



**CHALMERS**  
UNIVERSITY OF TECHNOLOGY

---

# **Towards a Circular Economy in the Pulp and Paper Industry**

Possible reuse of solid residues from kraft pulp  
mills as fertilizer to the forest

Master's thesis in cooperation with Pulp Competence Centre, Stora Enso AB

**SUSANNE BJÖRKQVIST**



# **Towards a Circular Economy in the Pulp and Paper Industry**

Possible reuse of solid residues from kraft pulp  
mills as fertilizer to the forest

SUSANNE BJÖRKQVIST

Department of Chemistry and Chemical Engineering  
Division of Forest Products and Chemical Engineering  
CHALMERS UNIVERSITY OF TECHNOLOGY  
Gothenburg, Sweden 2015

Towards a Circular Economy in the Pulp and Paper Industry-  
Possible reuse of solid residues from kraft pulp mills as fertilizer to the forest  
SUSANNE BJÖRKQVIST

©SUSANNE BJÖRKQVIST, 2015.

SUPERVISORS:

Maria Björk, Rickard Wadsborn

EXAMINER:

Hans Theliander

Department of Chemistry and Chemical Engineering  
Division of Forest Products and Chemical Engineering  
CHALMERS UNIVERSITY OF TECHNOLOGY  
Gothenburg, Sweden 2015

## Acknowledgment

I had the opportunity to meet many helpful people during my thesis time and I am very thankful to those who have supported me:

*Maria Björk and Rickard Wadsborn*, my supervisors at Stora Enso Pulp Competence Centre, for giving me the opportunity to conduct this master's thesis and for their inspiration, guidance and support throughout the work.

*Professor Hans Theliander*, my examiner and supervisor at Chalmers University of Technology, for interesting discussions and valuable knowledge.

*Doctor Cecilia Mattson* for daily encouragement and help when needed.

*Tommy Friberg* for all assistance and guidance in the laboratory work.

*Tomas Gustafsson* for the guided tour at the pulp mill which gave me a better picture of the kraft pulp process.

*Kajsa Winberg* for her answers to all my stupid questions and for her invaluable company through good times as well as bad times.

And finally I would like to thank all the people at the divisions Forest Product and Chemical Engineering and Chemical Environmental Science for creating a fun and pleasant time!

Gothenburg 2015-05-29

Susanne Björkqvist

## Abstract

To obtain a sustainable forestry and to move towards a more circular economy the solid residues from the kraft pulp mill could be recycled to the forest. The residues contain many nutrients that enter the mill within the wood and therefore the use as a fertilizer can be advantageous.

Problems that may arise when recycling are leaching of heavy metals and sulfate from the residues. Also a rapid increase of the pH in the soil may occur if the leaching rate of base cations are too fast. Therefore this thesis investigate; the leaching rate of the nutrients calcium, sodium and magnesium for self-hardening pellets of different compositions and pressure applied, the durability of the pellets in a transport simulation and leaching of sulfate from fly ash and the leaching of cadmium from fly ash and green liquor dregs. Four different residues (fly- and bottom ash from bark boiler, green liquor dregs and lime mud) from three different kraft pulp mills in Sweden and Finland have been the raw material for the investigation.

The pellets produced had two different compositions, one consisting only fly ash and one with a mixture of lime mud, fly ash and green liquor dregs. Two different pressures were applied when the pellets were produced, 30 MPa and 10 MPa, to investigate the difference in leaching rates and all pellets were stored in carbon dioxide for the self-hardening reaction to occur. The leaching of the pellets was performed in a modified column-pHstat test developed in the Ph.D. work by Mahmoudkhani (2005) and the leachates were analyzed in atomic adsorption spectroscopy. Leaching of cadmium and sulfate was performed in different batch leaching tests and analyzed in atomic absorption spectroscopy and ion chromatography. The transport simulation was examined in a shaker for 12 hours.

The result showed that the sodium leached fast at the beginning for both fly ash pellets and mixed pellets which indicate that the self-hardening reaction does not affect the sodium leaching. The magnesium leached from the fly ash pellets varied but in the leaching of mixed pellets the magnesium had the same leaching trend as sodium. Calcium was leached in a more constant rate than the two other metals and it is probably due to the self-hardening reaction. The different pressures applied when the pellets were produced do not influence the leaching rates for none of the substances.

The sulfate leached from the fly ash showed that it could be a problem with sulfate leaching from fly ash, it depends on where it is deposited. However, the leaching of cadmium was almost non-existent for all test which indicates on stable cadmium compounds in the residues.

At last the transport simulation of the pellets showed a high durability during the rough simulation which is advantageous if the pellets should be transported to the forest.

Keywords: Solid residues, Kraft pulp mill, Leaching, Inorganic nutrients, Pellets, Cadmium, Transport simulation

# Table of Contents

Acknowledgment.....	I
Abstract.....	II
1. Introduction.....	1
1.1 Objective.....	2
1.2 Thesis outline.....	2
2. Theoretical background.....	3
2.1 Circular- and bio based economy.....	3
2.2 The biorefinary concept and circular economy in pulp and paper industry.....	4
2.3 Kraft pulp process.....	5
2.4 Recovery process.....	6
2.5 Solid residue streams.....	8
2.6 Recycling back to the forest.....	9
2.7 Problems with cadmium and sulfate in nature.....	11
2.7.1 Cadmium.....	11
2.7.2 Sulfate.....	12
3. Experimental background.....	13
3.1 Leaching.....	13
3.1.1 Batch leaching test.....	13
3.1.2 Column leaching test.....	14
3.1.3 pH-stat leaching test.....	14
3.1.4 Modified column pH-stat test.....	14
4. Experimental methods.....	15
4.1 Physical and chemical characterization of raw material.....	15
4.2 Pellets preparation.....	15
4.2.1 Fly ash pellets.....	15
4.2.2 Mixed pellets.....	15
4.3 Column-pHstat leaching test.....	15
4.4 Batch leaching test.....	16
4.4.1 Cadmium.....	16
4.4.2 Sulfate.....	16
4.5 Atomic absorption spectroscopy.....	17
4.6 Ion chromatography.....	17

4.7 Transport simulation .....	17
5. Results and discussion .....	18
5.1 Physical and chemical characteristics of the residues .....	18
5.1.1 Chemical composition .....	18
5.1.2 Dry content .....	19
5.2 Leaching of soluble species .....	19
5.2.1 Fly ash pellets .....	20
5.2.2 Mixed pellets .....	22
5.2.3 Lower pressure .....	24
5.3 Leaching of cadmium.....	26
5.4 Leaching of sulfate.....	27
5.5 Transport simulation .....	28
6. Conclusion .....	29
References.....	30

# 1. Introduction

The world is at the beginning of a large challenge with growing population and large amount of waste generated with resource depletion as one of the consequences. To solve this, the linear economy used today, with the consumer pattern of “take-make-dispose”, has to be abandoned and a more circular economy has to be implemented where materials are reused and recycled.

Many business leaders, industries and governments have realized that striving against a circular bio-based economy will give them economic and environmental advantages in forms of lower resource costs and more secure supply chains. One of them is the pulp- and paper industry which has reached relatively far in the transition towards a circular bio-based economy due to resource- and energy efficiency and the recycling of fibers.

There is still more to achieve before the pulp- and paper industry can be seen as a circular bio-based industry and one issue is the reuse of the solid residues obtained from a kraft pulp mill. The kraft pulp process is the largest pulping process worldwide, representing 90% of the chemical pulp produced and over 60% of the pulp from virgin fibers (Saltberg, 2009). The process creates several solid residues where the main ones are green liquor dregs (green liquor sludge), lime mud, lime slaker grits, wastewater treatment sludge and boiler ashes (Monte, et al., 2009).

A large fraction of the solid residues are today placed at landfill deposits. However, new legislations against landfill deposits are established with high fees and difficulties to get new disposal sites as consequences (Pöykio, et al., 2006). The high costs for disposal together with the ambition of a circular bio-based economy enables the companies to find new application for their solid residues. Some of the uses of the residues found in the literature are neutralization agent for acidic wastewater, hardener in filling mine cavities, soil enrichment agent (Nurmesniemi, et al., 2007), raw material for concrete, sealing material for landfill areas, raw material for paper fillers and filling material in road banks (Mahmoudkhani, 2005).

Another application for the solid residues could be as a fertilizer to the forest since all solid residues from the kraft pulp mill contain inorganic materials, such as potassium (K), calcium (Ca), magnesium (Mg) and phosphorous (P), which enter the mills mainly with the wood (Mahmoudkhani, 2005). The recycling of residues would reduce the negative impact of harvesting on soil nutrient status which is important for a future sustainable forestry. The residues are also alkaline due to the presence of calcium carbonate and can therefore be used as a substitute for lime in acidified forests (Mahmoudkhani, 2005).

One problem that needs to be solved before the recycling is possible is that the residues have to be in forms, for example pellets or granules, which are easy to spread and transport. The leaching behavior of the agglomerates need to be characterized and controlled to prevent a pH chock for the soil. Another problem with recycling the residues back to the forest is the content of heavy metals in the residues, especially cadmium. Most of the heavy metals enter the mill with the wood but can also originate from the process chemicals or from corrosion (Pöykiö, et al., 2006). Whether the cadmium is leached and how much it is leached from the

residues are important knowledge because if it is soluble it may be accessible for the vegetation which is highly disadvantageous. There can also be a problem with leaching of sulfate from the fly ashes due to that it acidifies the soil which makes some metals more soluble, for example heavy metals.

### **1.1 Objective**

The aim of this thesis is to evaluate the possibility to recycle the solid residues from three different kraft pulp mills located in Sweden and Finland back to the forest. To achieve this the residues have to be in a format that is easy to spread and transport and the leaching behaviors of important nutrients such as calcium, sodium and magnesium and contaminants, such as cadmium and sulfate, need to be known. Therefore the following issues will be investigated in this thesis:

- The leaching behavior of calcium, magnesium and sodium from pellets with different composition and producing pressures.
- The pellets durability in a transport simulation.
- The leaching of cadmium from green liquor dregs and fly ashes from bark boilers.
- The leaching of sulfate from fly ashes from bark boiler.

### **1.2 Thesis outline**

The thesis start with a theoretical background where the circular bio-based economy, kraft pulping process, why the residues should be recycled back to the forest and the problems with recycling are described in more detail. Thereafter comes experimental background where different leaching methods are defined and the methods chosen for this thesis are motivated.

In the experimental method section the pellets production, chemical characterization and the leaching tests performed in this thesis are described. After this follows a presentation and discussion of the results achieved, starting with physical and chemical characterization of the residues followed by the leaching behavior for the different pellets, then the leaching of cadmium and sulfate and at last the transport simulation.

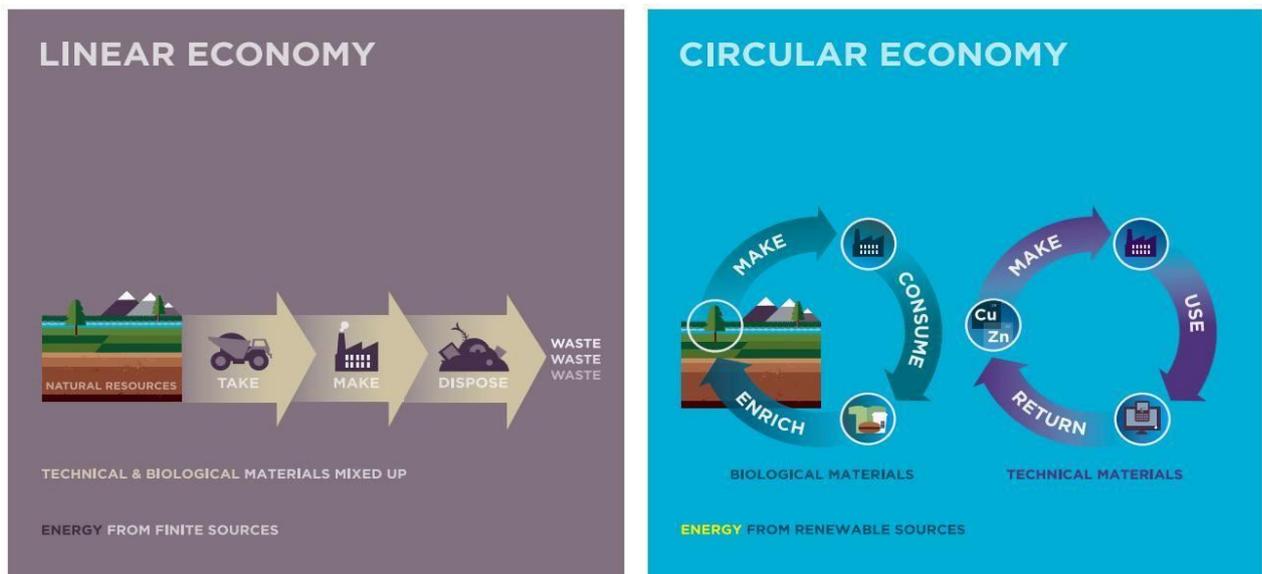
In the last section conclusions drawn from the result are presented and these are coupled back to the report's aims to see if these have been achieved.

## 2. Theoretical background

This section will give background information of the research subject. It will start with 2.1 Circular- and bio based economy, followed by 2.2 The biorefinery concept and circular economy in pulp and paper industry, 2.3 Kraft pulp process, 2.4 Recovery process, 2.5 Solid residue streams, 2.6 Recycling back to the forest and finished with 2.7 Problems with cadmium and sulfate in nature.

### 2.1 Circular- and bio based economy

Until today the world's economy has been linear, which means that it operates on a “take-make-dispose”-model where every product has an end of life, see Figure 1 (European Commission, 2014). This generates a lot of wastes and according to the European Commission an EU-citizen generate an average amount of 4.5 tons waste per year. Half of all the waste ends up in landfill disposal and these rates of resource consumption are not sustainable (European Commission, 2014). Therefore there is a lot of focus today on how to reach a circular economy, see Figure 1.



**Figure 1** Illustration of the difference between linear economy and circular economy. (Source: Ellen MacArthur Foundation, 2015)

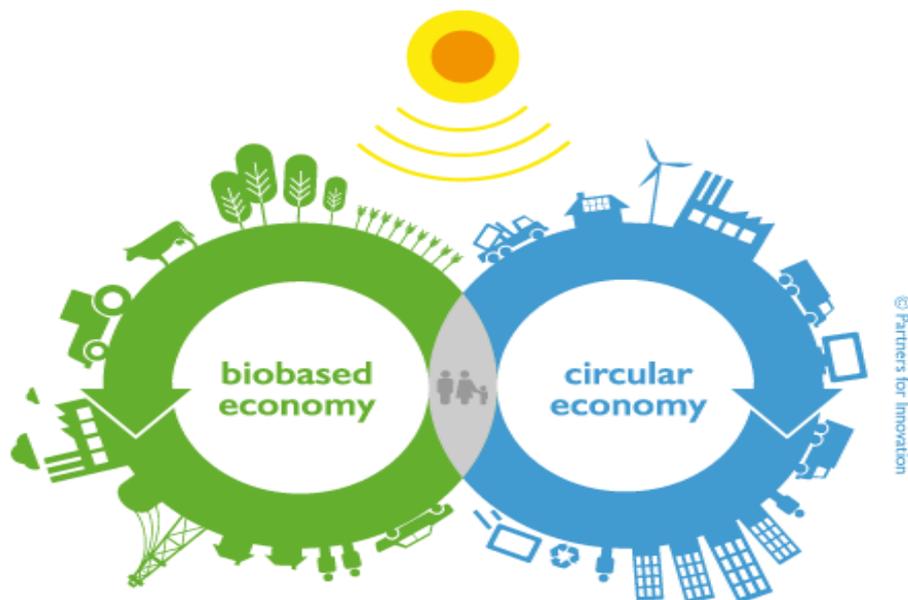
The circular economy has a focus on reusing, repairing, refurbishing and recycling of existing materials and products. It maximizes the use and value of the products which are beneficial for both the environment and the economy (House of Commons- Environmental Audit Committee, 2014). Materials that are considered as waste today should instead be seen as resources causing the residual waste close to zero (European Commission, 2014). This thinking is not new, there have been several similar approaches such as ‘cradle-to-cradle’ and ‘industrial ecology’ which are inspired from biological cycles on how to take care of waste and optimize the use of resources. The unique with circular economy is that it describes everything in processes, or ‘cycles’, where the resources are repeatedly used and their value are maintained as far as possible (House of Commons- Environmental Audit Committee, 2014). The circular economy implies that the industries should copy how nature takes care of

waste, so called biomimicry. The processes should work as an organism where processed nutrients can be fed back into the cycle.

Another concept is the bio-based economy which instead has the definition:

*“production paradigms that rely on biological processes and, as with natural ecosystems, use natural inputs, expend minimum amounts of energy and do not produce waste as all materials discarded by one process are inputs for another process and are reused in the ecosystem”*  
(European Commission, 2011)

The definition shows that the bio-based economy almost has the same approach as the circular economy but with the focus on organic raw material for production of materials, energy, chemicals and fuel (Partners for Innovation, 2015). These two concepts are reinforcing each other, see Figure 2, and together they are creating a strong position for the industries that are managing both of them.



**Figure 2** The interconnection between bio-based economy and circular economy.  
Source: (Partners for Innovation, 2015)

## 2.2 The biorefinery concept and circular economy in pulp and paper industry

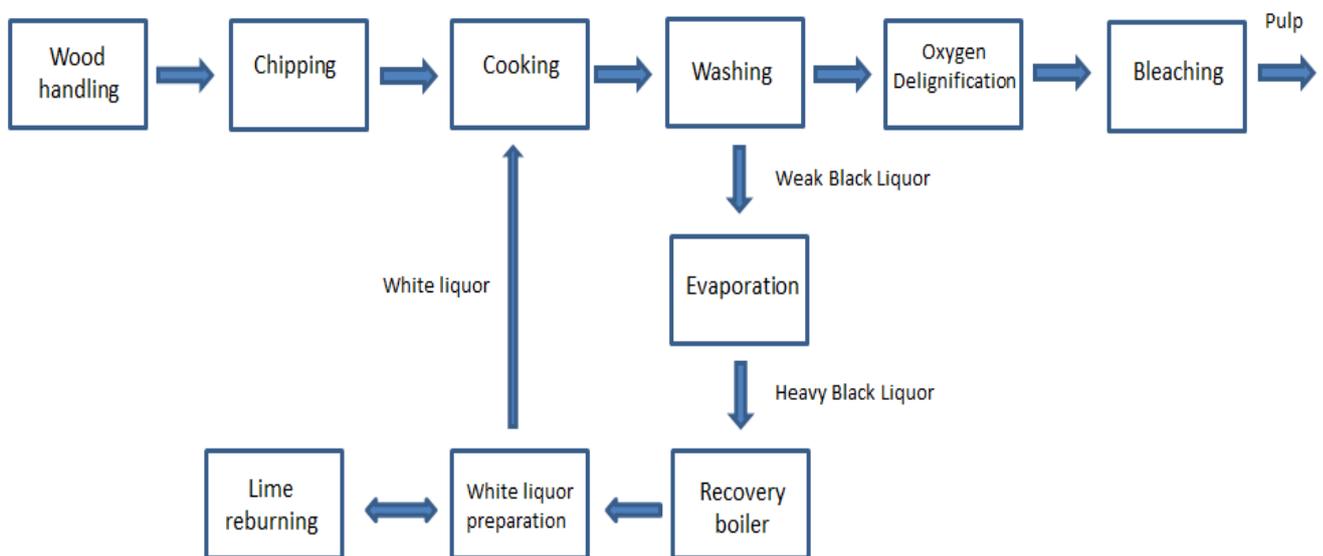
According to CEPI (Confederation of European Paper Industries) the pulp- and paper industry has a promising future for circular economy due to that it already has advancing resource efficiency and it is inherently sustainable with a renewable and recyclable raw material as base (CEPI, 2014). By recycling the papers at their end of life the loops are closed and no waste goes to landfill. The fibers can however not be recycled indefinitely and therefore new virgin fibers have to be added to the process and thereby the loops are continued. CEPI (2014) also claims that the pulp- and paper industry is the core of the European bio-based economy because the raw material is organic and it can produce biofuels to replace crude oil and bio-based products which is essential in a bio-based economy.

The recovered products from the pulp and paper industry are not just paper and pulp. Various of innovative products can be produced, such as chemicals from resins and renewable energy from the bark (CEPI, 2014). Excess electricity is also often sold to the grid and process steam is pumped to nearby houses as district heating (ibid). This is called the biorefinery concept and it started to be used for 15-20 years ago. A biorefinery is a process where biomass is converted to products that used to be fossil based (Berntsson, et al., 2014). That the pulp mills convert from pure pulp producers to more biorefineries depends not just on need of bio-based products but also on the demand for the pulp and paper industries in Europe to find more valuable products so they can compete with the Asian and South Americas markets.

To reach a total bio-based and circular economy and to close all the loops one issue the pulp and paper industry has is the disposal of waste. The focus for both the bio-based economy and the circular economy are that it should be zero amount of waste. The residues from one process should be an input for another process or it should be reused in the ecosystem, see the definition for bio-based economy.

### 2.3 Kraft pulp process

The kraft pulp process, also called the sulfate process, is a chemical pulping process with sodium hydroxide (NaOH) and sodium sulfide (Na<sub>2</sub>S) as active cooking chemicals (Gierer, 1980). An illustration of the process is shown in Figure 3 and it shows the process steps from handling of wood, through chipping into wood chips, impregnation/cooking in the digester, washing and bleaching to the final end product as bleached pulp.



**Figure 3** Kraft pulp process

Figure 3 also shows the important feature of the chemical recovery area where the cooking chemicals and energy are recovered (Saltberg, 2009). The recovery area will be described more in next section, 2.4 Recovery process, and that section also describe how some of the solid waste streams are obtained.

*The white liquor*, which is the cooking liquor, contains the active cooking chemicals and it is achieved from the recycling process. The main goal of kraft pulping is to remove lignin, which is the polymer that glues the fibers together, and liberate the fibers. As the lignin is broken down the white liquor is turning black/brown and is therefore called the *black liquor*. (Ziesig, 2014)

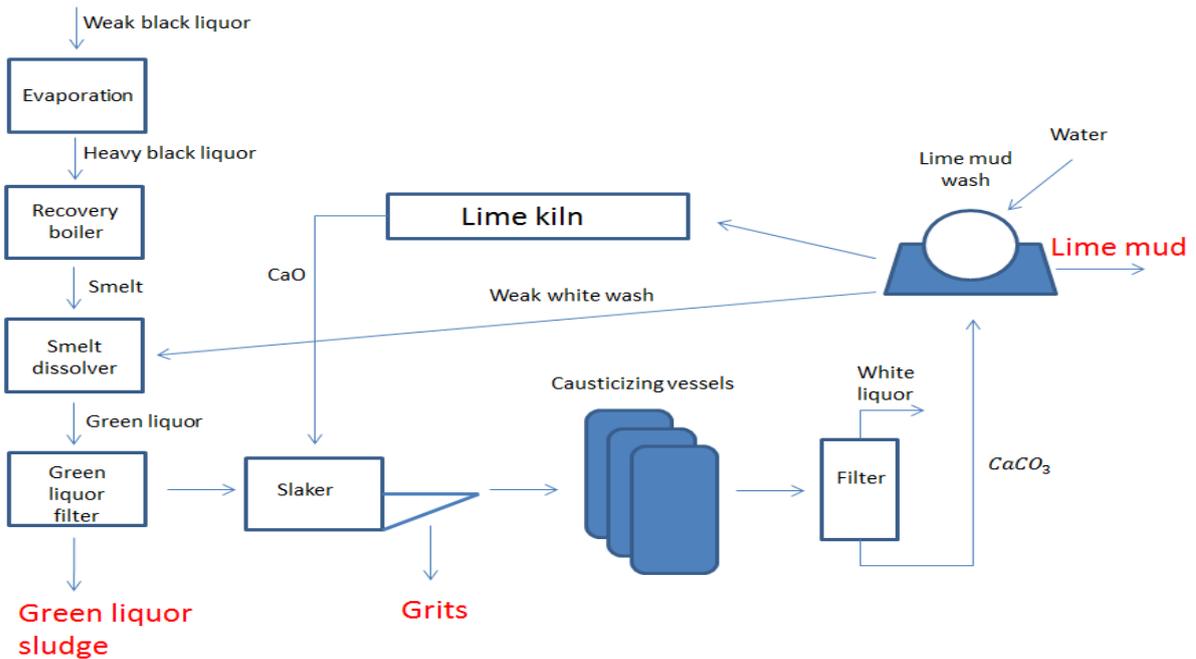
In the kraft pulping process the cellulose- and hemicellulose polymers are liberated through delignification. This is achieved by cleavage of ether linkages and by introducing charged phenolate groups which makes the lignin fragments soluble in the cooking liquor (Saltberg, 2009). The most important delignification reaction is the cleavage of the  $\beta$ -O-4-linkages in the phenolic structure of lignin (Saltberg, 2009).

During pulping, an unwanted end-wise degradation of hemicellulose and cellulose takes place, so called peeling reaction (Sjöström, 1993). This leads to losses of cellulose and hemicellulose, especially to hemicelluloses due to their lower degree of polymerization and their amorphous structure which give them a higher reactivity (ibid). The peeling reaction will continue until a stopping reacting occur and convert the reducing end group into a stable carboxylic acid group (ibid). A secondary peeling reaction can also start if the polysaccharides undergo an alkaline hydrolysis. The alkaline hydrolysis cleaves the glycosidic linkage in the polymers and this leads to the formation of a new reducing end-group (ibid).

All lignin is not removed in the digester due to the high degradation of cellulose and hemicellulose. Therefore some lignin has to be removed in the bleaching sequence if a white pulp is desired because lignin gives the pulp a darker color (Sjöström, 1993). The bleaching is performed in a sequence, so called bleaching line, consisting of three to six bleaching steps with different bleaching chemicals. The bleaching chemicals are for example chlorine dioxide, hydrogen peroxide, ozone, acids with EDTA and peracetic acid (Suess, 2010). Prior to the bleaching line the pulp is often pre-bleached in an oxygen delignification step. The oxygen delignification reduces the amount of lignin without reducing the pulp strength and it also reduces the amount of bleaching chemicals needed (Suess, 2010). Magnesium (Mg) is normally added to the oxygen delignification and hydrogen peroxide bleaching due to that magnesium inhibit the carbohydrate degradation and decreases the chemical use (Hälldal, 2004). Later the magnesium end up in the green liquor dregs which is described more in next section.

## **2.4 Recovery process**

One advantage the kraft pulp process has compared to the other pulping methods is its ability to effectively recover the process chemicals (Tran, et al., 2008). Up to 97% of the process chemicals are recovered in the kraft recovery process (ibid) and a schematic view of the process can be seen in Figure 4.

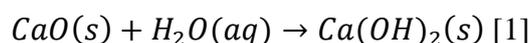


**Figure 4** Chemical recovery process

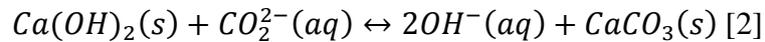
After the digester the pulp is washed and the cooking liquor, now as weak black liquor because of the dissolved lignin and often organic constituents turned it black, is separated from the pulp and sent to the recovery system. In the first step of the recovery system the weak black liquor is evaporated in multi-effect evaporators to attain a high concentration to make an efficient combustion of the black liquor in the recovery boiler (Tran, et al., 2008). This concentration is usually 70% solids or higher the liquor is now called heavy black liquor. The black liquor (mixed with electrofilter ash) is sprayed with liquor guns into the lower part of recovery boiler where it is burned in a reduced atmosphere due to that the airports at the recovery boiler are located at different heights (ibid). This leads to incomplete combustion but  $\text{Na}_2\text{S}$  is formed (ibid). Above the liquor guns the atmosphere is oxidizing because of added air from the airports higher up. This leads to combustion of carbon monoxide, methane and hydrogen (Theliander, 2008). When the flue gases leave the furnace they are led through superheaters where heat is exchanged and the flue gases are cooled down. Thereafter the gas passes a boiler tube bank and an economizer before it reach an electrostatic filter where the fly ash is collected (ibid).

The products from the recovery boiler are flue gases, heat used to produce high pressure steam and salt smelt (Theliander, 2008). The molten salt smelt consist mainly of  $\text{Na}_2\text{S}$  and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) (Tran, et al., 2008) and it is dissolved in weak white liquor from lime mud wash and thereby forms the green liquor (Theliander, 2008).

The green liquor is then filtered to separate the small solid particles in the green liquor, called the green liquor dregs (Theliander, 2008). The green liquor is then transported to the causticizing plant where burned lime mud, calcium oxide ( $\text{CaO}$ ), is added to the green liquor (ibid). The calcium oxide is slaked to calcium hydroxide through following reaction [1] (ibid):



After that, the causticizing reaction, reaction [2], starts where calcium hydroxide reacts with carbonate ions and form calcium carbonate (lime mud) and hydroxide ions (Theliander, 2008):



After the causticizing a suspension consisting of white liquor and lime mud is obtained. The white liquor and the lime mud are separated by filtration and the white liquor is recycled to the digester (Theliander, 2008). The lime mud is sent to a lime mud wash because it still contains some white liquor that has to be removed (ibid). Then the lime mud is transported to the lime kiln where it is heated to above 850°C, which makes the lime mud decompose into calcium oxide and carbon dioxide through the following reaction [3] (ibid):



The calcium oxide is sent to the slaker reaction again and thereby the lime cycle is closed.

## 2.5 Solid residue streams

As mentioned in 1. Introduction the major fraction of the total solid residues from the kraft pulp mill is bio sludge from wastewater treatment, fly and bottom ash from bark boiler and green liquor dregs and lime mud from the causticizing process (Nurmesniemi, et al., 2007). To get a better understanding of the specific streams a more detailed explanation will be presented in this chapter.

*Waste water sludge:* The kraft pulp mill is a water intensive industry but with an increased closure of the mills more water is recycled today. Still a considerable amount of waste water is produced according to Nurmesniemi et al. (2007), which needs to be treated before it is discharged to surrounding water sources. With an increased recirculation of the water the impurities are also concentrated and need to be removed. The waste water is often both primary and secondary treated and this results in waste water sludge, also called bio sludge. The primary treatment is usually sedimentation in a clarifier to remove suspended solids followed by a secondary treatment, a biological treatment, where micro-organisms are used to reduce the organic pollutants. The primary waste stream consists of wood fibers and an inorganic fraction and the secondary waste stream consists mainly of microbial biomass but also some inorganics, including macro nutrients (nitrogen, phosphorus) and micro nutrients (iron, zinc). The waste water sludge is often burned, together with the bark and wood residues, in the bark boiler (Nurmesniemi, et al., 2007) or incinerated in the recovery boiler (KAM report A100, 2003).

*Causticizing process:* During the chemical recovery process (see 2.4 Recovery process) the non-process elements (NPE) such as metals and other insoluble materials from the black liquor are separated from the green liquor in a filtration step, forming green liquor dregs. NPEs are elements, such as potassium, chloride, aluminum, magnesium and calcium etcetera, that can be harmful in various parts of the process (Parthasarathy, et al., 1999). The NPEs have to be removed before they reach a level that can cause damage, such as operation problems. This is why the green liquor filtration/clarification step is important if a high

quality pulp is desired and it is therefore often called the kidneys of the kraft pulp process (Nurmesniemi, et al., 2007) . The green liquor dregs consists mainly of calcite ( $\text{CaCO}_3$ ) (Monte, et al., 2009) and sodium carbonates (Taylor, et al., 2007) but has a relative high content from heavy metals, such as cadmium (Nurmesniemi, et al., 2007).

Another residue from the causticizing process is lime mud. Most of the lime mud is recycled but a few percent may be taken out. The lime mud mainly consists of calcium carbonate but also magnesium, phosphorous and sodium (Mahmoudkhani, 2005). It is however relatively free of contaminants, such as heavy metals (Pöykio, et al., 2006).

*Bark boiler:* Some of the steam to the process is produced by combustion of all types of appropriate burnable material, such as waste water sludge, bark and other wood residues. During combustion both fly- and bottom ash are produced as solid residues and almost all nutrients from the fuel are retained there (Nurmesniemi, et al., 2007). The quality of the ash depends on several factors such as tree species, part of the tree that is burned, temperature of combustion etcetera (Nurmesniemi, et al., 2007). Both ashes consists of calcite/calcium oxide and potassium salts (Monte, et al., 2009) but sodium silicates and magnesium oxide are also present (Steenari, et al., 1999). Some elements, such as potassium, sodium and heavy metals, are easily volatilized at high combustion temperature which leads to higher concentration of these elements in the fly ash in comparison with the bottom ash (Mahmoudkhani, 2005). The heavy metals in the tree species are also accumulated in the bark and therefore the heavy metal concentration in the bark boiler fly ash can be a potential problem if the ashes are supposed to be spread back to nature (ibid)

## **2.6 Recycling back to the forest**

The ashes from the bark boiler, the lime mud and the green liquor dregs all contain nutrients from the wood that are removed during harvest and enter the kraft pulp mill with the wood. One of the areas of utilizing these solid residues from the kraft pulp mill is to use their properties as a fertilizer to the forest and thereby also reduce the negative effects of harvesting of wood on soil nutrient status (Mahmoudkhani, 2005). All of the residues are alkaline due to their content of calcium carbonate and the residues can therefore also be used as a substitute for lime in acidified forests which is a problem for many forests in Europe (ibid).

The properties of the residues have to meet the forest's specific requirements e.g. different forests have different growth rate and therefore different requirements of the fertilizer may be needed. Properties that can be varied are e.g. composition and leaching rate of the residues and therefore the requirements of the land must be known before the residues can be used (Mahmoudkhani, 2005). One way of controlling the leaching rate is to make aggregates of the residues by pelletization or granulation (ibid). This is also advantageous when it comes to transport and spreading as pellets and granules are both easy to transport and spread if they are stable enough.

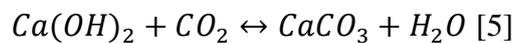
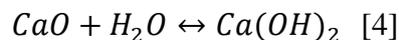
Today the fly ash is the only residue that is used as a fertilizer but not at any great extent, only 10% of all fly ash was recycled in Finland year 2008 (TAPIO, 2008). The reason for this, according to TAPIO (2008), is that companies performing the recycling are missing and that it is hard to decide which ash that is suitable as fertilizer. Some minimum threshold values and

guidelines have been set in Sweden and Finland for different substances in the fly ash, see Table 1, where the unit is how many gram substance per kilo dry ash the ash must contain. In Finland there are no threshold values for potassium and phosphorous alone instead these amount together represents the threshold limit.

**Table 1** Minimum limits for substances in ash recycled to the forest

<b>Nutrient</b>	<b>Sweden g/kg DS</b>	<b>Finland g/kg DS</b>
Calcium	125	60
Potassium	30	K+P 10
Magnesium	15	-
Phosphorus	7	K+P 10
Zinc	0.5	-

Potential problems with recycling residues to the forest are; rapid pH and ion concentration increase and the risk of spreading heavy metals to the soil according to Mahmoudkhani (2005). The rapid increase of pH and ion concentration is a problem for the upper soil horizon and on the surface of the vegetation. One way to solve this problem is to transform the solid residues into minerals, e.g. ash can be treated by self-hardening. This is mostly applicable to residual materials with high calcium oxide content which biofuel residues often have. In the self-hardening reaction calcium oxide reacts with water and calcium hydroxide is formed, see reaction [4]. Calcium hydroxide then reacts with carbon dioxide from the surrounding air and form calcium carbonate, see reaction [5] (Mahmoudkhani, 2005).



The formed calcium carbonate has lower solubility than calcium hydroxide which make the self-hardening reaction preferable when the ashes should be recycled back to the forest. Reaction [4] is rapid and exothermic but the carbonation of calcium hydroxide, reaction [5], requires a water phase where the reactants can be dissolved and transported (Mahmoudkhani, 2005). Therefore it is important that the water content in the ash is sufficient for reaction [5] to occur.

Another way to solve the problem with rapid pH increase is thermal treatment which makes the solid material less reactive. The thermal treatment can also remove some heavy metals e.g. arsenic and cadmium, by vaporization that occurs during the high temperature treatment (Mahmoudkhani, 2005). The drawback is that there is a need of very high temperatures, up to 800°C, to get the most advantageous sintering result. Therefore the leaching results obtained with only the self-hardening reaction, which is a much cheaper and simpler method than thermal treatment, will be investigated in this work.

## 2.7 Problems with cadmium and sulfate in nature

In this section the problems with the cadmium and sulfate contents in the residues are described, starting with 2.7.1 Cadmium followed by 2.7.2 Sulfate

### 2.7.1 Cadmium

The definition of a heavy metal is a bit vague but the most common definition is that a heavy metal has to have a density over  $5 \text{ g/cm}^3$  (Järup, 2003). The main heavy metals that are associated with damage to human health are lead, cadmium, mercury and arsenic with kidney damage and lung damage as some example of consequences of exposure. Heavy metals have been used for a long time for different applications and although the environmental and health effects are known, the exposure of heavy metals continues. Even though there is a decrease of heavy metals emissions in developed countries there are still an increase of emissions in some developing countries. (Järup, 2003)

There are two main environmental problems with heavy metals according to Guinee et al (2000). First, they are toxic to humans and ecosystems and even small doses can have harmful effect on the health. The second problem is that they are non-degradable which mean that once they have ended up in the environment they will stay there and accumulate in soils and food chains (Guinee, et al., 2000). Thereby the concentration will increase and lead to a harmful dose for animals and humans. Heavy metals are also often more soluble in acidic solutions which increase their availability for the vegetation in acidified soils (Kim, 2005).

The cadmium emissions have increased a lot in the 20<sup>th</sup> century due to that cadmium-containing products, such as nickel-cadmium batteries, often are dumped together with other household waste instead of being recycled (Järup, 2003). Direct inhalation of cadmium fumes can be life threatening and cadmium exposure can also cause kidney damage and cancer (ibid).

There are studies done to investigate where cadmium accumulate in the tree and how the concentration in the trees varies with latitude. Cadmium seems to accumulate mostly in the bark of the trees and thereafter the branches (KAM report A100, 2003). This makes the fly ash one possible cadmium source because bark and branches are often burned in the bark boiler and volatile elements, such as cadmium, end up in the fly ash. Cadmium concentration in the trees also decrease towards the northern part of Sweden and the explanation is probably that the cadmium uptake in the vegetation is favored by a low pH and the acidified soil in southern Sweden makes the cadmium more available to the forest (KAM report A100, 2003).

Cadmium in the green liquor dregs is probably found in the stable form cadmium sulfide (CdS) due to the high amount of sulfides in the green liquor dregs. In some mills there are also a precipitation of cadmium from the electrofilter ash with the green liquor dregs, forming cadmium sulfide (KAM report A100, 2003) The cadmium in the ash has been found as cadmium carbonate ( $\text{CdCO}_3$ ), in more insoluble forms  $\text{Ca}_x\text{Cd}_{1-x}\text{CO}_3$  (Steenari, et al., 1999), as sulfides and in the residual fraction (Camerani, 2001). According to Camerani (2001) more than 70 % of the cadmium was found in the residual fraction and the leachable cadmium carbonate was only found in the smallest particles.

Due to all the impacts cadmium causes to living beings threshold limits have been set for recycling of ash to the forest. There are only cadmium limits for the ash due to that ash is the only residue that is used as a commercial fertilizer today. The limits are 17.5 mg cadmium/kg dry ash in Finland and 30 mg cadmium/kg dry ash in Sweden (Haglund, 2008). These limits should be applicable for the green liquor dregs and lime mud as well and due to that no limits for green liquor dregs and lime mud exists the ash limits will be used in this work.

### 2.7.2 Sulfate

Sulfate ions are, on another hand, harmless to humans in aqueous solution if not the concentration of the ions is very high (Åkerlund, et al., 2006). The problem with leaching sulfate ions from landfill deposits is, according to Åkerlund et al (2006), the negative impact on drinking water. The limit of sulfate in drinking water is 100 mg/l in Sweden and this concentration has no negative impact on human health but is set as a limit because of the corrosive properties of the sulfate ions. High concentration of sulfate ions will also have an acidifying effect on the soil which impact the mobilization of metal ions and disturb the trees uptake of nutrients (ibid). Therefore new leaching limits have been set 2004 for hazardous waste and inert waste by Naturvårdsverket in Sweden and these limits can be seen in Table 2 where L/S is the ratio between liquid/solid of the leaching test (Åkerlund, et al., 2006).

**Table 2** Limits for sulfate ions in landfill waste

<b>Sulfate L/S 10 [L/kg]</b>	<b>Leached amount/Total amount dry material [mg/kg]</b>	<b>Cause</b>
Landfill deposits leaching limits for hazardous waste	50 000	Drinking water quality in adjacent wells
Landfill deposits leaching limits for non-hazardous waste or hazardous waste which is deposited on non-hazardous deposits	20 000	Drinking water quality in adjacent wells
Landfill deposits leaching limits for inert waste	1000	Drinking water quality in adjacent wells

One of the residues that can get problem with the threshold values for hazardous waste are fly ashes from combustion (Åkerlund, et al., 2006) and therefore the sulfate concentration of the ashes from the kraft pulp mill will be examined in this thesis.

### 3. Experimental background

In this section leaching (3.1 Leaching) is described in an overview at first followed by description of different leaching methods; 3.1.1 Batch leaching test, 3.1.2 Column leaching test, 3.1.3 pH-stat leaching test and 3.1.4 Modified column pH-stat test.

#### 3.1 Leaching

Leaching is a method where soluble components are removed from a solid matrix (Kim, 2005). It can be described easily with equation [6]:



There are several different leaching methods developed within the European leaching test framework such as batch leaching tests, column leaching tests and pHstat leaching tests (Mahmoudkhani, 2005). In this work batch leaching tests and a modified column-pHstat leaching test developed within the Ph.D. work of Mahmoudkhani (2005) are used. The modified column-pHstat leaching test (which is described in section 3.1.4 Modified column pH-stat test) is used because of drawbacks in the standard tests. The different standard leaching tests and their drawbacks will be described more under each section.

Results from leaching experiments are often defined as concentration in the leachate (mg/L) or as the leached amount from the solid (mg/kg) (Kim, 2005). In many methods the L/S ratio is used to quantify the amount solid material and the volume leachant. L/S ratio is the volume leachant over the amount solid, often expressed in L/kg (Kim, 2005).

##### 3.1.1 Batch leaching test

In batch leaching tests the solid material is placed in a given volume of leachant solution for a set period of time (Kim, 2005). Different L/S ratios can be used but most common is an L/S ratio between 2-200 L/kg (Mahmoudkhani, 2005). Parts that can differ between the methods are if the vessel is open or closed, if it is shaken, agitated or stand still and the set of time (Mahmoudkhani, 2005). The vessels are often shaken to make sure a constant contact between leachant and the sample is obtained (Kim, 2005). When the end time of the test is reached the liquid is removed and analyzed.

There are also different serial/sequential batch methods. They can be used in many various ways, e.g. in a two-step standardized batch leaching test a small L/S ratio is applied in the first step for a short period and then in the second step a larger L/S ratio is applied for a longer period (Mahmoudkhani, 2005) or in a sequential leaching test a single sample can be leached with different leaching fluids (Kim, 2005).

One problem with the batch leaching methods is that the pH is changed over time. This strongly influence the kinetics of dissolution reaction (Mahmoudkhani, 2005). The particles can also disintegrate due to the shaking which affect the leaching rate (ibid).

### 3.1.2 Column leaching test

Column leaching tests are aimed to simulate the groundwater's way through a porous bed made of granule material (Kim, 2005; Mahmoudkhani, 2005). In the test the leachate is passed through a column packed with the studied solid material. The flow can either be continuous or intermittent and it can either be up-flow or down-flow direction (Kim, 2005). The flowrate is often faster in comparison with natural conditions but it has to be slow enough to attain measurable concentrations (Kim, 2005).

The drawback with column leaching test is the risk of channeling which is when the flow of the liquid is not evenly distributed over the column (Mahmoudkhani, 2005). This can result in particles not to be exposed to the liquid in the same way in every test (ibid).

### 3.1.3 pH-stat leaching test

A pH-stat leaching test is a single batch leaching test where the pH is held constant through addition of acid or base (Mahmoudkhani, 2005). The pH-stat leaching test is used when the leaching of the compounds has to be determined under pH-controlled conditions (Mahmoudkhani, 2005).

### 3.1.4 Modified column pH-stat test

Mahmoudkhani (2005) combined the column test and the pH-stat test in the modified column-pHstat test. The solid material is placed in the middle of a chamber and the leachant is continuously pumped in an up-flow direction through the chamber. The leachant is circulated back to the storage vessel after it has met the solid material, see Figure 5. In the storage vessel the pH is measured with an electrode and there is an addition of acid or base when needed.

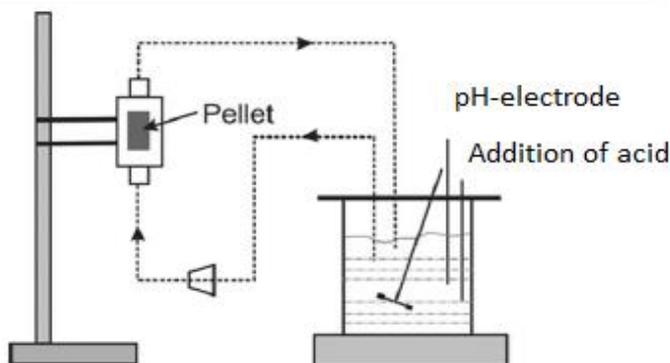


Figure 5 Column-pHstat leaching test

## 4. Experimental methods

In this section the methods used in this thesis are presented, starting with 4.1 Physical and chemical characterization of raw material, followed by 4.2 Pellets preparation, 4.3 Column-pHstat leaching test, 4.4 Batch leaching test, 4.5 Atomic absorption spectroscopy, 4.6 Ion chromatography and 4.7 Transport simulation.

### 4.1 Physical and chemical characterization of raw material

The dry content in the residues was analyzed when the residues arrived using a drying scale (Sartorius MA 30). To attain the chemical composition of the residues an ICP-AES (Inductively coupled plasma atomic emission spectroscopy) analysis was performed at an external lab (Innventia AB).

### 4.2 Pellets preparation

Two types of pellets were made, one containing fly ash from bark boiler and the other using a mix of green liquor dregs, lime mud and fly ash from bark boiler. The mixed pellets were made in relations to how much of the different residues the pulp mills produced during one year.

#### 4.2.1 Fly ash pellets

The fly ashes from the different pulp mills where dried in an oven at 105°C over night to get a comparable amount in the pellets since all fly ashes had different dry contents, see Table 5 in 5. Results and discussion. The dried ashes were mixed with deionized water at a ratio of 3:1 w/w and then 1.3 gram of the wet ash was pressed to pellets in a hydraulic hand press at a pressure of either 30 MPa or 10 MPa. The pellets were stored in a 100% carbon dioxide atmosphere for 4 days for the self-hardening reaction to occur, see reaction [4] and [5]. After the storage the pellets had a height of  $6.4 \pm 0.2$  mm, a diameter of  $10.2 \pm 0.1$  mm and a weight of  $1.16 \pm 0.07$  g.

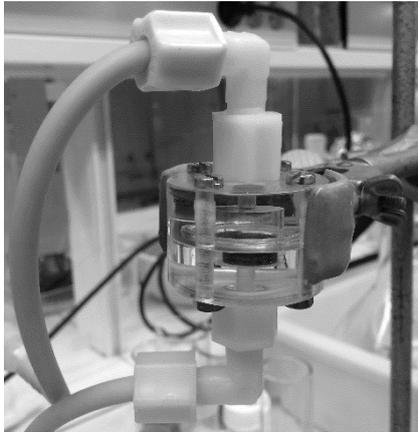
#### 4.2.2 Mixed pellets

Both the fly ashes from the bark boilers and the green liquor dregs were dried in an oven at 105°C over night to get comparable amount in the pellets due to differences in dry content from the different pulp mills, see Table 5 in 5. Results and discussion. The green liquor dregs were grounded to achieve finer particles. The ashes and the green liquor dregs were both mixed with deionized water at a ratio of 2:1 w/w. The lime muds were used as they arrived since the dry content of the lime muds where very similar, see Table 5 in 5. Results and discussion. A mixture of 40% lime mud, 37% fly ash and 23% green liquor dregs was blended and 1.3 g of the mixture were pressed to pellets in a hydraulic hand press at a pressure of either 30 MPa or 10 MPa. The pellets were stored in a 100% carbon dioxide atmosphere for 4 days for the self-hardening reaction to occur, see reaction [4] and [5] in 2. Theoretical background. After storage the pellets had a height of  $6.54 \pm 0.3$  mm, a diameter of  $10.24 \pm 0.08$  mm and a weight of  $1.04 \pm 0.04$  g.

### 4.3 Column-pHstat leaching test

A modified column-pHstat test developed within the Ph.D. work of Mahmoudkhani (2005) (see 3.1.4 Modified column pH-stat test) was used in this study. The pellets were placed in a

chamber, see Figure 6, and the leachant was pumped with a peristaltic pump upwards through the chamber at a constant flow rate at 75 ml/min.



**Figure 6** Pellet within the chamber

The leaching tests started with 400 mL of deionized water acidified with nitric acid to a pH of 5 in a 500 mL beaker. The pH was held constant at pH 5 (-0,2 units) during the test with an automatic addition of 0,1 M nitric acid from an auto burette (Titroline-alpha). Nitric acid (HNO<sub>3</sub>) was chosen because it simulates acid rain water in a proper way. The temperature was held constant at 25°C (±2 degrees) and the leachant was properly stirred with a magnetic stirrer. The beaker had a plastic lid to reduce the water loss with holes for inserting pH-electrode and pipe for addition of acid. Each test was performed in 80 hours and during this time samples were taken out regularly and analyzed for Na, Ca and Mg concentrations using atomic absorption spectroscopy (Thermo Scientific, iCE 300 series), see section 4.5 Atomic absorption spectroscopy. Some tests continued after 80 hours to see a longer perspective.

The Cd concentration was also measured with atomic absorption spectroscopy for all leaching samples but due to very low concentration in the leachates the amounts were below the detection limit. Therefore no results for Cd will be presented for the column-pHstat test, instead a batch leaching test was performed, see below.

#### **4.4 Batch leaching test**

In this section the two different batch leaching test performed in this thesis will be presented, first the batch test for cadmium followed by the sulfate test.

##### **4.4.1 Cadmium**

To analyze how much cadmium that was leached from the fly ashes and the green liquor dregs, batch leaching tests were performed in two different solutes; deionized water and deionized water acidified with HNO<sub>3</sub> to pH 5. Both the fly ashes and the green liquor dregs were dried at 105°C over night and then 20 gram of the dry materials were placed in a 200 mL volumetric flasks. 100 mL of the solute was added and the flask was shaken until everything was mixed. The flask was stored in room temperature for 48 hours and was shaken from time to time during the days. After 48 hours the leachate was filtered with a 0.45 µm membrane and thereafter the cadmium concentration was analyzed using atomic absorption spectroscopy (Thermo Scientific, iCE 300 series), see section 4.5 Atomic absorption spectroscopy. Four of the samples were sent to an external lab (Innventia AB) to verify the results from the atomic absorption spectroscopy in an inductively coupled plasma-optical emission spectroscopy (ICP-OES).

##### **4.4.2 Sulfate**

To analyze the sulfate content leached from the fly ashes a standard batch leaching test (EN 12457-2) was performed at L/S ratio 10 L/kg. 20 gram of each fly ash was placed in a 500 ml volumetric flask and thereafter 200 ml deionized water was added. The flasks stood on a

shaker ( $125 \text{ min}^{-1}$ ) for 24 hours and then the leachate was filtered with Munktells filter paper. The sulfate concentrations were then analyzed by ion chromatography (850 Professional IC), see section 4.6 Ion chromatography, and recalculated to g/kg dry substance.

#### 4.5 Atomic absorption spectroscopy

For detection of metal ions in the leachates Thermo Scientific, iCE 300 series atomic absorption spectroscopy with flame and hollow cathode lamps was used. The metal ions that were analyzed were sodium (Na), Calcium (Ca), Magnesium (Mg) for the column-pHstat leachates and cadmium (Cd) for the batch leachates. Standards, wavelength and fuel- and support gas used for the different metals are shown in Table 3.

**Table 3** Values for atomic absorption spectroscopy

Metal	Standards [mg/L]	Wavelength [nm]	Fuel gas/Support gas
Sodium	5, 20, 50, 100	330,3	Acetylene/Air
Magnesium	5, 10, 20, 50	202,6	Acetylene/Air
Calcium	5, 20, 50, 100	239,9	Acetylene/Nitrous oxide
Cadmium	0.1, 0.5, 1, 2	228,8	Acetylene/Air

#### 4.6 Ion chromatography

The content of sulfate ( $\text{SO}_4^{2-}$ ) in the leachate from the batch leaching test was analyzed with an 850 Professional IC from Metrohm equipped with a Metrosup A Supp7 column. The eluent was a 3.6 mM  $\text{Na}_2\text{CO}_3$ -solution. The standards used to obtain the calibration curve were 100, 200, 500 and 1000 mg/L.

#### 4.7 Transport simulation

To analyze how the pellets are affected by a truck transport a simulation of a rough transport was done. Five ash pellets and one mix pellet (30 MPa) were put in a 200 ml glass flask and the flask was placed at a shaker at  $225 \text{ min}^{-1}$  for 12 hours. Pictures were taken after 0, 2, 7 and 12 hours.

## 5. Results and discussion

In this section the results are presented and discussed. The three kraft pulp mills investigated are referred to as Pulp mill A, Pulp mill B and Pulp mill C. The results starts with 5.1 Physical and chemical characteristics of the residues followed by 5.2 Leaching of soluble species, 5.3 Leaching of cadmium, 5.4 Leaching of sulfate and at last 5.5 Transport simulation results.

### 5.1 Physical and chemical characteristics of the residues

The chemical characterization of the residues was performed by ICP-AES (Inductively coupled plasma atomic emission spectroscopy) at an external laboratory (Innventia AB) and the result is presented in 5.1.1 Chemical composition. The physical characterization was measuring of the dry content and that result is presented in section 5.1.2 Dry content.

#### 5.1.1 Chemical composition

The compositions of the residues were analyzed at an external laboratory using ICP-AES (Inductively coupled plasma atomic emission spectroscopy). The result is shown in Table 4 where all units are gram substance per kilo dry residue except for cadmium which is milligram cadmium per kilo dry residue.

**Table 4** Result from the ICP-AES (Inductively coupled plasma atomic emission spectroscopy). LM- Lime mud, GLD- Green liquor dregs, FA- Fly ash and BA- bottom ash. Note the unit at cadmium.

Sample	Al [g/kg]	Ba [g/kg]	Ca [g/kg]	Cu [g/kg]	Fe [g/kg]	K [g/kg]	Mg [g/kg]	Mn [g/kg]	Na [g/kg]	P [g/kg]	S [g/kg]	Si [g/kg]	Zn [g/kg]	Cd [mg/kg]
LM Pulp mill A	0,3	0,3	468	0	0,3	0,5	7,6	0,9	7,1	3,8	0,5	1,7	0,1	1,6
GLD Pulp mill A	3,1	1,1	259	0,3	3,8	2,8	93	31	21	1,4	13	16	3,8	18,5
FA Pulp mill A	27	2,2	231	0,1	15	50	22	14	26	18	26	11	2,4	9,6
BA Pulp mill A	24	1,7	74	0	7	39	7,5	4,1	13	4,1	0,4	95	2	2,5
LM Pulp mill B	1	0	470	0	0,4	0,3	6,4	0	6,9	0,1	0,6	1,5	0	0,6
GLD Pulp mill B	3,7	0,2	408	0,2	4,7	1,1	24	24	10	0,2	7,2	11	1,6	11,2
FA Pulp mill B	23	1,4	92	0,1	6,8	21	6,6	4,2	20	5,8	9,3	23	0,9	4,8
BA Pulp mill B	15	0,8	30	0	3,7	21	2,7	1,8	13	1,8	0,3	109	0,8	2,5
LM Pulp mill C	0,2	0,2	544	0	0,1	0,3	3,3	0,1	8,5	3,5	0,2	0,3	0	0,6
GLD Pulp mill C	2,5	0,2	255	0,2	3,4	3	78	16	55	1,6	11	1,4	1,4	12,3
FA Pulp mill C	33	1,5	194	0,1	94	32	19	5,2	20	19	23	71	1,2	8,3
BA Pulp mill C	27	0,7	40	0	6,7	30	3,5	1,3	13	2,2	0,3	87	0,7	2,5

The results are mostly as expected with high calcium (Ca) content in the lime mud, green liquor dregs and fly ash and high cadmium (Cd) and magnesium (Mg) content in the green liquor dregs for all mills. The magnesium content in the green liquor dregs does not only originating from the wood chips but also from magnesium addition in the oxygen bleaching.

This can be seen as disadvantageous because the recycled content will be higher than the withdrawn amount. However there is no upper limit for the amount of magnesium in ash recycled to the forest, see Table 1, so there is no problem today but it might be a problem in the future. The fly ash has the highest phosphorous (P) content of the residues and quite low cadmium content which is advantageous if the ash should be used as a fertilizer.

The cadmium levels for all residues are below Sweden's limit (30 mg/kg DS) and only one residue, green liquor dregs from Pulp mill A, violate Finland's threshold value (17.5 mg/kg DS). This means that all residues could be used as fertilizers in Sweden and that the green liquor dregs have to be mixed with other residues to be recycled in Finland. To solve the problem with cadmium in green liquor dregs new methods to remove cadmium needs to be investigated. The mills precipitating cadmium from the electrofilter ash in the green liquor dregs may also investigate new methods for this purpose even though the cadmium precipitated does not contribute much to the total amount of cadmium in the green liquor dregs.

The magnesium (Mg) content in the fly ash and green liquor dregs from Pulp mill B is low in comparison with the other mills and this result will be discussed later in sections. The phosphorous amount in the lime mud from Pulp mill B is also low in comparison with the other mills which is a bit surprising because the phosphorous in the process is usually found in the lime mud. The sulfur (S) content in the fly ashes also deviate a bit for the different mills and that result will be discussed more in section 5.4 Leaching of sulfate. There is also a high iron (Fe) content in the fly ash from Pulp mill C but the reason and consequences for this will not be discussed in this thesis.

### 5.1.2 Dry content

The dry content was measured for all residues and the result is shown in Table 5.

**Table 5** Dry content of the residues in % w/w

Mill	Fly Ash [%]	Lime Mud [%]	Green Liquor Dregs [%]
<b>Pulp mill A</b>	99,46	67,63	29,76
<b>Pulp mill B</b>	85,17	73,67	46,56
<b>Pulp mill C</b>	77,11	72,47	45,81

The result shows that the dry content for green liquor dregs and fly ashes varies quite a lot but a more even distribution for the dry contents is found for the lime muds. This result established the decision to dry the green liquor dregs and fly ash before the pellets were made so the pellets would have as uniform content as possible.

## 5.2 Leaching of soluble species

The results from the column-pHstat test is presented below, first the fly ash pellets followed by the mixed pellets and at last a comparison between pellets produced by different pressures will be demonstrated.

### 5.2.1 Fly ash pellets

Figure 7, Figure 8 and Figure 9 demonstrate how the compounds sodium, magnesium and calcium are leached from fly ash pellets in the column-pHstat test. The first graph in each figure shows how much of each compound that is leached relative to how much of each compound the pellets contained from the beginning. The second graph shows how much of each compound that is leached relative to dry starting material. The tests for Pulp mill A and Pulp mill B were executed for 80 hours, see Figure 7 and Figure 8. To investigate the consequence of a longer time perspective the test for Pulp mill C was performed for 200 hours, see Figure 9.

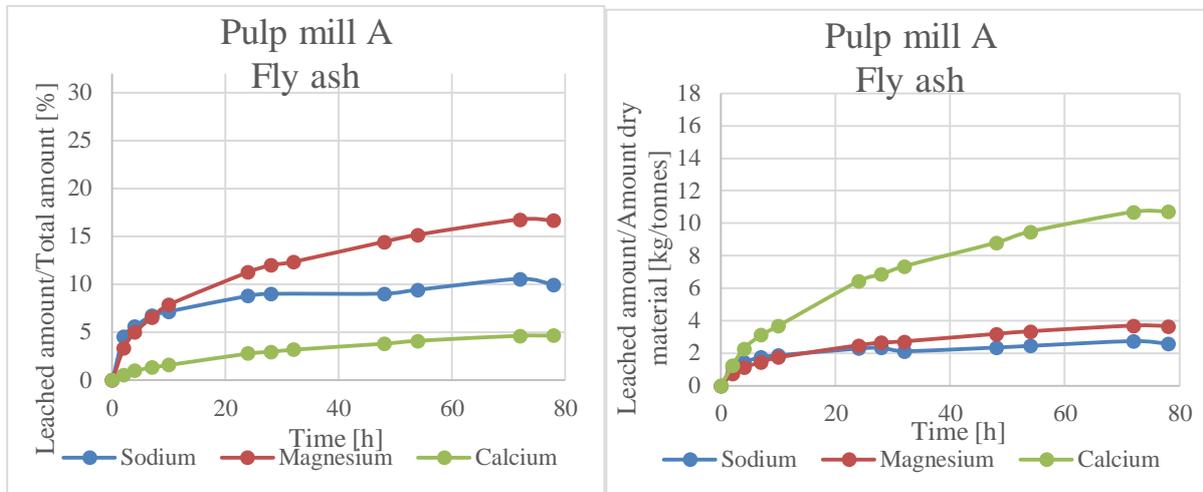
The tests indicate the same leaching behavior for sodium and calcium where sodium is leached fast at the beginning and after around 20 hours the leaching rates start to decrease and calcium has a more linear leaching rate over the whole period. The leaching behavior of magnesium on the other hand varies for the different mills and the reason will be discussed more in the last paragraph of this section.

Based on the amounts in the starting material calcium is leached to the lowest degree of the three substances in all tests, which is visualized in the graphs to the left in the figures, where only 10% of the total calcium is leached at the most. This is probably due to the self-hardening reaction which transform calcium oxide to the less soluble calcium carbonate, see reaction [4] and [5]. The self-hardening reaction appear to decrease the calcium leaching but in comparison with Mahmoudkhani's (2005) thermal treatment, where only 2% of the calcium was leached after 80 hours, the thermal treatment appears more efficient .

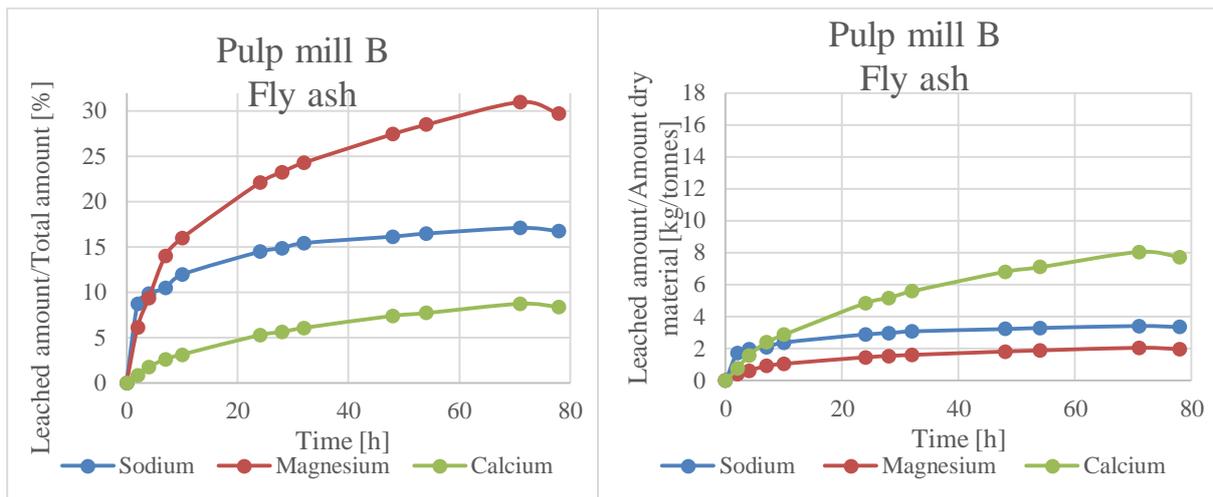
The fast leaching of sodium the first hours is disadvantageous if the ash should be used as a fertilizer due to rapid pH increase in the soil. The self-hardening reaction does not seem to slow the leaching of sodium down unfortunately. However, it is only 10-20 % of the total sodium content that is leached which may be explained by the fact that sodium is mostly present as sodium silicates and feldspar in the ash (Steenari, et al., 1999) rather than the more soluble forms sodium carbonate or sodium sulfate. This is both advantageous and disadvantageous if the ash should be used as fertilizer. Advantageous because the pH increase will not be that large due to the amount leached is small and disadvantageous because most of the sodium will be in forms the vegetation cannot take up. Potassium is however a more important nutrient for the trees than sodium but Mahmoudkhani (2005) has showed that sodium and potassium shows the same leaching trends and therefore only sodium was analyzed.

Results that are unexpected are the leaching rates for magnesium. The results deviate for the different mills and the leaching rate is higher than expected due to that the magnesium in ash should be in the low soluble forms magnesium oxide (MgO) and magnesium silicate according to the literature (Steenari, et al., 1999). One leaching rate that is particularly high is the magnesium leaching for Pulp mill B, see Figure 8, where the percentage of magnesium leached is 30 %. One possible explanation can be that Pulp mill B's ash simply contain more soluble magnesium than the other mills. Another explanation could be the low magnesium content in the ash from Pulp mill B analyzed at the external lab, see Table 4, which makes the

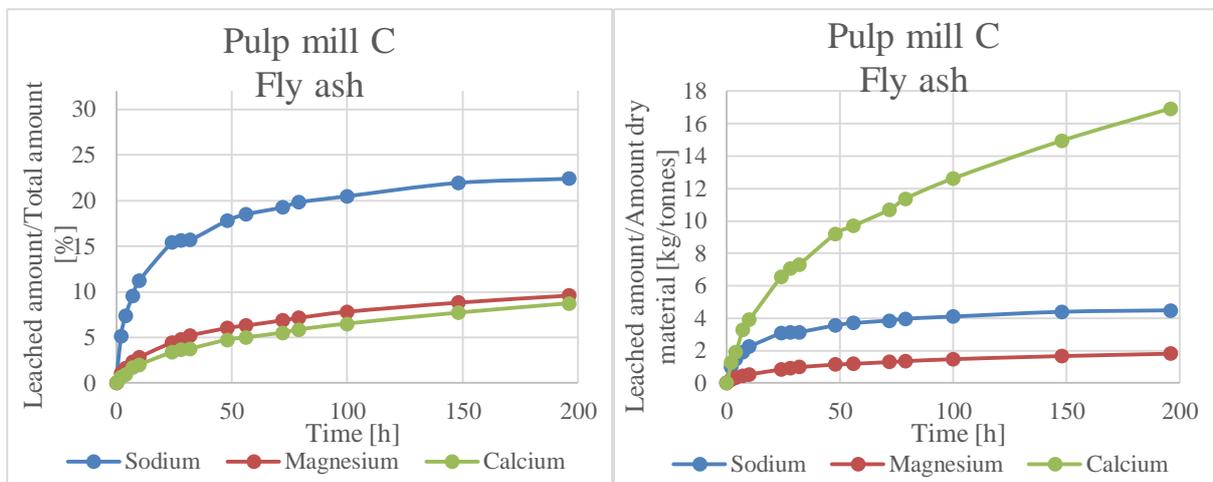
leaching percentage high. If the total amount would be as Pulp mill A's or Pulp mill C's ash the leaching percentage would be 9-11% after 80 hours which can be seen as a more reasonable result.



**Figure 7** Leaching results for fly ash pellet from Pulp mill A



**Figure 8** Leaching results for fly ash pellet from Pulp mill B



**Figure 9** Leaching results for fly ash pellet from Pulp mill C

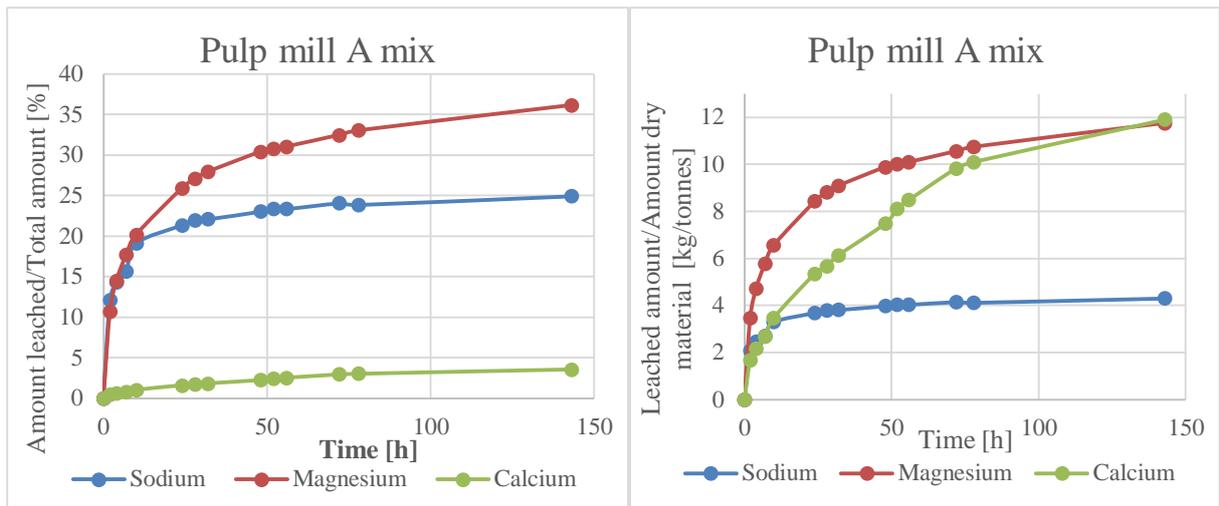
### 5.2.2 Mixed pellets

The results for the mixed pellets are shown in Figure 10, Figure 11 and Figure 12. The first graph in each figure shows how much of each compound that is leached relative to how much of each compound the pellets contained from the beginning. The second graph shows how much of each compound that is leached relative to dry starting material. Here Pulp mill B's and Pulp mill C's tests were performed for 80 hours and Pulp mill A's test was performed for 150 hours to get an indication of a longer leaching time.

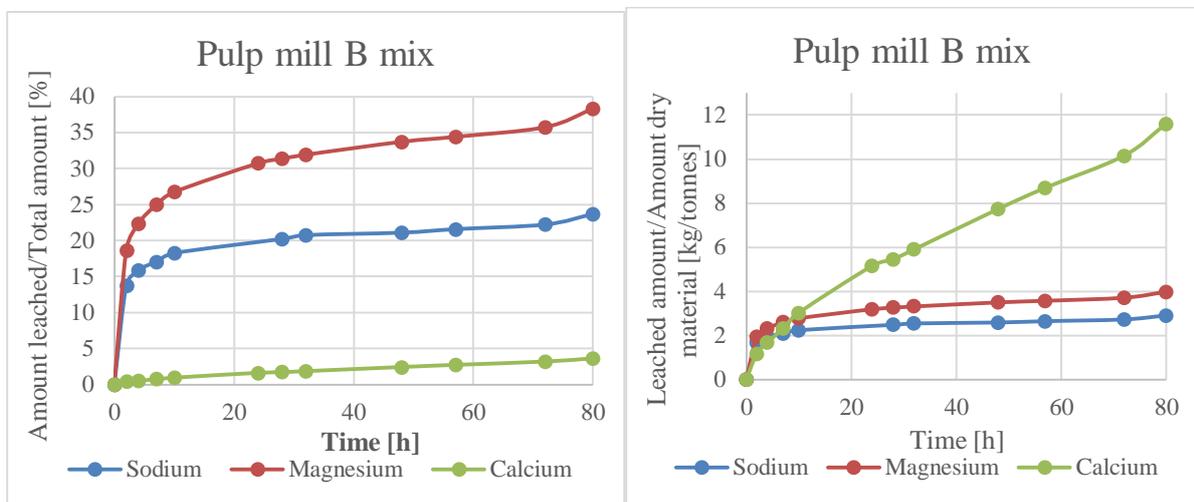
For the mixed pellets all compounds show the same leaching patterns for all three pulp mills where sodium and magnesium are leached fast in the beginning and then decrease and calcium is leached at a more constant rate. In comparison with the ash pellets there is more magnesium leached for the mixed pellets, both in percentage and in amount. This indicates that magnesium is in more soluble forms in the green liquor dregs and in the lime mud which is supported by Taylor et al. (2007) which claim that some magnesium in the lime mud and green liquor dregs is magnesium carbonate. Taylor et al. (2007) also claims that 50% of the magnesium in the green liquor dregs is in the silicate forms diopside ( $\text{CaMgSi}_2\text{O}_6$ ) and pargasite ( $\text{NaCa}_2\text{Mg}_3\text{Fe}^{2+}\text{Si}_6\text{Al}_3\text{O}_{22}(\text{OH})_2$ ) which explains why not all magnesium is leached. There is also quite a lot of magnesium leached from Pulp mill A's pellet in comparison with the other mills, see graph to the right in Figure 10, and this is probably due to a large amount of magnesium in the green liquor dregs from Pulp mill A, see Table 4.

Around 25% of the sodium is leached for all three pulp mills. This result is also confirmed by Mahmoudkhani (2005). The sodium amount leached per dry material is slightly higher in the mixed pellets compared to the ash pellets even though the total sodium amount is lower in the mixed pellets. This might be explained by that sodium is in more soluble forms in the green liquor dregs and lime muds than in the ash. It was mentioned in the previous section that much of the sodium in the ash probably occurs as insoluble silicate compounds but in green liquor dregs the sodium is mostly found in different carbonates and as sodium chloride according to Taylor et al. (2007) which can be the explanation for more leached sodium. This is also indicated by the result for Pulp mill C's mixed pellet, see graph to the right in Figure 12, where the highest amount of sodium is leached for the three mills and Pulp mill C also had the highest content of sodium in the green liquor dregs and lime mud but not in the ash, see Table 4.

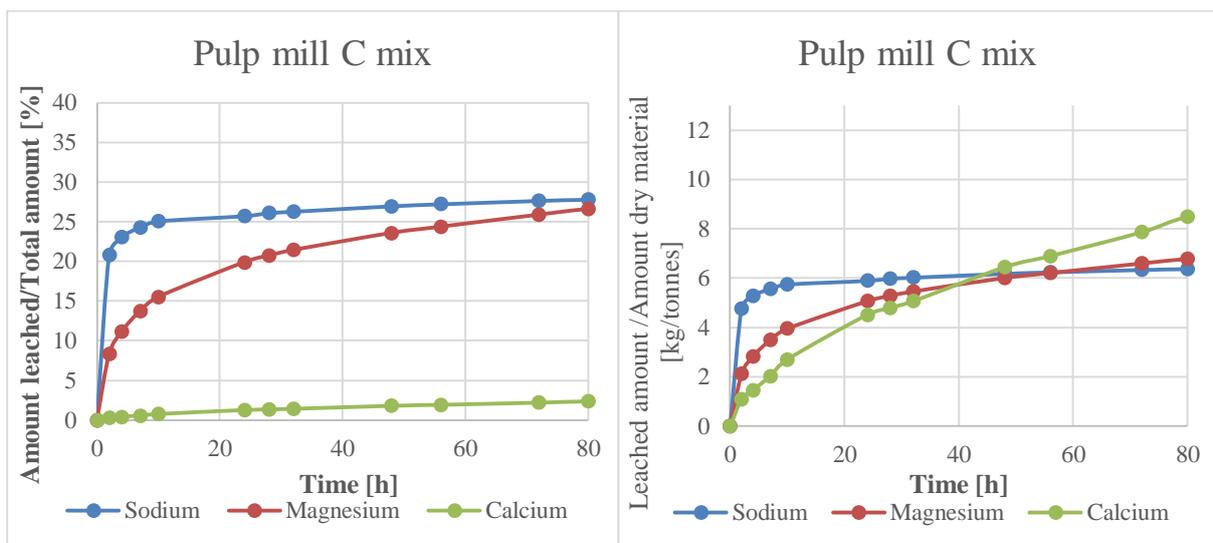
The calcium is even less leached in percentage for the mixed ash pellets compared to ash pellets but the amount leached per dry material is almost the same. The mixed pellets contained more calcium than the ash pellets due to the lime muds and the green liquor dregs having high calcium content, see Table 4, which makes the leached percentage lower. The interesting result here is that the amount leached per kilo dry material is not increasing when the content of calcium increased. This is due to that the leaching of calcium is dependent on the concentration of  $\text{H}^+$ -ion, according to Mahmoudkhani (2005), and this concentration is the same all the time because of constant pH. This explains how the amount leached calcium is almost the same in every test independently of the start amount of calcium. A slow leaching rate of calcium is preferable if the residues should be used as fertilizer in the forest since that prevents a pH shock for the vegetation.



**Figure 10** Leaching results for mixed pellet from Pulp mill A



**Figure 11** Leaching results for mixed pellet from Pulp mill B



**Figure 12** Leaching result for mixed pellet from Pulp mill C

### 5.2.3 Lower pressure

To investigate how much the applied pressure when producing the pellets influences the leaching rates some pellets with lower applied pressure were produced. A comparison between ash pellets produced with lower pressure (10 MPa) and higher pressure (30 MPa) was done and the results are shown in Figure 13 and Figure 14. A mixed pellet was also produced with an applied pressure of 10 MPa and the leaching result was compared with a mixed pellet with producing pressure at 30 MPa and these results are shown in Figure 15 and Figure 16.

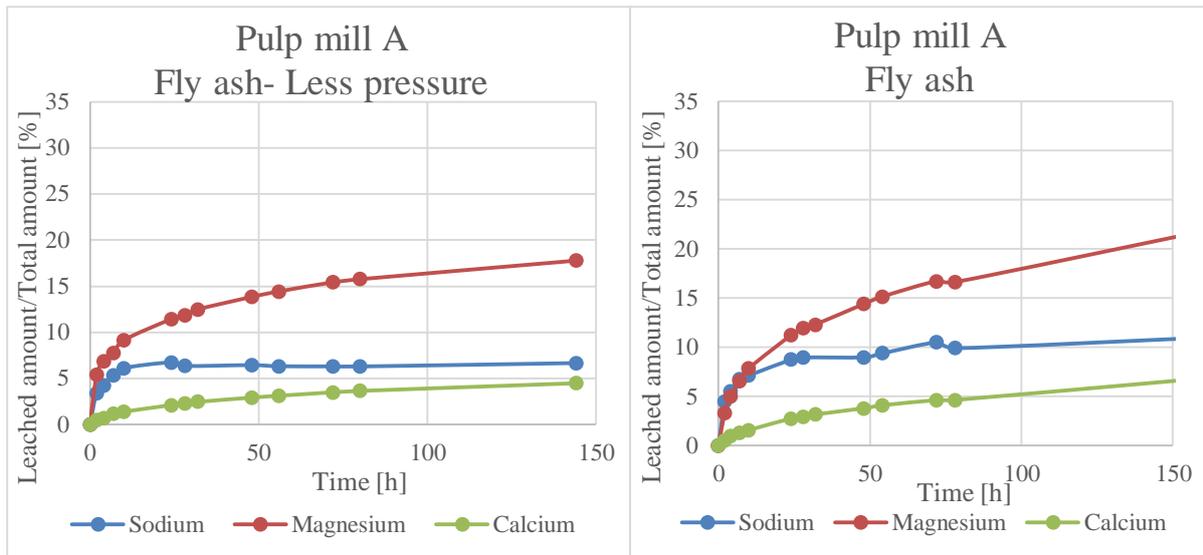


Figure 13 Comparison between fly ash pellets produced with 10 MPa and 30 MPa

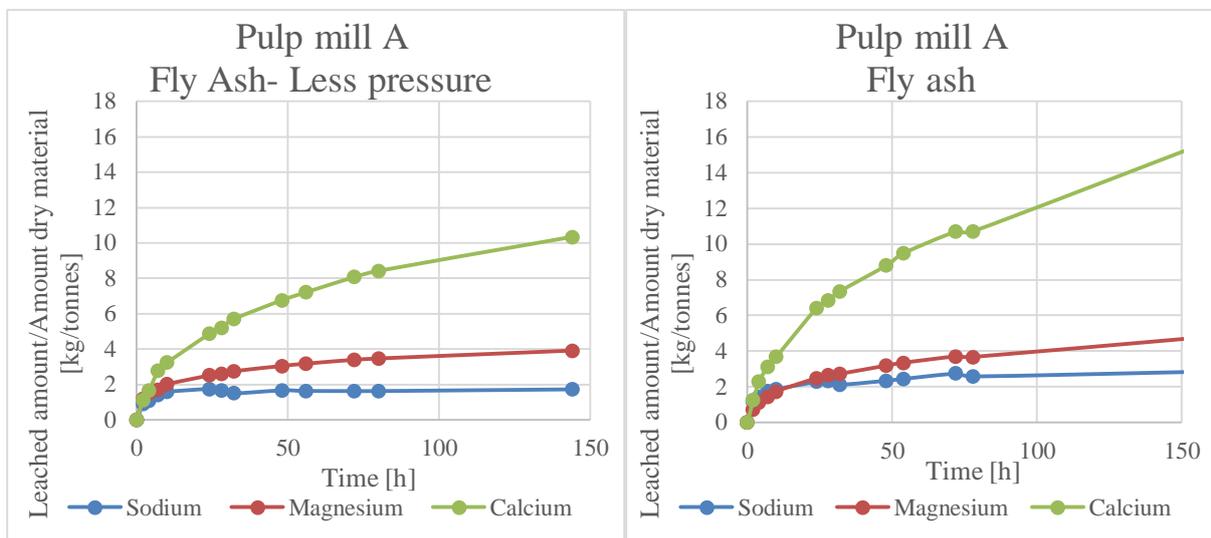
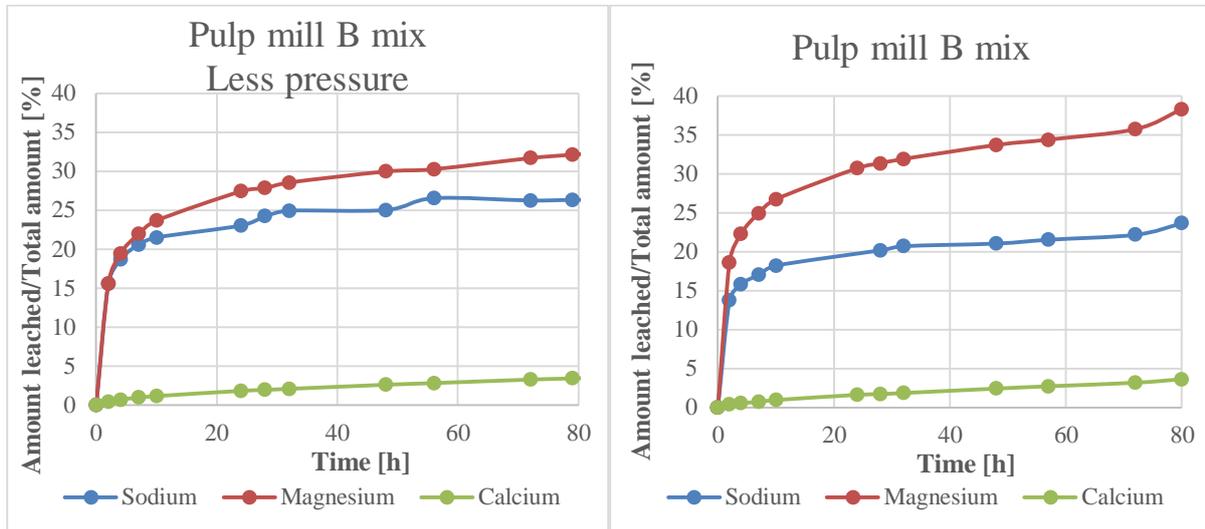


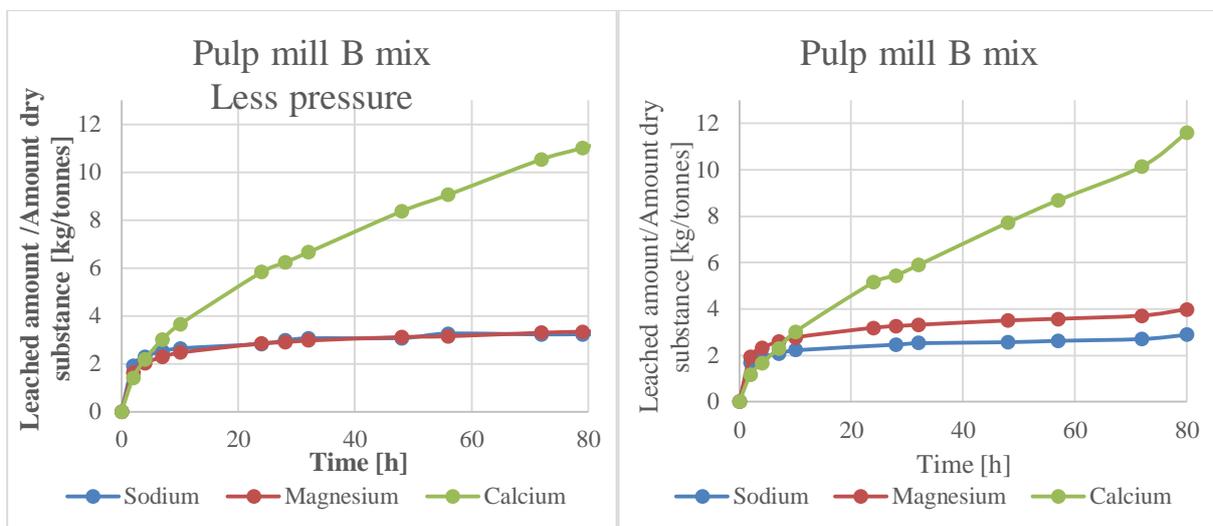
Figure 14 Comparison between fly ash pellets produced with 10 MPa and 30 MPa

As Figure 13 and Figure 14 shows there are no significant differences in leaching rates for the different pressures. The expected results would be that leaching rates increased with lower pressure because of less dense pellets but that result cannot be concluded from this trials. The result shows on the contrary a small increase of leached ions at the higher pressure but the increase is so small it is negligible.

The comparisons between the mixed pellets are shown in Figure 15 and Figure 16. The results for the mixed pellets are, as for the ash pellets, that there is no significant difference between the leaching rates for the different pressures. There is a small increase of sodium ions leached for the lower pressure but at the same time a small decrease of magnesium ions. The leaching of calcium ions are almost identical. The differences in leaching rates for magnesium and sodium is so small that no conclusion can be drawn from it.



**Figure 15** Comparison between mixed pellets produced with 10 MPa and 30 MPa



**Figure 16** Comparison between mixed pellets produced with 10 MPa and 30 MPa

To sum it up the conclusion of the lower pressure trials is that there are no significant differences between the leaching rates for low or high applied pressure. The leaching rates are almost the same for the different pressures in both cases. As it was mentioned above the expected result was an increased leaching rate for the lower pressure but no such conclusion can be drawn since there was both a small increase and decrease in leaching rates for the lower pressure.

### 5.3 Leaching of cadmium

In this section the results of the batch leaching tests for cadmium are presented, the fly ash tests in Table 6 and the green liquor dregs tests in Table 7. Both the measured results from atomic absorption spectroscopy (AAS) and from inductively coupled plasma-optical emission spectroscopy (ICP-OES) are presented in the Tables 5 and 6 but since only four samples were sent for verification to external lab the other tests results for the ICP-OES are presented as not available in the tables (N/A).

The results shows that only a small amount of the cadmium is leached for both residues but with a small increase of leaching for the fly ash. This is an expected result because cadmium can be found as cadmium carbonates in the fly ash which is more soluble than the most common form in green liquor dregs; cadmium sulfide.

Cadmium is more leachable in acid solution which should result in more cadmium leached at pH 5 than in water. This cannot be concluded from the conducted results for the fly ash or green liquor dregs because the leaching increased at pH 5 for two mills but decreased at pH 5 for one mill, see Table 6 and Table 7. This probably depends on the low concentration of acid (0.01 mM HNO<sub>3</sub>) and because the pH was not held constant over time. It would be preferable to perform tests with constant pH of 5 in the batch tests to see how the cadmium behave in acid solutions for a longer time.

The results from the cadmium leaching are highly desirable because they indicates that the cadmium found in the solid residues is stable which means that they will not be available for vegetation uptake if the residues are recycled back to the forest. However more trials with lower pH have to be conducted to investigate if these results also are applicable at lower pH-values.

**Table 6** Leaching of cadmium from fly ash (FA). The tests were performed in batch leaching tests L/S 5 L/kg for 48 hours. ICP-OES was not performed for all leachates, therefore they are presented as not available (N/A)

Sample	Total amount cadmium [µg]	Leached amount cadmium AAS [µg]	Leached amount cadmium ICP-OES [µg]	Leached amount/Total amount [%]
Pulp mill A FA pH 5	192	5.02	<10	2.61
Pulp mill A FA water	192	4.91	<10	2.56
Pulp mill B FA pH 5	96	3.9	N/A	4.06
Pulp mill B FA water	96	3.97	N/A	4.14
Pulp mill C FA pH 5	166	4.93	N/A	2.97
Pulp mill C FA water	166	4.78	N/A	2.88

**Table 7** Leaching of cadmium from green liquor dregs (GLD). The tests were performed in batch leaching tests L/S 5 L/kg for 48 hours. ICP-OES was not performed for all leachates, therefore they are presented as not available (N/A)

Sample	Total amount cadmium [µg]	Leached amount cadmium AAS [µg]	Leached amount cadmium ICP-OES [µg]	Leached amount/Total amount [%]
Pulp mill A GLD pH 5	370	6.72	<10	1.82
Pulp mill A GLD water	370	6.60	<10	1.78
Pulp mill B GLD pH 5	224	6.55	N/A	2.92
Pulp mill B GLD water	224	6.57	N/A	2.93
Pulp mill C GLD pH 5	246	8.86	N/A	3.60
Pulp mill C GLD water	246	8.95	N/A	3.64

## 5.4 Leaching of sulfate

The leaching results for sulfate from the standard batch leaching tests are presented in Table 8. The results shows that none of the fly ashes violates the threshold values for landfill deposits for hazardous waste which was 50 000 leached sulfate per total amount dry ash [mg/kg], see

Table 2. The ash from Pulp mill A however shows higher values than allowed for landfill deposits for non-hazardous waste or hazardous waste which is deposited on non-hazardous deposits which was 20 000 leached sulfate per total amount dry ash [mg/kg], see

Table 2. This confirms Åkerlund, et al. (2006) statement that fly ashes may have problems with the leached sulfate but the result in this study indicates that it is only if they are placed on deposits for non-hazardous waste.

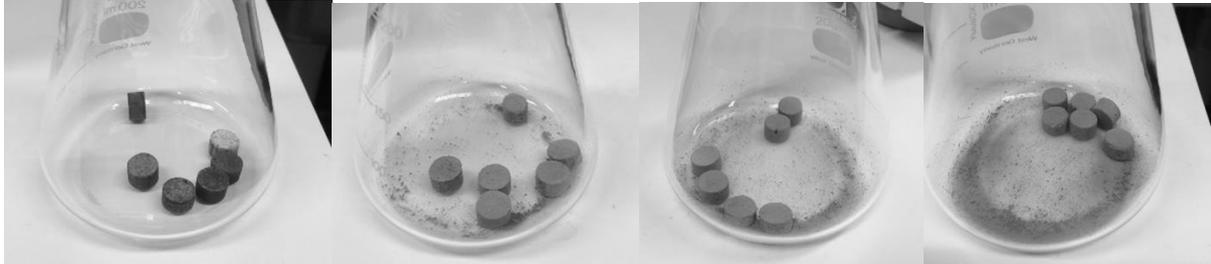
The sulfate concentration varies for the different ashes which is expected due to that they contained different amount of sulfur; Pulp mill A's fly ash contained 26 g sulfur/kg dry material, Pulp mill B's contained 9,3 g sulfur/kg dry material and Pulp mill C's contained 23 g sulfur/kg dry material, see Table 4. However the total amounts of sulfate in the ashes are not known and thereby it is hard to estimate how much of the sulfate that is leached.

**Table 8** Leaching of sulfate from fly ash (FA). The tests were performed in batch leaching tests L/S 10 L/kg for 24 hours.

Sample	Leached sulfate [mg/L]	Leached sulfate [mg]	Leached sulfate/Total amount dry ash [mg/kg]
Pulp mill A	2367	473	23 666
Pulp mill B	1376	275	13 761
Pulp mill C	1834	367	18 337

## 5.5 Transport simulation

The result of the transport simulation is shown in the pictures in Figure 17. The first picture is at the starting point of the test, second picture is after two hours, third picture is after seven hours and the last picture is after twelve hours.



**Figure 17** Pictures of the pellets (30 MPa) and how well they manage a truck transport. First picture is before the test began and thereafter the pictures are after 2, 7 and 12 hours.

As Figure 17 shows, the pellets manage the transportation simulation well. The transportation simulation was very rough to attain an extreme environment for the pellet but still they were almost intact after 12 hours which is a good result. This is an important feature for future transportation to the forest because the wanted product has to be easy to spread and at the same time not dust. This result shows that the pellets fulfill these criteria well.

The pellets tested in the simulation were produced at a pressure of 30 MPa so it would be interesting to see how well the pellets produced at 10 MPa had managed the simulation as well. This has not been investigated in this work but can be recommended for further studies.

## **6. Conclusion**

The conclusions drawn from the obtained results are that some leaching trends for the different substances can be seen for both the fly ash pellets and the mixed pellets, where sodium is leached fast at the beginning and then decreases whereas calcium is leached at a more constant rate. The leaching of magnesium in the mixed pellets showed the same trend as the sodium but for the ash pellet no conclusion for the magnesium can be drawn. The pressure applied when the pellets are produced does not influence the leaching rate to any greater extent.

The leaching of sulfate from the fly ash may be a problem, it depends on where the ash is deposited. The leaching of cadmium on the other hand was almost non-existent for both the green liquor dregs and the fly ash which indicates that the residues may be allowed to be recycled back to the forest.

At last, the pellets durability during the transport simulation was very good which indicates that they could manage a truck transport in the future.

## References

- Åkerlund, E., Wadstein, E., Rosqvist, H., & Kockum, P. F. (2006). *Hälso- och miljörisker vid deponering av avfall som lakar höga halter av klorid och sulfat*. Linköping: STATENS GEOTEKNISKA INSTITUT.
- Berntsson, T., Sanden, B., Olsson, L., & Åsblad, A. (2014). *Vad är ett bioraffinaderi?* Gothenburg: Chalmers University of Technology.
- Camerani, M. C. (2001). *Quantification and Speciation of Cadmium in Fly Ash*. Gothenburg: Chalmers University of Technology.
- CEPI. (2014). *Resource efficiency in the pulp and paper industry - Making more from our natural resources*. Bryssel: Confederation of European Paper Industries.
- European Commission. (2011). *Bio-based economy For Europe: State of play and future potential – Part 2*. Luxembourg: European Union.
- European Commission. (2014). *The circular economy- connecting, creating and conserving value*. ISBN: 978-92-79-37810-2.
- Gierer, J. (1980). Chemical aspects of kraft pulping. *Wood Science and Technology*, 4(241-266).
- Guinee, Haes, & Voet. (2000). General Introduction. In Bergh, Bouman, Kandelaars, Lexmond, Moolenaar, Boelens, . . . Voet, *Heavy Metals: A Problem Solved?* (pp. 3-10). Springer Science+Business Media Dordrecht.
- Haglund, N. (2008). *Guideline for classification of ash from solid biofuels and peat utilised for recycling and fertilizing in forestry and agriculture*. Oslo: Nordic Innovation Centre.
- Hälldal, A. (2004). *Utveckling av metod för att förutsäga "farliga" metallers effekt på peroxidblekning*. Luleå: Luleå University of Technology.
- House of Commons- Environmental Audit Committee. (2014). *Growing a circular economy: Ending the throwaway society*. London: House of Commons.
- Järup, L. (2003). Hazards of heavy metal contamination. *British Medical Bulletin* 68, 167-182.
- KAM report A100. (2003). *Ecocyclic Pulp Mill - "KAM" Final Report 1996-2002*. Stockholm: STFI.
- Kim, A. G. (2005). *LEACHING METHODS APPLIED TO THE CHARACTERIZATION OF COAL UTILIZATION BY-PRODUCTS*. Pittsburgh, Pennsylvania: National Energy Technology Laboratory, US Department of Energy.
- Mahmoudkhani, M. (2005). *Recycling Inorganic Residues fom Wood-based Industries to the Forest*. Gothenburg: Chalmers University of Technology.

- Monte, M. C., Fuente, E., Blanco, A., & Negro, C. (2009). Waste management from pulp and paper production in the European union. *Waste Management* 29, 293-308.
- Nurmesniemi, H., Pöykiö, R., & Keiski, R. L. (2007). A case study of waste management at the Northern Finnish pulp and paper mill complex of Stora Enso Veitsiluoto Mills. *Waste Management* 27, 1939-1948.
- Parthasarathy, G., & Krishnagopalan, G. (1999). Effluent reduction and control of non-process elements towards a cleaner Kraft pulp mill. In *Clean Products and Processes 1* (Vols. 264–277). Springer-Verlag.
- Partners for Innovation. (2015). *Towards a biobased and circular economy*. Hämtat från Partners for Innovations: <http://www.partnersforinnovation.com/en/vision/> den 12 05 2015
- Pöykiö, R., Nurmesniemi, H., & Kuokkanen, T. (2006). Green liquor dregs as an alternative neutralizing agent at a pulp mill. 4(37-40).
- Pöykio, R., Nurmesniemi, H., Kuokkanen, T., & Perämäki, P. (2006). The use of a sequential leaching procedure for assessing heavy metal leachability in lime waste from the lime kiln at a causticizing process of a pulp mill. *Chemosphere* 65, 2122-2129.
- Saltberg, A. (2009). *Inorganic ions in wood chips*. Gothenburg: Chalmers University of Technology.
- Sjöström, E. (1993). *Wood Chemistry*. Elsevier Inc.
- Steenari, B.-M., Karlsson, L., & Lindqvist, O. (1999). Evaluation of the leaching characteristics of wood ash and the influence of ash agglomeration. *Biomass and Bioenergy*(119-136).
- Suess, H. U. (2010). *Pulp Bleaching Today*. Walter de Gruyter.
- TAPIO. (2008). *Göddling med aska*. ISBN 978-952-5694-37-6: Skogsbrukets utvecklingscentral Tapio.
- Taylor, K., & McGuffie, B. (2007). Investigation of non-process element chemistry at Elk Falls mill - green liquor clarifier and lime cycle. *PULP & PAPER CANADA*, 108(2).
- Theiliander, H. (2008). The recovery of cooking chemicals: the white liquor preparation plant. i *Cellulose Technology* (s. Chapter 30). Fibre and Polymer Technology, KTH.
- Tran, H., & Vakkilainen, E. K. (2008). *The Kraft Chemical Recovery Process*. TAPPI.
- United States Environmental Agency. (2001). *Pulping and Bleaching System NESHAP for the Pulp and Paper Industry: A Plain English Description*. United States Environmental Agency.

Ziesig, R. (2014). *Towards a Pure Kraft Lignin*. Gothenburg: Chalmers University of Technology .