore when constructing the limits for purification of process waters the reference values should be selected so that they can be applied to multiple cases even though they exceed the requirements set for process conditions in some of the parameters. For example, the European Commission has presented values for the required degree of purification for purified effluents when discharged to surface waters. According to EC the resulting purified liquid effluents should meet the following requirements for maximum levels set for direct discharge to surface waters from pulp and paper manufacturing presented in the table 7.[39,51]

**Table 7. Liquid effluent requirements for direct discharge to surface waters.[39][51]**

| Parameter | Maximum Value |
|---|---|
| **pH** | 6-9 |
| **COD [mg/l]** | |
| - Kraft pulp mills | 300 |
| - Sulfite pulp mills | 700 |
| **AOX [mg/l]** | |
| General | 40 |
| Target values for: | |
| - Retrofit | 8 |
| - New mills | 4 |
| **Total phosphorus [kg/T]** | 0,05 |
| **Total nitrogen [kg/T]** | 0,4 |

These values state the required limits for the used water prior it can be released to soil from the mill. Therefore some of the parameters may be higher than is actually needed for process conditions, hence achieving these presented parameter requirements should provide sufficient degree of purity. When re-using the cleaned process waters in white liquor preparation the most relevant parameter usually is the reduction in organic matter or COD. For example, in lime mud washing it is required that the COD-level is reduced at least by over 40 %, further advantages can be gained when the reduction in COD is over 60 %. As an example the COD values acceptable for white liquor preparation is 1500 mg/l and in the acidic effluents the COD value is usually between 800 to 2200 mg/l depending on the used effluent stage and pre-treatments for the effluent. When comparing these reductions in COD-levels to the assumed original values of COD, these presented requirements for direct discharge to surface waters could serve as sufficient guidelines when considering the reuse of process waters.[49,52]

The presented method has some open question to be verified, for example in the resulting change of pH that can be achieved by purely addition of lime mud and how much additional pH lifters are needed in order to reach the desired pH levels. Some estimations can be done based on the studies done by Milosevich & Hill, who reported that when using lime mud to acidic effluents the dissolution of lime mud becomes difficult after pH has reached 4 and additional alkali such as NaOH had to be used. This would suggest that by only using lime mud the desired change in pH can be reached but it will take considerable amount of time and using additional chemicals might make it economically unappealing.[53]

## 3.4 Ultrasonic applications

Ultrasound has multiple purposes when considering its usefulness in the lime mud recycling. Most common industrial applications in use that use ultrasound include, for example mechanical cleaning, enhancing chemical reactions or using ultrasound in enhancing dewatering. From these methods the potential of chemical reaction enhancing or dewatering purposes are the most interesting when considering the potential of ultrasound for lime mud.

### 3.4.1 Using ultrasound for mechanical cleaning of the lime mud

When estimating the use of ultrasound in lime mud recycling, assumptions are based on the fact that calcite crystals are covered by impurity fractions that could potentially be separated from the calcite core by using ultrasound and by doing so improve the overall purity of the calcite. Based on the conducted SEM analysis this is unlikely to be possible. Because as was seen from the figures 10-13, the scale of the calcite crystals is in the range of few micrometers, with possible impurity fractions on the surface of the calcite crystals even smaller. When the liquid-solid system is subject to ultrasound, the pressure waves produced by ultrasound cause bubble cavitations' affecting the solid particles in the system. These shockwaves are likely to cause fractures in the produced calcite agglomerates that might just result into increase of issues caused by smaller particles. This rules the mechanical cleaning of the lime mud particles virtually impossible due to the lack of control in the mechanical cleaning, which would likely result into breakage of the calcite crystal structure that would cause reduction in agglomerate sizes and result in losses of calcium carbonate during the lime cycle by dusting in the lime kiln.[31,54]

### 3.4.2 Using ultrasound for enhancing causticization grade

Because the use of ultrasound is likely to cause breaking of the produced calcite agglomerates, it is not beneficial to use it in the later stages of lime cycle with aim to enhance lime mud purity through mechanical cleaning. However ultrasound and its cavitation energy could be potentially harnessed earlier in the recovery system. The ultrasound could potentially be used in enhancing the causticization efficiency by increasing the usage ratio of calcite crystals during recausticizing or using ultrasound in enhancing dewatering of the lime mud. Alternatively ultrasound has been also investigated to enhance microbiological activity during anaerobic phases when used as a pre-treatment method. This enhancement is likely due to the cavitation energy breaking the organic compounds in the organic mass making the bacteria degradation of the mass easier.[54,55,56]

The potential of using ultrasound for increasing causticization efficiency comes from the increase in speed and conversion grade of the un-reacted calcium hydroxide particles. As was presented earlier in the reaction 2, during the causticization calcium hydroxide particles react with sodium carbonates producing during the reaction calcium carbonates. These calcium carbonates have residual calcium hydroxide within the particles due to diffusion limiting the full conversion. Ultrasonic energy could be used in enhancing the carbon dioxide to better access the un-reacted $Ca(OH)_2$ core in the reaction and by doing so increasing the conversion grade of calcium carbonate. The use of ultrasonic cavitation energy will cause the breakage of the calcium carbonate layer during the causticization, hence allowing the increase in efficiency. In small scale tests, acoustic intensity of 7.1 $W/cm^2$ with input energy of 17 W was reported to cause fractures in the calcite crystals. By the acoustic intensity is given the amount of energy emitted by the used probe. This energy is strongly dependant on the distance to the target, therefore when in large scale industrial applications, in order to still maintain the desired effect on the calcite crystals, not only the amount of the input energy has to be lifted, but there should also be ways to reduce the distance between the emitting probe and processed surface. This could be achieved by, for example sufficient agitation within the vessel or alternatively using multiple input locations for the acoustic energy. When considering the implementation of ultrasound for causticization care has to be taken as it is also likely to produce smaller agglomerates, having increased amount of fractures and defects. This might increase risk of plugging and dust formation in the later stages of the recovery system. In order to avoid this, only short impulses should be used in the causticization, this is also likely to maintain the required input energy at minimum.[54,56]

### 3.4.3 Using ultrasound for enhancing the dewatering of lime mud

Ultrasound could also potentially be used in enhancing the dewatering of lime mud, however it is unlikely efficient enough to implement it as a separate filtration stage, more likely the implementation of ultrasound into dewatering should be incorporated into existing dewatering steps. One possible implementation place could be within the vacuum filtration systems of the washed lime mud, where the vibration caused by high intensity ultrasonic energy would improve the effect of the static pressure. Here the alternating stresses caused by ultrasound to the cake may enhance the migration of the liquid. This has been tested on an experimental laboratory scale setup by Gallego-Juárez et al. seen in the following figure 19.[57]

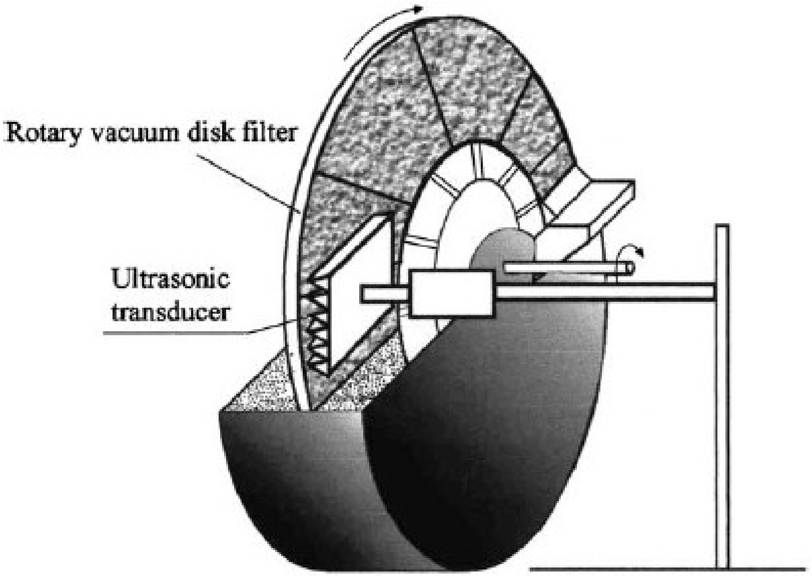


**Figure 19. Schematic of a experimental ultrasonic assisted filtration set-up.[57]**

From the figure 19 can be seen that the acoustic energy is transmitted via mechanical contact between the rotary filtrate disc and the transducer. The efficiency of the ultrasonic assisted filtration set-up is largely dependent on several factors to be balanced for the optimal implementation of ultrasonic assisted filtration. Such factors are, for example the particle size of the processed suspension, the applied power and also the used treatment time. Processing smaller particles increases efficiency of the system whereas larger particle sizes allow the use of higher input powers, without having the risk of filter cake becoming unstable. The use of higher input powers consumes also more electricity but overall it should be compensated by the achieved increase in the dewatering level. Achieving higher treatment time also raises the dewatering level; however this requires the optimization of the rotating speed of the filtration system. By process optimization it might be even possible to achieve dry-content close to 90% for the lime mud prior entering the lime kiln. Overall these improvements gained in the dewatering would likely increase the efficiency of the lime kiln and by doing so increase the intake amount of NPE’s that will be incinerated into dusts and removed by ESP-system; risks however exist in the potential dusting issues causing plugging in the electrostatic precipitators.[57]

## 3.5 Alternative uses for the discharged lime

Alternative uses are also considered as viable recycling methods of the used lime mud. As these methods are alternative, they mean that the lime mud has to be removed and it no longer can serve its purpose in the main processes of the chemical recovery system. The removed lime mud however still has the potential in several uses such as serving agricultural needs in soil conditioning, fertilizing or acting as a catalyst in hydrogen production. The most un-desired result for lime mud is the disposal to landfills, as with this method all the potential of the spent lime mud is lost. However in some cases it can be the most cost efficient method for using the spent lime mud and therefore attempting to change the potential waste status of the removed lime mud can have financial impact on the pulp mills economy. When considering the lime mud as waste and disposing the removed lime mud from the process to landfill, it has to fulfil several limits concerning certain metals and anions. These limits vary greatly depending on the location and present regulations, for example in Finland the values set by regulative officials are gathered in the following table 8.[58,59]

**Table 8. Element concentration limits in different waste types in Finland.[58]**

| Element | Limits in wastes as [mg/kg] in dry-matter (L/S 10 l/kg) | | |
|---|---|---|---|
| | Permanent waste | Normal waste | Hazardous waste |
| **Arsenic (As)** | 0,5 | 2 | 25 |
| **Mercury (Hg)** | 0,01 | 0,2 | 2 |
| **Cadmium (Cd)** | 0,04 | 1 | 5 |
| **Chromium (Cr)** | 0,5 | 10 | 70 |
| **Copper (Cu)** | 2 | 50 | 100 |
| **Lead (Pb)** | 0,5 | 10 | 50 |
| **Nickel (Ni)** | 0,4 | 10 | 40 |
| **Zinc (Zn)** | 4 | 50 | 200 |
| **Barium (Ba)** | 20 | 100 | 300 |
| **Molybdenum (Mo)** | 0,5 | 10 | 30 |
| **Antimony (Sb)** | 0,06 | 0,7 | 5 |
| **Selenium (Se)** | 0,1 | 0,5 | 7 |
| **Chloride ($Cl^-$)** | 800 | 15 000 | 25 000 |
| **Sulphate ($SO_4^{2-}$)** | 1000 | 20 000 | 50 000 |
| **Organic carbon (TOC)** | 30 000 | 5 % | 6 % |

It can be seen from the table 8 when compared to the table 5, where the lime mud from several mills were analyzed, that of the detected metals Barium is problematic in the case of disposing lime mud as permanent waste. However as the conducted analysis had the minimum detection limit of 0.01 % equal to 100 mg/kg, which means that in the conducted analysis most of the hazardous heavy metals weren't detected, but when compared to other results found from the literature some elements such as chromium, lead, nickel and zinc can easily set the disposable lime mud under the category of hazardous waste. Of course it has to be noticed that the amount of some impurities is mainly function of environmental growing conditions, which means that if using raw material originating from polluted locations the amount of potentially hazardous impurities rises.[58,59]

### 3.5.1 The use of lime mud in soil conditioning or for fertilizers

The usefulness of lime mud in soil conditioning either as fertilizer raw material or for enhancing soil pH levels has been widely studied in the literature. The main ideological purpose with the recycling of lime mud as soil conditioner or as fertilizer is in attempting to return majority of the elements that were removed during harvesting of the forest back to the soil and by returning these elements to the soil, fulfil their life cycle. The use of lime mud for soil condition also takes benefit from the high alkalinity of the lime mud, which is beneficial in locations where the soil is acidic and therefore un-suitable for, for example agricultural needs. In addition to the lime mud's effect on raising the soil pH level it also adds calcium and magnesium together with other important nutrients into the soil. When combining all these effects, studies have shown that the same effect on soil conditioning can be achieved by using less lime mud, when compared to commercial ground limestone. Based on the studies conducted by Pöykiö et al. the liming value of lime mud would yield significant savings in soil conditioner consumption. In the reference case approximately 0.8 tonnes of lime mud waste would be required for replacing 1 tonne of commercial ground limestone.[60,61,62]

When considering the use of lime mud waste as fertilizer the key factor would be to achieve controlled leachability of the contained elements and especially of the contained trace amounts of heavy metals under environmental conditions. In lime mud, different fractions contain different amounts of available elements to the environment and according to Pöykiö et al. lime mud can be divided to five categories based on the leachability of metals to the environment. These categories are presented in the following table 9.[60,62]

**Table 9. Classification of lime mud into categories based on the different leachable fractions.[62]**

| Category | Description | Releasable elements |
|---|---|---|
| **1. Water-soluble fraction** | Labile elements, readily leachable and potentially bioavailable in the environment. | Cr, Zn, Ba, S |
| **2. Exchangeable fraction** | Metals adsorbed on lime waste or on major components of lime waste. Elements are most readily available to biota. | Cr, Zn, Ba, S |
| **3. Easily reduced fraction** | Elements strongly bound to the oxides of Mn and Fe. Potentially bioavailable. | Ba, S, Fe, Mn, Ni |
| **4. The oxidizable fraction** | Elements occurring as oxidizable minerals and released under oxidizing conditions. Potentially released through biodegradation. | Cr, Zn, Fe, Mn, Al, Ni, V, Ba, S, Pb |
| **5. The residual fraction** | Non-mobile fraction containing metals retained within the crystal lattice of minerals and inside crystallized oxides. Released as a result of long-term effects such as weathering. | Pb, Cr, Zn, Fe, Mn, Al, Ni, V, Ba, S |

Based on the presented table 9 some of the elements such as barium, chromium and sulphur are released from the lime mud to the environment during multiple stages and great proportion of the elements in the lime mud would seem to be released from the lime mud under oxidizing conditions, for example during biodegradation. However when evaluating the most harmful metals and most of the toxic metals, it can be seen that they are assumedly not to release under short-term environmental effects. Instead long-term effects such as weathering, would suggest that some treatment is required for the lime mud in-order to prevent the possible soil contamination caused by these elements and also to control the leachability of the beneficial elements. This controlled, slow leachability over a long period of time would beneficially affect the soil for several years; although this most likely requires pre-treating, such as compressing the lime mud into pellets. The use of fertilizers are highly regulated and for example the EU directive states the maximum concentrations of heavy metals that are on average released from the fertilizer into the soil. These maximum harmful metal concentrations for fertilizers are presented in the table 10.[60,62]

**Table 10. Maximum concentrations for harmful metals in fertilizers.[63,64]**

| Element | Maximum concentration in fertilizers (mg/kg avg.) | |
|---|---|---|
| | In general usage | In forest usage |
| **Arsenic (As)** | 25 | 50 |
| **Mercury (Hg)** | 1 | 1 |
| **Cadmium (Cd)** | 1,5 | 15 (by-product) / 25 (ash) |
| **Chromium (Cr)** | 300 | 300 |
| **Copper (Cu)** | 600 | 600 |
| **Lead (Pb)** | 100 | 100 |
| **Nickel (Ni)** | 100 | 100 |
| **Zinc (Zn)** | 1500 | 4500 |

When comparing the values seen in the table 10 to the analyzed lime mud values in the table 5, it can be seen that the toxic elements such as arsenic, mercury, lead and cadmium may exceed the presented maximum values in the case of general use of fertilizers unless the lime mud is pre-treated in order to reduce these elements, which however can be very hard to achieve with attempting to also maintain sufficient cost efficiency. When compared the analyzed lime mud to values found from the literature it can be verified that the presumed elements are likely to cause problems in fertilizers, for example the Samoa pacific mill reported arsenic and cadmium values of 33.75 and 2.525 mg/kg, which would restrict the use of the lime mud as general fertilizer. Based on these values the lime mud would however be suitable, in most cases for forest fertilizing.[65]

As there is potential risk of exceeding the maximum allowed concentration values for some elements when considering the fertilizers in general usage, the lime mud would have to be pre-treated with attempt to reduce these concentrations. However, achieving this economically might prove to be difficult. Instead there also exists separate limits for waste product addition to soil in agricultural use and in the tables 11 and 12 is presented maximum heavy metal concentrations when waste sludge, for example lime mud is used in agriculture. The following table 11 gives the values that exist in the USA for the concentration limits.

**Table 11. Concentration limits for land application of waste set by the 40 CFR Part 403 in the US.[61,66]**

| Element | Ceiling heavy metal concentration limits for land application (mg/kg) | Annual allowed pollutant loading rate (kg ha$^{-1}$ 365d$^{-1}$) |
|---|---|---|
| **Arsenic (As)** | 75 | 2.0 |
| **Mercury (Hg)** | 57 | 0.85 |
| **Cadmium (Cd)** | 85 | 1.9 |
| **Chromium (Cr)** | 3000 | 150 |
| **Copper (Cu)** | 4300 | 75 |
| **Lead (Pb)** | 840 | 15 |
| **Nickel (Ni)** | 420 | 21 |
| **Zinc (Zn)** | 7500 | 140 |

In the following table 12 are for comparison the similar values for the European Union.

**Table 12. Concentrations limits for land application of sludge when used in agriculture set by the European council directive 86/278/EEC.[67]**

| Element | Limit values for heavy-metal concentrations in sludge for use in agriculture (mg/kg) | Annual allowed pollutant loading rate in 10 years average (kg ha$^{-1}$ 365d$^{-1}$) |
|---|---|---|
| **Arsenic (As)** | - | - |
| **Mercury (Hg)** | 16-25 | 0,1 |
| **Cadmium (Cd)** | 20-40 | 0.15 |
| **Chromium (Cr)** | - | - |
| **Copper (Cu)** | 1000-1750 | 12 |
| **Lead (Pb)** | 750-1200 | 15 |
| **Nickel (Ni)** | 300-400 | 3 |
| **Zinc (Zn)** | 2500-4000 | 30 |

It can be seen from the tables 11 and 12 that these allowed limit concentration values are substantially higher when compared to the concentration limits for fertilizers seen in the table 10. Therefore if the lime mud is to be used as general fertilizer means and the strict concentration limits are not met, it is also possible to use it in very similar purpose but with different labelling. This is assumed to be in the end, branding issue as the regulations obviously require the product to be indicated as waste instead of fertilizer, which might be difficult to prove for the market as a product having similar beneficial effect. It is also worth noticing that there can be seen major difference between the respective values of USA and EU, for example in the case of mercury that has over twice as big maximum allowed limit in the USA when compared to values EU and these values are likely to differ in other parts of the world also.[67]

### 3.5.2 Energy source as catalyst in bio-waste based $H_2$ production

Most recently there have also been studies for the use of lime mud as catalyst for hydrogen gas production from bio-waste. The process of producing hydrogen gas from the food waste highly depends on the bacterial activity. During the bacterial induced degradation of food waste the bacteria release gaseous hydrogen to their macro-environment that can be gathered. The bacterial activity can be enhanced by addition of metal cations, from which the most beneficial in the case of hydrogen gas fermentation was determined to be calcium, iron and manganese. Therefore the usefulness of lime mud for catalyst purpose is because all of these elements are usually present in the lime mud and in most cases also in sufficient concentrations. Also the research conducted by Zhang et al. showed that the addition of lime mud not only increased the amount of produced gaseous hydrogen but it also facilitated the fermentation reaction. The use lime mud was proven to synergistically enhance the gaseous hydrogen fermentation process having not only the amount but also the speed and stability significantly enhanced.[68] This presented method could prove to be beneficial for additional energy source production as it could be assumedly used also in consuming all the organic wastes generated in the area in addition to the use of food wastes when processing these fractions into hydrogen gas that could be further used as an alternative or additional energy source.

# 4 Principles for estimating the economic feasibility

When attempting to achieve maximum efficiency in the recycling of lime mud with having minimum financial input the requirement is in using primarily methods that would passively fulfil the recycling needs for the given input stream. This suggests that for the recycling process minimum amount of added chemicals, external energy or operating costs should be required. Therefore the economic feasibility for the presented methods is ultimately decided by the impact of the different considered actions on the final prices of the lime mud, which can vary depending on the goal for recycling. Roughly speaking, lime mud can have three different prices depending on its end-of-life uses. These uses can be recycling the spent lime mud back to process suitable raw-material, disposing the lime mud as land-fill-waste or producing alternative products from the lime mud; and respectively the prices associated to these categories can yield into positive, negative or zero prices for the recycling of lime mud.

The different prices based on these presented uses for lime mud can include various cost elements depending on the complexity of the operation or the required additional equipment purchases. For example, the following cost elements could be considered as the most relevant in many of the presented cases: cost of disposal, cost of reuse and cost of selling. In general, the cost of disposal includes the total costs generated from different performed actions related to waste disposal, which needs to be fulfilled prior to disposing the used lime mud as waste. Cost of reuse can be combined from the costs generated by different methods used for recycling the lime mud when attempting to fully return it to the chemical recovery system. Finally the cost of selling, consists of costs generated from actions that are needed prior to selling the spent lime mud as, for example land fertilizer. These cost elements can vary depending on the location of operations, for example in some parts of the world cost of disposal may be substantially less when compared to other locations.

## 4.1 Example for estimating the economic feasibility of alternative uses for the discharged lime

The evaluation of economic feasibility is very case sensitive due to different plant operation conditions, specifications or other factors. Therefore as an example is presented the required estimation chain for the case of producing alternative products such as fertilizer that could include the following chain of consideration.

Considering the lime mud as un-usable within the chemical recovery system, will result in need of finding alternative uses for this spent product. Based on this thesis the possible uses could be, using the removed lime mud either directly as fertilizer, raw material for fertilizers or as catalyst used in the energy production. For alternative methods, the evaluation of economic feasibility focuses mainly on the costs of selling. This is because with the alternative uses for the lime mud key things to be considered are arguably; will there be interest in expanding the mill product category to products requiring complex processing prior to reaching usable product state, for example in the case of producing soil conditioners or fertilizer pellets from the lime mud? The relevant costs could include, for example investments in new equipment and also increase in energy consumption. In some cases it might be unlikely that the Kraft mill would find the required investments in-order to produce additional products, appealing enough when considering that extending the product category to such alternative products might be quite far away from the core of business. Thus selling the separated lime mud waste to third parties might be the most cost efficient way.

Selling the lime mud – that can be ultimately considered as process waste – as raw-material for alternative product manufacturing might be troublesome, as there can be regulations limiting this in some regions. To ensure better utilization of process waste fractions EU has began encouraging the use of waste residues in alternative products by offering regulations when reusing waste fractions, for example spent lime mud can be regarded as by-product or end-of-waste instead of waste if some conditions are fulfilled for the substance. These conditions according to the waste framework directive include that the further use of the substance should be certain, the substance should be usable directly without further processing other than normal industrial practise, the substance is produced as an integral part of a production process and further use does not violate any laws. Alternatively end-of-waste status requires that the substance is commonly used for specific purposes, there is clear market or demand for the substance, it fulfils the technical requirements for the purposes and meets the existing legislation and standards applicable to products and the use of the substance will not lead to overall adverse environmental or human health impacts. When considering all these criteria in the waste framework directive, the lime mud may fulfil the requirements that are required for by-product status when used as fertilizer. Things to be considered are, will the possibly needed pre-treatments for the lime mud fulfil these conditions for being directly usable without any further processing other than normal industrial practise? The decision to use the lime mud in production of alternative products could possibly yield, in best cases positive price for the removed lime mud if the demand for this type of raw-material can be verified in the fertilizer production, at minimum such alternative uses should generate at least zero price for the pulp mill for the spent lime mud in-order for this kind of operation to be worth considering. The zero-price can be the case where the possibly required treatments would cause the lime mud to be undesirable as a costly raw-material but instead acceptable as a free-to-acquire raw-material for the fertilizer producers, hence removing the need of disposing costs for the Kraft pulp mill.[69,70]

As was seen from the given example there are many factors to be considered prior and during the implementation and similar chain of estimation would be required for every presented method in this thesis. Also numerical data is ultimately required in order to complete detailed analysis and give necessary exact estimates of the economic feasibility when considering the implementation of the given technological solution. However as the nature of this thesis was to simply gather and present the possible solutions, such information required for detailed economical estimates were not acquired.

# 5 Summary

During this thesis, extensive literature survey was conducted with having goal in finding new possibilities to be further researched in recycling of used lime mud. Lime mud samples were analyzed using XRF and XRD analyses by VTT in order to compare the literature results on the common elemental composition of lime mud. Samples of lime mud were also analyzed by using SEM, in order to verify detailed crystal structures.

The methods that were presented in this thesis included the following: altering the local solution parameters in attempt to reduce specific impurity by affecting to its solubility, against the normal procedures attempting to produce local conditions that would enhance precipitation of aluminosilicate scales on controlled surfaces that can be easily enough removed from the system and once cleaned returned back to the recovery system, addition of magnesium salts or alternatively aluminium in order to remove these elements as hydrotalcite at filters, microbiological processing methods, usage of acidic effluents in processing used lime mud, ultrasound and also possible alternative uses were studied for the spent lime mud.

The results of this thesis yielded several promising methods to be further investigated in the future. Many of the presented methods are likely to show their most potential when used together as one recycling step for the spent lime mud, also the potential of using some of these recycling methods in order to produce purified water instead of focusing on cleaning the lime mud was identified as potential use of these methods.

Finally brief analysis on the economy of these presented methods was introduced. The estimation of the economical feasibility was not conducted in large scale, with having detailed cost information on a industrial scale for all of these methods because it was assumed to be outside from the original purpose of this thesis and acquiring such information during the thesis was not possible. Instead different guidelines for cost elements to be considered when implementing new technology were given.

# 6 Conclusions

The results of this thesis are very promising. In the beginning of the thesis, the goal was set on finding new possibilities for recycling the used lime mud that could ultimately lead, through further study and experimental testing into possible adaptation of new recycling methods for Kraft recovery systems. The conducted literature survey proved that there indeed exists several potential recycling methods for processing the used lime mud either back to process viable form or alternatively to be used in other purposes. Some of the methods presented in this thesis have already been studied extensively in the literature before, but apparently haven't made their way as permanent solution for reducing impurities; there might be several reasons for this. One likely reason could be, for example when looking the progress in environmental regulations during the past 100 years. The shift in more environmental friendly, non-polluting Kraft pulping is relatively new with the regulations set by the environmental officials beginning to tighten. Therefore when considering some of these methods, for example the addition of magnesium salts as permanent solution for reducing the aluminium concentration in the lime cycle. They have most likely been very costly to be used as permanent solution for recycling relatively inexpensive material, lime mud in an industrial scale. However the future would suggest that with the tightening environmental regulations there will be interest in focusing resources for also optimizing these already studied methods together with finding new possibilities for recycling the spent lime mud.

When considering the presented solutions for the recycling of the spent lime mud it is fairly obvious that some of the presented methods are not likely to show their full potential when considered as a singular processes; instead many of them are likely to be useful when considered together. For example, in the case of processing lime mud with microbiological methods, incorporating the biological treatment methods together with the acidic effluents is most likely to be the most efficient way to use two of these produced waste streams. Consecutive use of bacteria and acidic effluents is likely to produce purified calcium carbonate to be re-used as lime mud in kraft recovery system but also purified water that could have the sufficient reduction in COD-levels – through bacterial consumption – that is required when re-using these liquids as process water in the white liquor preparation. The remaining separated waste fraction from the combinative use of these two methods might also fulfil the given solubility limits for further use as a fertilizer or alternatively as waste to be used in agriculture and soil conditioning material. Also during the process water cleaning is assumed to take place, which is considered in many parts of the world as highly valuable resource. Additionally considering the further potential of lime mud in its alternative processes, introduces economically interesting results if improvements in the purity of lime cycle could open the possibility of using the re-burnt lime from the lime cycle directly as raw material for PCC manufacturing. This could generate obvious synergy advantages if, for example the capacity of the lime kiln could also be used in manufacturing PCC-lime.

Because the nature of this thesis was set to be purely theoretical and based strictly on the conducted literature survey, none of these methods were experimentally tested. Some of the presented methods on literature were tested earlier in an industrial scale, with having promising results, while lacking the economical feasibility without proper optimization. Hence it is hard to accurately estimate the exact way some of these presented new methods would ultimately work in small scale or in an industrial scale based on purely the literature cases. Based on this thesis, suggestions for further studies should be on investigating the possibilities and requirements of implementing the presented methods either as singular recycling step or as combinative recycling processes for processing the spent lime mud.

# References

1. Clarke, F. W., Washington, H. S. *The composition of the Earth's crust,* U.S. Geol. Survey Professional Paper 127. U.S. Geol. Survey Washington, DC, 1924 [Referred 02.02.2013]

2. Boynton, Robert S. *Chemistry and technology of lime and limestone*. New York: Wiley, 1980. [Referred 01.02.2013] ISBN 0-471-02771-5

3. Nordkalk *Product sheets for Limestone 8-16 VK, Calcium oxide QL 0-8 LV & QL 0-15 VT SILVA* Nordkalk 2012 & 2013 [Referred 28.06.2013]

4. Naqvi, M., Yan, J., & Dahlquist, E. *Black liquor gasification integrated in pulp and paper mills: A critical review.* Bioresource Technology. Vol. 101:21 2010 pp. 8001-8015 [Referred 04.03.2013]. DOI:10.1016/j.biortech.2010.05.013 ISSN 0960-8524

5. Gullichsen, Johan. & Fogelholm, Carl-Johan. *Papermaking science and technology. Book 6B, Chemical Pulping.* Helsinki, Fapet, 2000 [Referred 07.02.2013] ISBN 952-5216-06-3

6. Gullichsen, Johan. & Fogelholm, Carl-Johan. *Papermaking science and technology. Book 6A, Chemical Pulping.* Helsinki, Fapet, 1999 [Referred 07.03.2013] ISBN 952-5216-06-3

7. Robert P. Green & Hough Gerald *Chemical recovery in the alkaline pulping process*. Atlanta (GA), TAPPI Press, 1992 [Referred 07.02.2013] ISBN 0-89852-255-2

8. Lindblom, Josefina. *Sintering in the kraft pulp mill: studies in the rotary kiln and recovery boiler.* Göteborg : Chalmers University of Technology, 1999 – (Doktorsavhandlingar vid Chalmers tekniska högskola, 1554). [Referred 07.02.2013] ISBN 91-7197-864-X – Diss. CTH Göteborg.

9. Ciullo, P.A. *Industrial Minerals and Their Uses - A Handbook and Formulary*. pp. 161-196. William Andrew Publishing/Noyes. 1996. [Referred 05.02.2013] ISBN 978-0-0809-4644-3

10. Sanchez, Dale R. *Recausticizing: Principles and practice.* Vector process equipment Inc. 2007: 2-1. [Referred 08.03.2013]

11. Lewko, Leonard A., & Blackwell Brian. *Lime mud recycling improves the performance of kraft recausticizing.* October 1991. Tappi Journal. [Referred 04.03.2013] ISSN 0734-1415

12. Tiljander, Pia. *Disintegration of lime mud particles during the causticizing operation.* Göteborg : Chalmers University of Technology, 1997. - (Doktorsavhandlingar vid Chalmers tekniska högskola, 1352). [Referred 07.02.2013] ISBN 91-7197-573-X. - Diss. CTH Göteborg.

13. Pat. US: 4,668,342. *Recausticizing Kraft Green Liquor* Blackwell B. R. Vancouver, Canada. App. 804087, 03.12.1985 Publ. 26.05.1987 pp. 10 [Referred 07.03.2013]

14. Andritz Oy, Fiber and chemical division, *Any Mill Recausticizing Operational Training*, Company internal material [Referred 07.02.2013]

15. Fardadi, Malahat. *Modelling dust formation in Lime Kilns.* Department of Mechanical and Industrial Engineering University of Toronto, 2010. Thesis for the degree of Doctor of Philosophy. Available online at http://hdl.handle.net/1807/32040 [Referred 20.02.2013]

16. Ulmgren, Per *Non-process elements in a bleached kraft pulp mill with a high degree of system closure – state of the art.* Nordic Pulp and Paper Research Journal Vol.12:1 1997 pp. 32-41[Referred 17.05.2013] ISSN 0283-2631

17. Stenius, Per *Papermaking science and technology. Book 3, Forest products chemistry – Structure and chemical composition of wood*. pp. 12-54 Helsinki, Fapet, 2000 [Referred 07.02.2013] ISBN 952-5216-00-4

18. Hyvönen, Anu *The effects of non-process elements in biosludge on the recovery cycles in kraft pulp mills* Master's Thesis 2009, Jyväskylä University [Referred 10.6.2013]

19. Doldán J., Poukka O., Salmenoja K., Battegazzore M., Fernandez V., & Eluén I *Evaluation of sources and routes of non-process elements in a modern eucalyptus kraft pulp mill* O Papel. Vol. 72:7 2011 pp. 47-52 [Referred 01.02.2013]. ISSN 0031-1057

20. Ulmgren, P. & Rådeström, R. *The Build-Up of Phosphorus in a Kraft Pulp Mill and the Precipitation of Calcium Phosphate from Green and White Liquors* Journal of Pulp and Paper Science Vol.23:2 1997 pp.52-58 [Referred 11.02.2013] ISSN 0826-6220

21. Taylor K. & McGuffie B. *Investigation of non-process element chemistry at Elk Falls mill – green liquor clarifier and lime cycle* Pulp & Paper Canada Vol.108:2 2007 pp. 27-32 [Referred 01.02.2013] ISSN 0316-4004

22. Lundqvist, Per *Mass and energy balances over the lime kiln in a kraft pulp mill* Master's Thesis 2009, Uppsala Universitet [Referred 07.02.2013] ISSN 1650-8300

23. Taylor K. & Bossons D. *Investigation of green lime mud at Harmac mill* Pulp and Paper Canada Vol.107:3 2006 pp. 37-40 [Referred 14.02.2013] ISSN 0316-4004

24. Ulmgren, Per *Processfrämmande grundämnen i kemikalieåtervinningen – Del 3. Processstörningar, åtgärdsrekommendationer och haltnivåer av processfrämmande grundämnen.* STFI, SCAN Forsk - Rapport 535, 1989 [Referred 13.02.2013]

25. Ribeiro J. C. T., Santos S. M. & Tran H. *Experience of low lime mud solids problems at a kraft pulp mill* O Papel. Vol. 69:6 2008 pp. 69-79 [Referred 13.05.2013]

26. Sheikholeslami R. & Zhou S. *Performance of RO membranes in silica bearing waters* Desalination Vol.132:1-3 2000 pp. 337-344 [Referred 08.04.2013] DOI:10.1016/S0011-9164(00)00169-7 ISSN 0011-9164

27. Saijonkari-Pahkala, Katri *Non-wood plants as raw material for pulp and paper* Academic Dissertation, University of Helsinki, 2001. [Referred 31.05.2013] ISBN 951-729-637-1

28. Xiaofei, Fan. *The Fates of Vanadium and Sulfur Introduced with Petcoke to Lime Kilns* Master's Thesis 2010, University of Toronto [Referred 31.05.2013] Available online at http://hdl.handle.net/1807/25572

29. Streisel, Robert C. *Chemical equilibrium of Nonprocess Elements in the Kraft Recovery Cycle* Oregon State University, 1988. Thesis for the degree of Doctor of Philosophy [Referred 13.05.2013]

30. Ulmgren, Per *The removal of aluminum from the recovery system of a closed kraft pulp mill* Nordic Pulp and Paper Research Journal Vol.2:1 1987 pp. 4-9 [Referred 3.6.2013] ISSN 0283-2631

31. Vehmaan-Kreula, Juhani *Coversations and email correspondence* 2013 [Referred 17.6.2013]

32. VTT Expert services *XRF & XRD analysis results report* [Referred 29.06.2013]

33. Haimi, Eero *SEM-analysis results* Aalto-University 2013 [Referred 05.07.2013]

34. Gunnarsson I. & Arnórsson S. *Amorphous silica solubility and the thermodynamic properties of* $H4SiO_4°$ *in the range of 0° to 350°C at* $P_{sat}$ Geochimica et Cosmochimica Acta Vol.64:13 2000 pp. 2295-2307 [Referred 10.6.2013] DOI:10.1016/S0016-7037(99)00426-3 ISSN 0016-7037

35. Gasteiger, H. A. William J. F. & Streisel R. C., *Solubility of aluminosilicates in alkaline solutions and a thermodynamic equilibrium model* Industrial & Engineering Chemistry Research Vol.31:4 1992 pp. 1183-1190 [Referred 7.6.2013] DOI:10.1021/ie00004a031 ISSN 0888-5885

36. Orava, Toni *Email correspondence & conversations held at UPM-kymmene, Kymi* 2013 [Referred 05.07.2013]

37. Park H. & Englezos P. *Sodium Aluminosilicate Crystal Formation in Alkaline Solutions Relevant to Closed Cycle Kraft Pulp Mills* The Canadian Journal of Chemical Engineering Vol.76:5 1998 pp. 915-920 [Referred 25.06.2013] DOI: 10.1002/cjce.5450760508 ISSN 1939-019X

38. Park Hyeon & Englezos Peter *Sodium-aluminum-silicate solids precipitation from the build-up of non-process elements in closed cycle kraft pulp mills* TAPPI Environmental Conference 1998 [Referred 13.05.2013]

39. Shammas, Nazih K. *Advances in Hazardous Industrial Waste Treatment – Waste Management in the Pulp and Paper Industry* Taylor & Francis Group, LLC. 2009 pp. 462-515 [Referred 11.6.2013] ISBN 978-1-4200-7231-0

40. European Commission, Integrated Pollution Prevention and Control (IPPC), *Reference Document on Best Available Techniques in the Pulp and Paper Industry*, European Commission, 2001. [Referred 11.6.2013]

41. European Commission, Integrated Pollution Prevention and Control (IPPC), *Reference Document on Best Available Techniques for the Waste Treatment Industries*, European Commission, 2006. [Referred 11.6.2013]

42. Madigan, M. T., Martinko, J. M., Parker, J. & Brock, T. D. *Brock Biology of Microorganisms*. Upper Saddle River, NJ Prentice Hall, Pearson Education. 10th edition 2003 [Referred 01.03.2013] ISBN 0-13-049147-0

43. Werner E.G. Müller *Molecular Biomineralization: Aquatic Organisms Forming Extraordinary Materials* Springer Verlag, 2011 [Referred 12.06.2013] ISBN 9783642212307

44. Puhakka, Jaakko E*mail correspondence* 2013 [Referred 31.05.2013]

45. Bhatti M. T. & Yawar W. *Bacterial solubilization of phosphorus from phosphate rock containing sulfur-mud* Hydrometallurgy Vol.103:1-4 2010 pp.54-59 [Referred 13.06.2013] DOI:10.1016/j.hydromet.2010.02.019 ISSN 0304-386X

46. Tang K., Baskaran V. & Nemati M. *Bacteria of the sulphur cycle: An overview of microbiology, biokinetics and their role in petroleum and mining industries* Biochemical Engineering Journal Vol.44:1 2009 pp.73-94 [Referred 13.06.2013] DOI:10.1016/j.bej.2008.12.011 ISSN 1369-703X

47. Rava, Eleonora. M. E. *Management of Hydrogen Sulphide Generation at a Kraft Paper Mill* Master's Thesis 2008, University of Pretoria [Referred 05.07.2013]

48. Stratful I., Brett S., Scrimshaw M. B. & Lester J. N. *Biological Phosphorus Removal, Its Role in Phosphorus Recycling* Environmental Technology Vol.20:7 1999 pp. 681-695 [Referred 19.06.2013] DOI:10.1080/09593332008616863 ISSN 0959-3330

49. FI 122812 B *Menetelmä nestevirtojen käsittelemiseksi sellutehtaalla* Andritz Oy, Helsinki, Finland. (Vehmaa, J., Pikka O. & Tervola, P.) App. 20070477, 15.06.2007. Publ. 16.12.2008. 36 pp. [Referred 19.06.2013]

50. Torre M., Rogriguez R. A. & Saura-Calixto F. *Study of the Interactions of Calcium Ions with Lignin, Cellulose, and Pectin* Journal of Agricultural Food and Chemistry Vol.40:10 1992 pp. 1762-1766 [Referred 17.6.2013] DOI: 10.1021/jf00022a007 ISSN 0021-8561

51. World Bank, *Pollution Prevention and Abatement Handbook,* World Bank Group, 1998 [Referred 11.6.2013] ISBN 0-8213-3638-X

52. Dahl, Olli *Evaporation of acidic effluent from kraft pulp bleaching, reuse of the condensate and further processing of the concentrate* Academic Dissertation, University of Oulu, 1999. [Referred 09.07.2013] ISBN 951-42-5208-X ISSN 0355-3213

53. Milosevich G. M. & Hill D.A., *Reduction of AOX in Bleach Plant Effluent by Addition of Mill Process Alkalis* Pulp and Paper Canada Vol.93:3 1992 pp. 61-67 [Referred 28.06.2013] ISSN 0316-4004

54. Wagterveld R. M., Boels, L., Mayer M. J. & Witkamp G. J. *Visualization of acoustic cavitation effects on suspended calcite crystals* Ultrasonics Sonochemistry Vol.18:1 2011 pp. 216-225 [Referred 19.06.2013] DOI:10.1016/j.ultsonch.2010.05.006 ISSN 1350-4177

55. Park N. D., Helle S. S. & Thring R. W. *Combined alkaline and ultrasound pre-treatment of thickened pulp mill waste activated sludge for improved anaerobic digestion* Biomass and Bioenergy Vol.46 2012 pp. 750-756 [Referred 19.06.2013] DOI:10.1016/j.biombioe.2012.05.014 ISSN 0961-9534

56. López-Periago A. M., Pacciani R., García-González C., Vega L. F. & Domingo C. *A breakthrough technique for the preparation of high-yield precipitated calcium carbonate* The Journal of Supercritical Fluids Vol.52:3 2010 pp.298-305 [Referred 20.06.2013] DOI:10.1016/j.supflu.2009.11.014 ISSN 0896-8446

57. Gallego-Juárez J. A., Elvira-Segura L. & Rodríguez-Corral G. *A power ultrasonic technology for deliquoring* Ultrasonics Vol.41:4 2003 pp. 255-259 [Referred 01.07.2013] DOI:10.1016/S0041-624X(02)00449-3 ISSN 0041-624X

58. Electronic Statutes of Finland 2006, N:o 202 *Valtioneuvoston asetus kaatopaikoista annetun valtioneuvoston päätöksen muuttamisesta* (2006) pp. 630-643 [Referred 24.06.2013]

59. McGuffie B. & Taylor K. *Non-process element mass balance improves recaust and lime kiln efficiency at Elk Falls mill* Pulp and Paper Canada Vol.108:3 2007 pp. 34-40 [Referred 27.06.2013] ISSN 0316-4004

60. Rothpfeffer, C. *From Wood to Waste and Waste to Wood – Aspects on Recycling Waste Products from the Pulp Mill to the Forest Soil* Uppsala, Swedish University of Agricultural Sciences, 2007. Doctoral thesis [Referred 25.06.2013] ISBN 978-91-576-7382-4

61. He J., Lange C. R. & Dougherty M *Laboratory study using paper mill lime mud for agronomic benefit* Process Safety and Environmental Protection Vol.87:6 2009 pp. 401-405 [Referred 05.07.2013] DOI:10.1016/j.psep.2009.08.001 ISSN 0957-5820

62. Pöykiö R., Nurmesniemi H., Kuokkanen T. & Perämäki P. *The use of a sequential leaching procedure for assessing the heavy metal leachability in lime waste from the lime kiln at a causticizing process of a pulp mill* Chemosphere Vol.65:11 2005 pp. 2122-2129 [Referred 08.07.2013] DOI:10.1016/j.chemosphere.2006.06.018 ISSN 0045-6535

63. Electronic Statutes of Finland 2006, N:o 539 *Lannoitevalmistelaki* (2006) pp. 1595-1607 [Referred 05.07.2013]

64. Knuuttila H., Kontturi M., Laurila E. & Ahlgrén M. *VISA – Selluteollisuuden kiintojätteen, viherlipeäsakan uudet käsittelymenetelmät* Confidential final report 2006 [Referred 05.07.2013]

65. Gu Y. & Edwards L. *Prediction of metals distribution in mill processes, Part 3 of 3: NPE management in kraft chemical recovery* Tappi Journal Vol.3:3 2004 [Referred 05.07.2013] ISSN 0734-1415

66. U.S. Environmental Protection Agency *40 CFR Part 503 - Standards for the Use or Disposal of Sewage Sludge* Federal Regulation 1993, 58(32) pp.9248-9415 [Referred 05.07.2013]

67. European Commission *Council Directive on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture – 86/278/EEC.* Official Journal of the European Communities 1986, No. 181 pp. 6-12 [Referred 05.07.2013]

68. Zhang J., Wang Q. & Jiang J. *Lime mud from paper-making process addition to food waste synergistically enhances hydrogen fermentation performance* International Journal of Hydrogen Energy Vol.38:6 2013 pp. 2738-2745 [Referred 05.07.2013] DOI:10.1016/j.ijhydene.2012.12.048 ISSN 0360-3199

69. Pajunen N., Watkins G., Husgafvel R., Heiskanen K. & Dahl O. *The challenge to overcome institutional barriers in the development of industrial residue based novel symbiosis products – Experiences from Finnish process industry* Minerals Engineering Vol.46-47 2013 pp. 144-156 [Referred 17.07.2013] DOI:10.1016/j.mineng.2013.03.008 ISSN 0892-6875

70. European Commission *Council Directive on waste and repealing certain Directives – 2008/98/EC.* Official Journal of the European Union 2008, No. 312 pp. 3-30 [Referred 18.07.2013]

# 7 Appendices

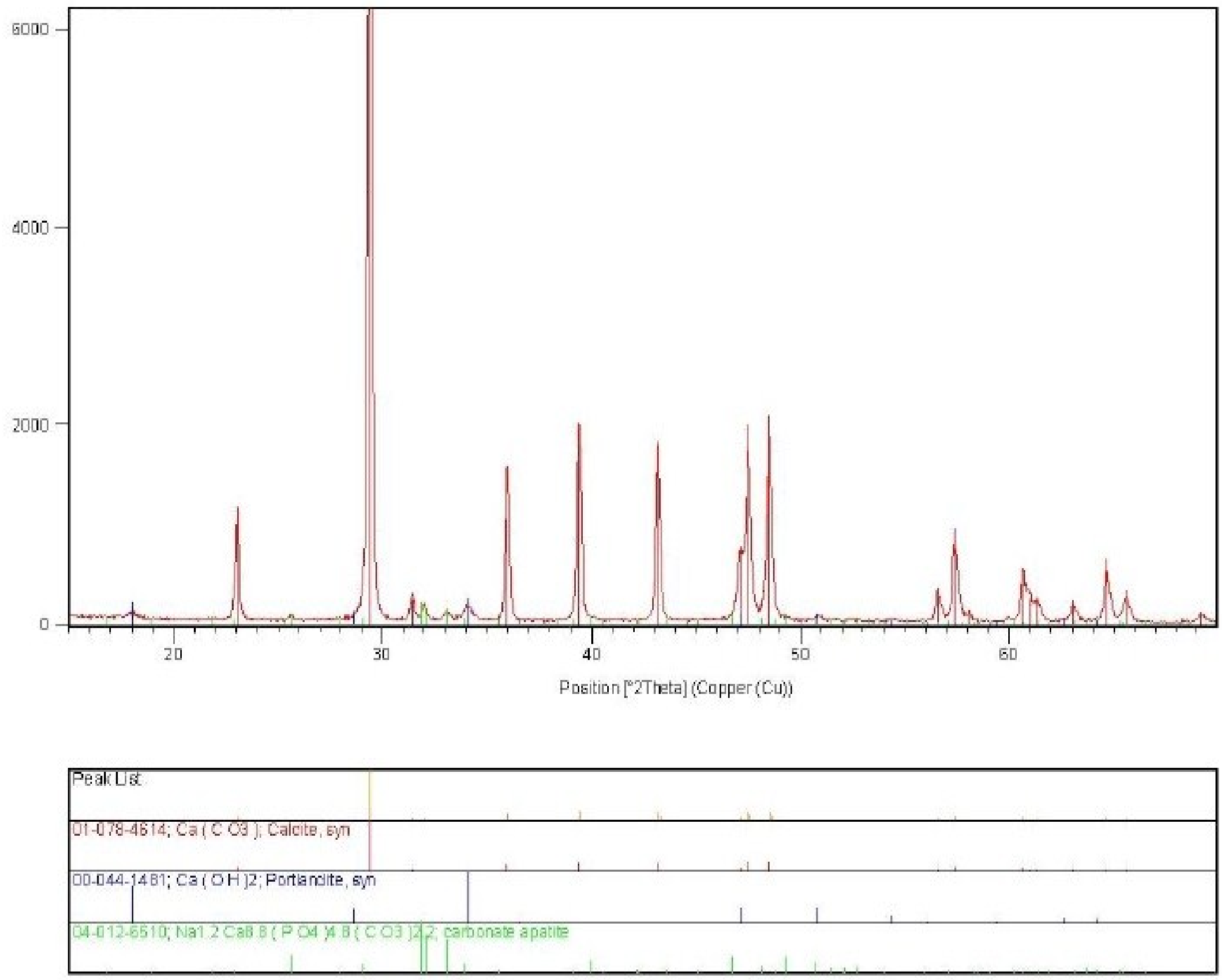
Appendix 1. XRD analysis – sample 2, ESP Dust

Appendix 2. XRD analysis – sample 3, Lime mud

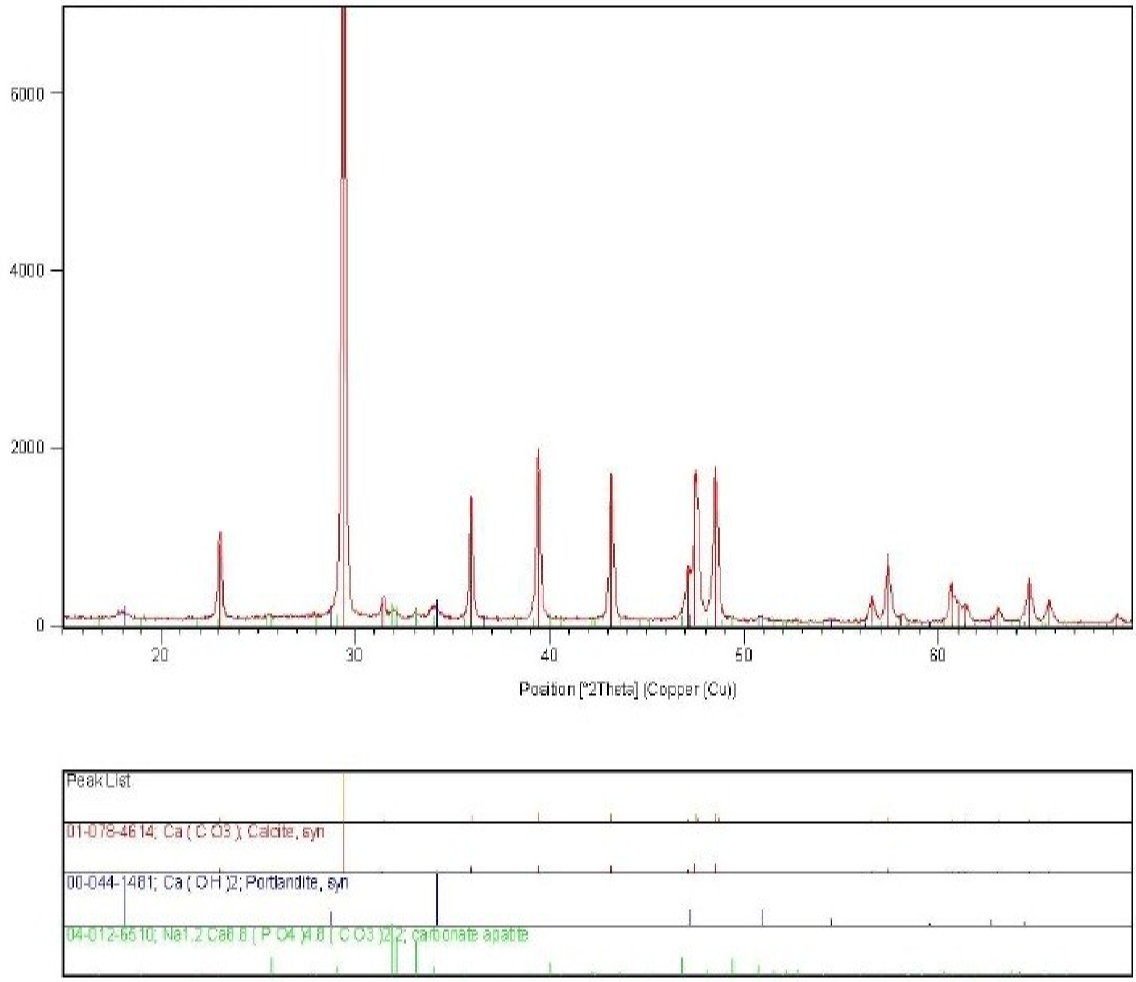
Appendix 3. XRD analysis – sample 4, ESP Dust

Appendix 4. XRD analysis – sample 5, Lime mud

Appendix 1.

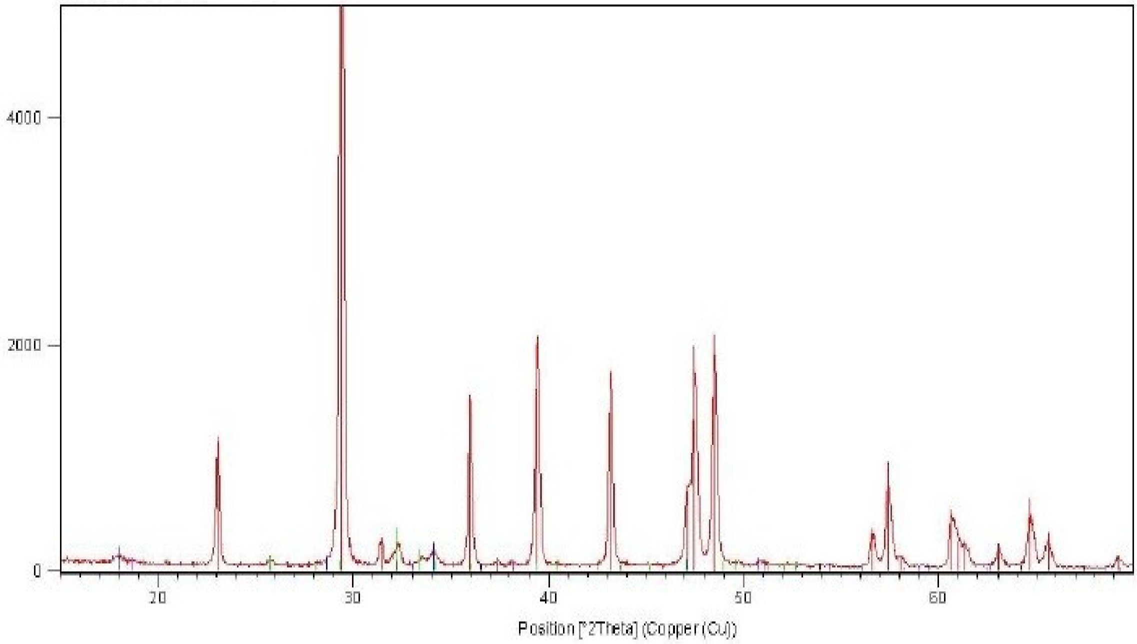

6000
4000
2000
0
20
30
40
50
60
Position [°2Theta] (Copper (Cu))
Peak List
01-078-4614; Ca ( C O3 ); Calcite, syn
00-044-1481; Ca ( O H )2; Portlandite, syn
04-012-6510; Na1.2 Ca8.8 ( P O4 )4.8 ( C O3 )2.2; carbonate apatite

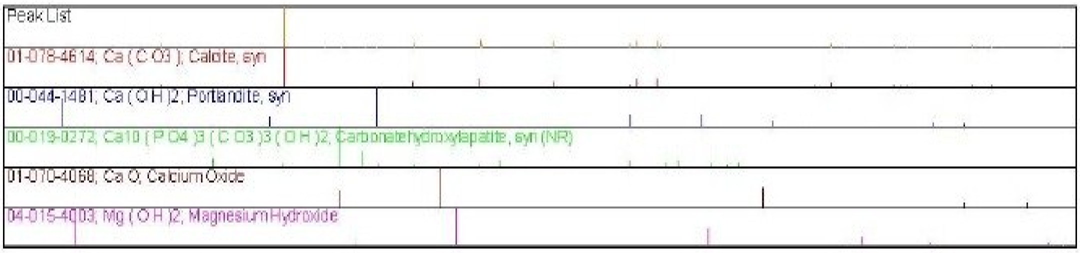
# Appendix 2.



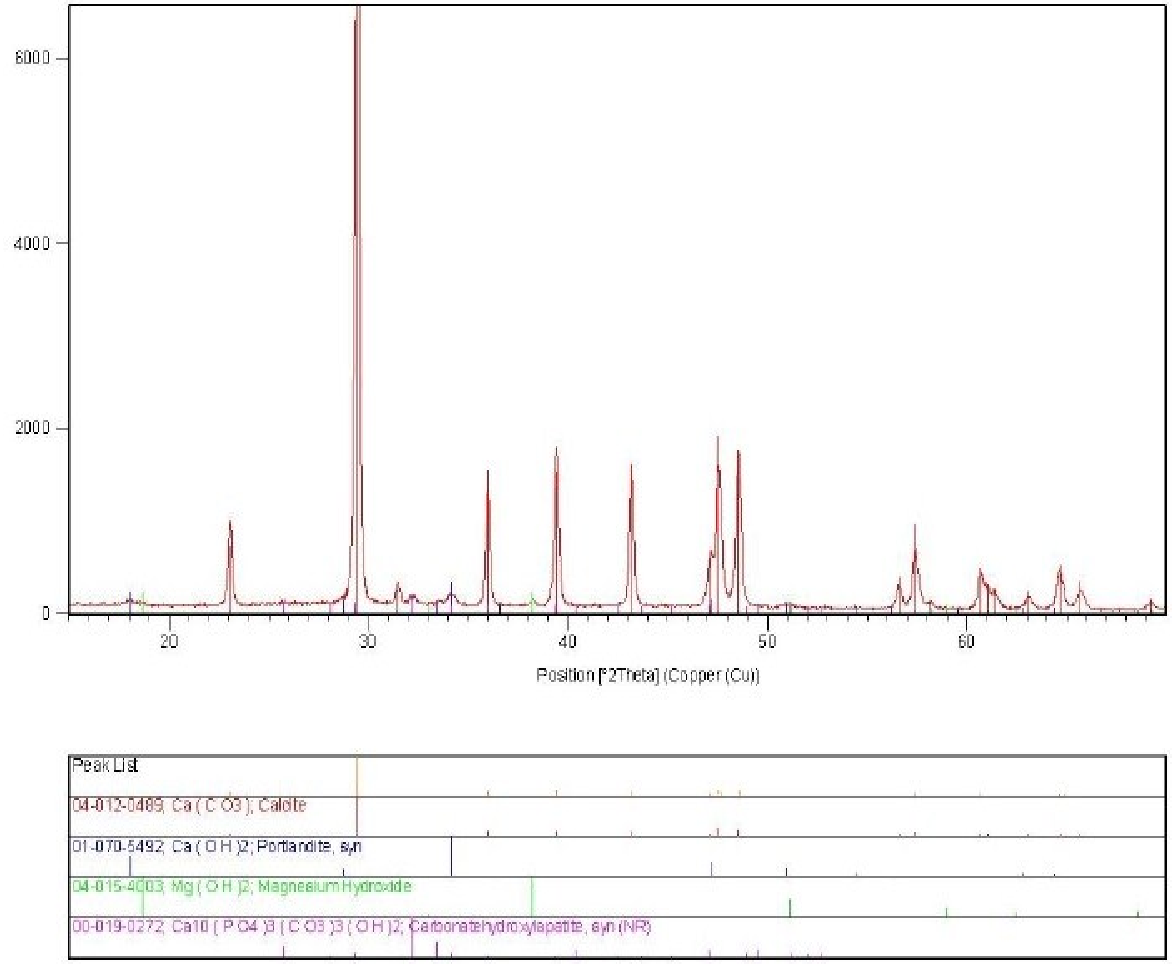
6000
4000
2000
0
20
30
40
50
60
Position [°2Theta] (Copper (Cu))
Peak List
01-078-4614; Ca ( C O3 ); Calcite, syn
00-044-1481; Ca ( O H )2; Portlandite, syn
04-012-6510; Na1.2 Ca8.8 ( P O4 )4.8 ( C O3 )2.2; carbonate apatite

Appendix 3.


4000
2000
0
20
30
40
50
60
Position [°2Theta] (Copper (Cu))


Peak List
01-078-4614; Ca ( C O3 ); Calcite, syn
00-044-1481; Ca ( O H )2; Portlandite, syn
00-019-0272; Ca10 ( P O4 )3 ( C O3 )3 ( O H )2; Carbonatehydroxylapatite, syn (NR)
01-070-4068; Ca O; Calcium Oxide
04-015-4003; Mg ( O H )2; Magnesium Hydroxide

Appendix 4.


6000
4000
2000
0
20
30
40
50
60
Position [°2Theta] (Copper (Cu))
Peak List
04-012-0489; Ca ( C O3 ); Calcite
01-070-5492; Ca ( O H )2; Portlandite, syn
04-015-4003; Mg ( O H )2; Magnesium Hydroxide
00-019-0272; Ca10 ( P O4 )3 ( C O3 )3 ( O H )2; Carbonatehydroxylapatite, syn (NR)