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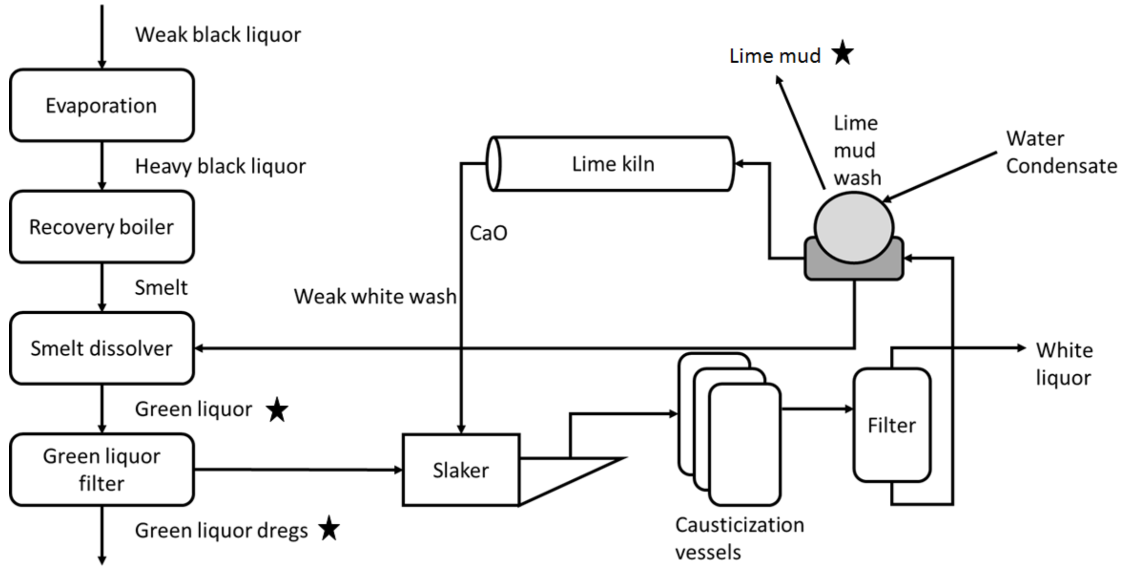

Separation and Utilization of Solid Residue Streams from Kraft Pulp Mills

Master's thesis in Innovative and Sustainable Chemical Engineering

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Department of Chemistry and Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2016

Master's thesis 2016

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Cover: A schematic of the chemical recovery process of a Kraft pulp mill.

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Abstract

Separation of solid residues serve as an important kidney of non-process elements in a kraft pulp mill. The separation and later utilization of these residues as a possible source of nutrients in the forest is of interest in this thesis. One such solid residue is green liquor dregs, which are removed from the green liquor by means of filtration. Green liquor with additions of iron and aluminum were filtered to see the effect of these ions on the average specific filtration resistance. Another residue is fly ash which comes from the bark burner, it contains a lot of nutrients as well as potentially problematic cadmium. Leaching experiments were performed on both fly ash and green liquor dregs in acidic conditions to study the leaching of cadmium.

A model system was set up where industrially produced green liquor was heated to 65 °C and iron ions or aluminum ions were added with constant stirring. The green liquor was then filtered with constant pressure filtration at 1 bar and 44 °C. The leaching experiments were conducted in acidic conditions using pH-stat titration.

The average specific filtration resistance of green liquor without any additional iron or aluminum was found to be $2.3 \cdot 10^{12}$ m/kg. The addition of iron ions to industrially produced green liquor at 65 °C decreased the average particle size. The results of the experiments show that a large addition of iron ions, 1190 mg/liter green liquor, to the green liquor increases the filtration resistance to $3.0 \cdot 10^{13}$ m/kg, which is an order of magnitude compared to native green liquor. An industrially more realistic addition of iron, 96.8 mg/liter green liquor, did not affect the filtration resistance significantly.

The average particle size of green liquor dregs with additional aluminum was increased compared to native green liquor dregs. Adding large amounts of aluminum, 350 mg/liter green liquor, decreased the filtration resistance. A small addition of aluminum, 35 mg/liter green liquor, caused a slight increase in filtration resistance for the green liquor used in this thesis. For this model system there is no indication that these amounts of aluminum would significantly increase the filtration resistance.

The preliminary leaching study indicated that cadmium is leached over time from both fly ash and green liquor dregs at acidic conditions. Which indicates that this could be a potential problem when utilizing the residues and further studies are required.

Keywords: Filtration, leaching, kraft process, solid residue, green liquor dregs.

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Everyone else at SIKT and KMV for being awesome people.

Cecilia Steen, Gothenburg, June 2016

Contents

List of Symbols

Nomenclature

α	specific filtration resistance [m/kg]
α_{av}	average specific filtration resistance [m/kg]
Δz	Thickness of the bed [m]
ϵ	Porosity [-]
μ	Viscosity [Pa s]
ϕ	Solidosity [-]
ρ_s	Solid density [kg/m^3]
A	Area [m^2]
c	mass of solids per unit volume of filtrate [kg/m^3]
P	Pressure [Pa]
R_m	Resistance of the filter media [m^{-1}]
t	Time [s]
u	Superficial flow velocity [m/s]
V	Volume of filtrate [m^3]

Abbreviations

AA	Active alkali (NaOH + Na_2S)
AAS	Atomic absorption spectroscopy
BS	Biosludge
DS	Dry solids
EA	Effective alkali (NaOH + ½Na_2S)
FA	Fly ash
GL	Green liquor
GLD	Green liquor dregs
LM	Lime mud
TTA	Total titratable alkali (NaOH + Na_2S + Na_2CO_3)

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Introduction

1.1 Introduction

The Swedish forest industry produces a range of products such as sawn timber, paper pulp, paper, paperboard and tissue. The value of the export of these goods was in the year 2013 118 billion SEK, and this is equal to 11 % of the total export value for all goods (Skogstyrelsen, 2014). In 2014 the Swedish production of paper pulp was 11.7 million tons and the production of paper and paperboard was 10.8 million tons(Skogstyrelsen, 2014), making this an important industrial sector in Sweden. The most common type of chemical pulp is kraft pulp. Kraft pulp production makes up 7.6 million tons of the yearly pulp production (Skogstyrelsen, 2014), and will be the focus of this thesis. All of these products have their origin in forest and each year 70.7 million m^3 of solid timber is harvested (VMU, 2015).

In today's society there is a move towards being more sustainable and using less fossil raw materials for chemicals, materials and fuels. One way to achieve this is the concept of biorefinery, in which wood and other plant material is used to produce high value chemicals and materials. There is also the possibility to produce fuel or oil from e.g. lignin which is under development or from extractives, such as tall oil, which is already a commercial product. Biomass growth is limited which means that the biomass has to be used effectively. The forest is a key resource in the strive towards becoming a fossil free society.

The forest industry faces two main problems related to the removal of nutrients due to harvest. The soil becomes acidified when important base cations, such as potassium, calcium, magnesium and sodium, are removed due to growth and harvest (Mahmoudkhani, 2005). The second problem is that growth is limited when important nutrients are limited in their availability.

One part of the trees that is currently to a large extent not used is the branches and tops, these are rich in nutrients and are today often left in the forest to decompose. However, research is being done to investigate using these parts as starting material in a biorefinery. When branches and tops are removed from the forest the impact on the acidification is greater (Swedish Environmental Protection Agency, 2007) and important nutrients are removed.

A kraft paper pulp plant generates a significant amount of solid residue, these residues include green liquor dregs, lime mud and fly ash. The metals and other elements that make up these residues occur naturally in the wood and bark. Currently the solid residues from pulp mills are partly deposited on landfills. This is costly and a waste of the nutrients present in the solid material. If the nutrients in the residue streams could be returned to the forest it would be both environmentally and economically beneficial.

However, when adding the green liqour dregs, lime mud and fly ash to the soil the pH may increase quickly which shocks the soil and the ecosystem(Mahmoudkhani, 2005). Another possible issue is high amounts of sulfate and the presence of cadmium in the residue streams. The cadmium comes into the residues from cadmium naturally occurring in the wood. Previous studies have examined how to reduce the pH shock to the soil, while also studying the leaching rate of sodium, calcium and potassium (Mahmoudkhani, 2005). The leaching rate can be controlled by producing e.g. pellets or granules from the solid residue streams. On the other hand little is known about how cadmium in these materials is leached in an acidic environment. Soil is naturally acidic and soil subjected to acid rain and mineral depletion is often more acidic. If the cadmium was to leach from the green liquor dregs and fly ash it would hinder the potential use in forests without actions taken to stabilize or remove cadmium.

Another issue is that at some pulp plant iron and aluminum are added to the waste water treatment to precipitate phosphorous. The resulting biosludge, which is the residue from the waste water treatment, has a high iron or aluminum content. The biosludge has no or little value as its heating value is very low, it may even have a cost as it would need to be landfilled. The biosludge can be incinerated in the recovery boiler as a way to dispose of the residue. It could potentially cause problems with the subsequent separations of green liquor dregs and lime mud. One area of interest is to see if the iron and aluminum changes the filterabilty of the green liquor, affecting the separation and recovery of these residue streams.

1.1.1 Aim

The thesis work aims to investigate filtration of green liquor to separate the dregs and the feasibility of using solid residue streams from a pulp mill as a potential fertilizer in forests, two mills (A and B) have been used as test mills. A residue stream in a kraft pulp mill is biosludge, which is produced in the waste water treatment. The biosludge at plant B contains a high amount of either iron or aluminum, which is added to precipitate phosphorus, the iron and aluminum could eventually effect the down stream separation operations. To model the effect on the green liquor filtration properties of iron and aluminum present in the biosludge, iron and aluminum will be added to the green liquor from plant A. The filtration properties of green liquor with ferrous iron or aluminum added will be investigated. It is also of interest to know if cadmium is leached from the solid residue streams generated at a pulp mill (plant A). The solid residue streams are green liquor dregs, lime mud and fly ash. The following research questions will be investigated in this thesis:

- What effects does iron have on the filtration properties of green liquor?
- What effect does aluminum have on the filtration properties of green liquor?
- At what rate at acidic conditions is cadmium leached from green liquor dregs and fly ash?

2

Background and Theory

2.1 Pulping

The pulp and paper industry is one of Sweden's most important industries. A variety of pulps can be produced, from mechanical to semi-chemical to chemical pulps. In mechanical pulping there is no removal of lignin, and the most common mechanical pulp product is newsprint. For finer paper applications it is important to remove the lignin which causes the paper to become yellow in sunlight, this is done in chemical pulping. There are several chemical methods of pulp production, which use different cooking chemicals, these are the sulfite, soda and kraft processes (Theliander *et al.* , 2002). The main production of chemical pulp is through the Kraft process in which wood is delignified with white liquor. Delignification is done to remove the lignin from the cellulose fibers, lignin is the glue which holds the fibers together(Brännvall, 2004). The active components of white liquor are hydroxide and hydrogen sulfide ions (Theliander *et al.* , 2002). The cooking chemicals are recovered through the chemical recovery process which is a cyclic process. This recovery process generates solid residues which need to be removed from the process as they contain non-process elements, NPEs. Some of the non-process elements are magnesium, manganese, iron, aluminum and silicon (Theliander *et al.* , 2002). Some of the problems associated with non-process elements are deposits, corrosion and an increased dead load. In the bleach plant transition metals also cause the hydrogen peroxide to decompose (Backlund, 2004). A simplified overview of the kraft pulping process is shown in Figure 2.1.

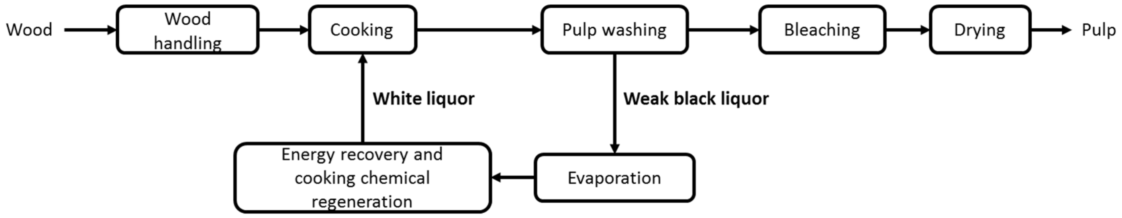


Figure 2.1: A simplified schematic of the kraft process

2.1.1 Chemical recovery cycle

In Figure 2.2 the chemical recovery cycle which is a vital part of the kraft process is represented. Without recovering the cooking chemicals the pulp mill would not be financially viable. The weak black liquor is evaporated to form heavy black liquor which is burned in the recovery boiler. The recovery boiler is both a boiler and a chemical reactor. It is divided into two parts, the upper and the lower. The upper part of the recovery boiler is where the lignin is burned and energy is recovered. The lower part of the recovery boiler is the first step in the chemical recovery cycle. The reducing conditions in the bottom of the boiler produce a smelt consisting of sodium carbonate (Na_2CO_3), sodium sulfide (Na_2S), sodium sulfate (Na_2SO_4) and sodium chloride (NaCl) (Theliander *et al.* , 2002). The sodium hydroxide in the white liquor still needs to be regenerated from sodium carbonate formed in the recovery boiler, which is done in the causticization vessels shown in Figure 2.2.

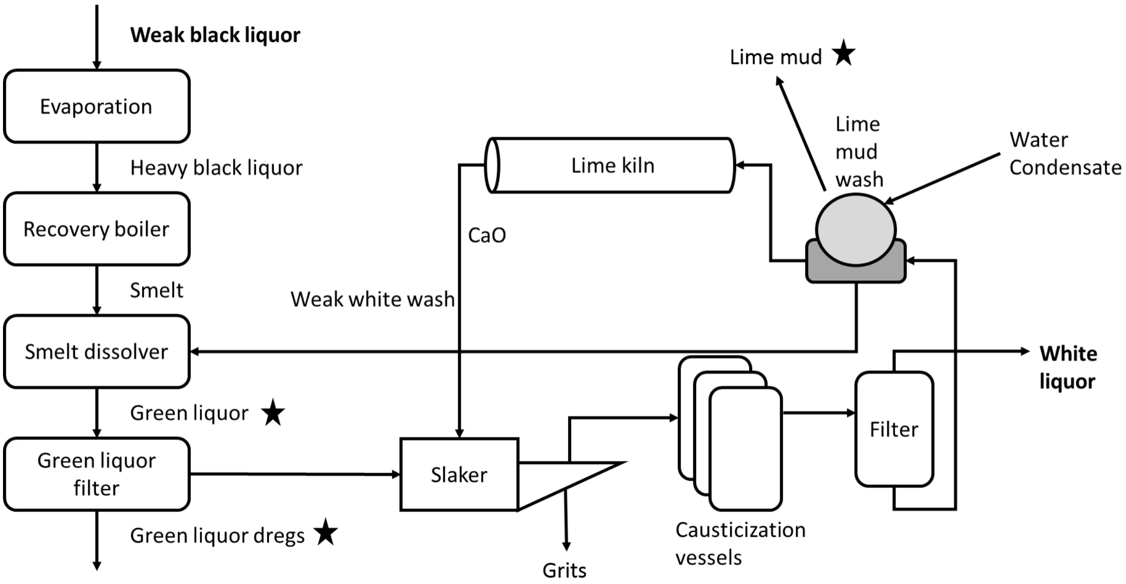


Figure 2.2: The chemical recovery process, sample points marked with a star

Green liquor is formed when the smelt from the recovery boiler is added to weak white wash. The green liquor is made up of mainly sodium, carbonate, hydrogen sulfide and hydroxide ions dissolved in water (Theliander *et al.* , 2002).

The Kraft process generates solid residues in the form of green liquor dregs and lime mud. Many non-process elements precipitate and form the green liquor dregs. The green liquor dregs are removed from the green liquor by means of filtration. The green liquor dregs serve as a kidney to remove the non-process elements from the process. The green liquor dregs consist of mostly Ca, Mg, C, and Mn, as well as some Al, Si, Fe, P and Ti (Theliander *et al.* , 2002).

The filtered green liquor is then transferred to the slaker where reburned lime mud, CaO, is added. The addition of CaO to the green liquor starts the slaking reaction, where CaO is turned into $Ca(OH)_2$ by reacting with water. The $Ca(OH)_2$ reacts with ${CO_3}^{2-}$ present in the green liquor and hydroxide ions, OH^-, and calcium carbonate, $CaCO_3$, are formed, this reaction is known as the causticization reaction. When the slaking is finished the suspension is moved to the causticization vessels, where the causticization reaction continues. The remaining green liquor is turned into white liquor. The Na_2CO_3 from the green liquor is turned into NaOH and the remaining lime mud becomes $CaCO_3$, which needs to be burned in the lime kiln in order to become regenerated. The lime mud and white liquor are separated by filtration and the lime mud is washed before it enters the lime kiln, the wash water becomes weak white wash which is used to dissolve the smelt in the smelt dissolver. The CaO regeneration reaction in the lime kiln is an endothermic reaction, where CO_2 is released and energy needs to be provided.

2.1.1.1 Composition of residual streams

Lidén found that the main components of the dregs are inorganic forms of calcium and magnesium (1995). The minor components of green liquor dregs are Mn, Na and Fe (Lidén, 1995). The total iron content of green liquor dregs varies between 3.1 and 7.7 g kg^{-1} (Pöykiö *et al.* , 2014) The precipitated iron in the dregs were found to be in the form of Fe_2O_3, where iron has an oxidation state of +3 (Lidén, 1995) Iron in green liquor dregs also occurs in the form of iron sulfide, FeS, with oxidation state +2 (Lidén, 1995). Lane and Empie studied green liquor dregs as a potential odor controlling agent and determined that the iron in the dregs is present in the forms FeS, Fe_2O_3 and Fe_2O_4 (2005).

The lime mud consists of almost exclusively calcium carbonate ($CaCO_3$), and is purged from the system to avoid the accumulation of phosporous (Mahmoudkhani, 2005). Another solid residue that is generated at a pulp mill is biosludge as a biproduct from the waste water treatment. Fly ash is generated in the bark burner, which burns the bark that is removed in the debarking of incoming wood. The bark contains high amounts of non-process elements, which do not enter the process as the bark is incinerated separately and the ash landfilled.

2.2 Filtration

To remove a solid phase from a suspension filtration can be used, filtration is often an energy effectient method for solid-liquid separation. Particles above the pore size of the filter will be retained on the filter media. As the filtration progresses smaller particles will also be trapped in the filter cake which is built up on top of the filter media. One possible driving force is a pressure gradient, either a higher pressure above the filter cake or a sub-atmospheric pressure below the filter cake. Other driving forces for filtration can be gravitational and centrifugal forces (Svarovsky, 2000).

Darcy (1856) formulated an equation for flow through a porous bed relating the flow rate to the pressure drop, this equation was later expanded by including the viscosity:

$$u = \frac{K}{\mu} \cdot \frac{\Delta P}{\Delta z} \tag{2.1}$$

where u is the superficial flow velocity through the bed, ΔP the pressure drop over the bed and Δz the thickness of the bed, μ the viscosity of the fluid. Where K, the permeability, is given by

$$K = \frac{1}{\alpha \rho_s \phi} \tag{2.2}$$

where α is the specific filtration resistance, ρ_s is the solid density, ϕ is the volume fraction of solids in the bed.

$$\phi = 1 - \epsilon \tag{2.3}$$

where ϵ is the porosity of the bed.

The classical filtration equation was derived from Darcy's work (1856) and is valid for a case where the filter cake is being formed and continues to grow during filtration. The classical filtration equation is shown below as equation 2.4 :

$$\frac{dV}{dt} = \frac{A^2 \Delta P}{\mu(\alpha_{av} c V + R_m A)} \tag{2.4}$$

where V is the filtrate volume, t the time, A the filtration area, α_{av} the average specific filtration resistance, c the mass of solids per unit volume of filtrate and R_m the resistance of the filter media. The equation 2.4 is valid for incompressible filter cakes, that is a filter cake which does not change its volume under pressure.

The equation can also be written in the form of equation 2.5.

$$\frac{dt}{dV} = \frac{\mu \alpha_{av} c}{A^2 \Delta P} \cdot V + \frac{\mu R_m}{A \Delta P} \tag{2.5}$$

where the slope of the line of V vs $\frac{dt}{dV}$ gives $\frac{\mu \alpha_{av} c}{A^2 \Delta P}$ and the intersect gives values for $\frac{\mu R_m}{A \Delta P}$. When written in this from equation 2.5 is useful in finding the average specific filtration resistance α_{av} and the filtermedia resistance R_m. α_{av} is a measure of the ease of filtration, a value of 10^9 indicates that the filtration is very easy and a filtration resistance of 10^{13} corresponds to a difficult filtration (Leu, 1986).

The integrated form of equation 2.5 is presented as equation 2.6

$$\frac{t_2 - t_1}{V_2 - V_1} = \frac{\mu}{A^2 \Delta P} \left[\frac{\alpha_{av} c}{2} (V_2 - V_1) + c \alpha_{av} V_1 + R_m A \right] \tag{2.6}$$

where the index 1 is the lower integration limit and 2 the higher integration limit. As the integrated form only takes an average of the changes in the filtration flow some important changes might be missed, therefore it is better to use equation 2.5.

Another way to separate solids from liquids is sedimentation, in which the particles are allowed to settle and the clarified liquid is removed from the surface. Some advantages with filtration is that it is faster than sedimentation, and it is cost efficient.

2.2.1 Filtration of Green Liquor

The separation of green liquor dregs from green liquor is difficult, the green liquor dregs form a filter cake which is relatively compressible (Sedin & Theliander, 2004). Both Sedin and Theliander as well as Mattsson and Richards (2010) have studied the average specific filtration resistance, α_{av}, of green liquor filtration and found that the results vary from 10^{12} and 10^{13} m/kg. The value of α_{av} depends on the chemical composition of the green liquor and varies from mill to mill.

Sedin and Theliander set up experiments with low pressure filtration, between 0.5 and 3 bars, of green liquor to study the effects of aluminum. They found that the more alumium that was added to the green liquor the lower the filtration resistance became (Sedin & Theliander, 2004). The average specific filtration resistance went from $\approx 8.5{\cdot}10^{12}$ with no aluminum added to $\approx 3.5{\cdot}10^{12}$ when 360 mg Al/ l was added (Sedin & Theliander, 2004).

Historically green liquor was settled instead of filtered, which means that the dregs were allowed to sediment and the clarified green liquor was removed. Advances in filtration has made it more economical to use filtration instead of sedimentation to separate green liquor dregs from the green liquor.

Experiments where Fe_2O_3 was added to synthetic smelt chemicals were conducted by Ellis and Empie (2003). The synthetic smelt chemicals had the same composition as smelts from four kraft pulp plants, the components were Na_2CO_3, Na_2S, Na_2SO_4, NaCl, $CaCO_3$, Fe_2O_3, $Mg(OH)_2$, MnO_2, SiO_2, Al_2O_3 and C (Ellis & Empie, 2003). They investigated the effect of non-process elements such as iron on green liquor dregs settling and filterability (Ellis & Empie, 2003). In experiments with 10 times the level of iron compared to a regular smelt the results showed that the settling and filterability of the dregs was markedly affected. The settling rate was found to be only 60% of the base case, and the relative permeability was only $\approx$ 15% compared to the base case (Ellis & Empie, 2003).

In the industrial filtration of green liquor a tube, casette or disc filter is commonly used. The difference between a tube filter and a casette filter is that the casette filter is pressurized (Wimby *et al.* , 1995). The filter is usually combined with a precoat of lime mud to help minimize the filtration resistance (Theliander, 2004).

2.3 Leaching

The removal of a soluble part of a solid with a liquid solvent is called leaching. The insoluble parts remain in the solid material. The leaching rate is affected by among other things the particle size and porosity of the solid material, but also the composition and pH of leachate and the temperature.

pH-stat leaching is a method in which the pH is kept constant by means of automatic titration and simultaneous pH measurements. It is often used to analyze soil samples, but can be used to assess the leachablity of metals from any solid sample.

Leaching experiments conducted by Pökiö et al. (2005) on fly ash from a pulp and paper mill found that in a five stage leaching test 84 % of the total cadmium was leached. The five stage sequential leaching procedure was also used to leach metals from green liquor dregs (Nurmesniemi *et al.* , 2005). The five sequential stages of the leaching test are: the water soluble fraction, exchangeable fraction, easily reduced fraction, oxidizable fraction and residual fraction (Nurmesniemi *et al.* , 2005)(Pöykiö *et al.* , 2005).

2.4 Non-Process Elements in solid residues

There are many non-process elements present in the solid residues, the three that will be discussed in this thesis are iron, aluminum and cadmium. These three elements, their origin and problems associated with them are described further in this section.

2.4.1 Iron

The iron present in the pulp process comes mainly from the stem wood, the levels depending on the type of wood and its origin (Saltberg, 2009). This iron is removed with the green liquor dregs which serves as a kidney for removing non-process elements, otherwise the iron would accumulate in the process. If the iron, is not removed from the process it causes problems in the hydrogen peroxide bleaching, as iron can be easily oxidized and the hydrogen peroxide forms radicals (Backlund, 2004). The hydrogen peroxide, which is the active bleaching chemical, catalytically decomposes when these peroxide radicals reduce the iron again (Backlund, 2004).

Iron which is soluble in water can be either in the form of ferrous hydroxide, ($Fe(OH)_2$, ferrous carbonate, $FeCO_3$, or ferrous sulfide, FeS (Stumm & Lee, 1960). In the presence of carbonates and sulfides the solubility of iron varies depending on the pH (Stumm & Lee, 1960).

In the 1950's the solubility of ferrous iron in a saturated sodium hydroxide solution was studied (Gayer & Woontner, 1956). Gayer and Wootner found that iron(II) precipitates as ferrous hydroxide ($Fe(OH)_2$) in basic solutions (1956). The solubility of $Fe(OH)_2$ was in pH 14 found to be about 0,4 mg/l (Gayer & Woontner, 1956)

Stumm and Lee determined the solubility of ferrous hydroxide in a solution with pH 9 to be approximately 2,6 mg/l (1960). While the two values differ the conclusion can be drawn that the theoretical maximum solubility of FeOH in a solution with pH between 9 and 14 should be at most 3 mg/l.

The solubility of iron in green liquor has not been previously studied. Green liquor which has a pH of about 14, should have a low concentration of soluble iron, according to the results of Stumm and Lee (1960), and Gayer and Wootner (1956). However, the effect of carbonate, sulfide and hydroxide ions on the solubility of iron has not been further studied.

2.4.2 Aluminum

Aluminum is a non-process element which occurs naturally in wood. High levels of aluminum can cause scaling and deposits on for example heat exchangers (Backlund, 2004). Aluminum can be used to precipitate phosphorous in the waste waster treatment. It enters the pulp process with the wood as well as in the recovery boiler when the biosludge is burned. Ulmgren (1987) studied adding magnesium to the process in order to remove aluminum. Magnesium and aluminum form hydrotalcite, which is a salt which in alkaline systems is only slightly soluble (Ulmgren, 1987). Correspondingly aluminum can be added in order to remove excess magnesium from the process.

2.4.3 Cadmium

The main source of cadmium found in soils is anthropogenic from phosphate fertilizers, atmospheric deposition from burning of fossil fuel and feed additives (Berndes *et al.* , 2004).

Cadmium is found in the soil and trees in Sweden (Berndes *et al.* , 2004). About 75 percent of the area of agricultural soils in Sweden has a cadmium content between 0.1 and 0.3 mg Cd kg^{-1} (Berndes *et al.* , 2004). Berndes et al. (2004) speculated that the net cadmium inflow would remain constant the coming decades, which would lead to an increase in cadmium levels.

Cadmium is present in fly ash and green liquor dregs from pulp mills (Pöykiö *et al.* , 2005; Manskinen *et al.* , 2011a). Manskinen et al (2011b) list the literature values of the cadmium concentration in green liquor dregs as being between 4.0 and 24 mg per kg dry solids.

3

Method

In this chapter the methods used for the investigation of filtration and leaching behavior will be presented and described.

3.1 Filtration

Green liquor will be filtered to determine the average specific filtration resistance. Either iron or aluminum will be added to the green liquor to assess whether there is a difference in filtration resistance between these additions and unaltered green liquor.

3.1.1 Starting material

The green liquor used in all of the experiments comes from the same pulp mill. The samples were collected by operators at the mill. After receiving the samples they were stored in a refrigerator (4 °C) until it was divided into smaller homogeneous samples. The green liquor needed to be heated in order to dissolve the precipitated salts which formed during storage in the refrigerator. Once the salts had dissolved the green liquor was transferred from the buckets into polypropylene-bottles (1000 ml).

The chemicals used are iron (II) sulfate heptahydrate ACS reagent $\geq$ 99 % and aluminum chloride hexahydrate ReagentPlus® 99 % both from Sigma Aldrich.

The filters used for most experiments were Sartorius regenerated cellulose membrane 0,45 μm filters. Other filters which were used were Whatman® glass microfibre filters grade: GF/A (pore size 1,6 μm). In both cases the filters rested on Munktell filter paper grade: 5 for support.

3.1.2 Experimental Equipment

In Figure 3.1 the experimental setup with the filtration apparatus is shown. The filtration apparatus is made of a insulated, baffled and well stirred tank which is connected to the filtration cell by a valve located close to the bottom of the tank. The tank is pressurized by connecting it to the high pressure air system. The pressure is regulated with a precision pressure regulator (IMI Norgren 11-818-100) and it is measured with a pressure transducer (Comark Type 3392 PG 10) with corresponding pressure meter (Comark C9550). The filtration cell has circular disk for mounting the filter paper, and gaskets to keep the liquid contained. The filtration cell is small to avoid settling effects. When the valve is opened the filtration starts and the amount of filtrate is logged using a digital scale (Mettler, Toledo PB5001-S) connected to a computer running LabVIEW. The temperature was also measured with a liquid-in-glass thermometer.

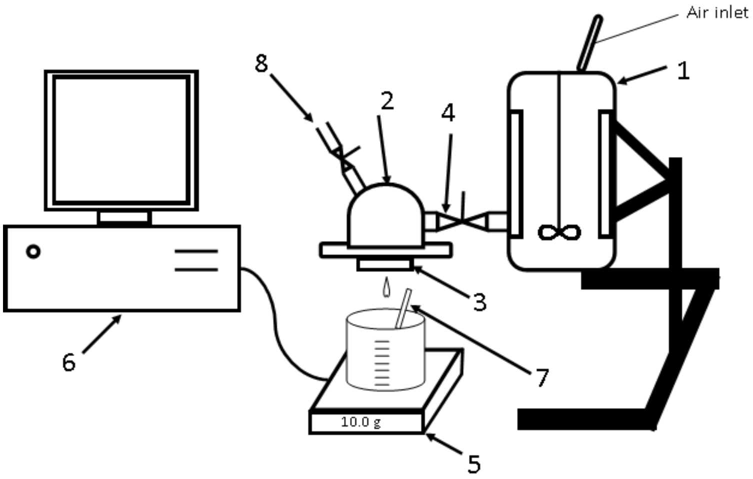


Figure 3.1: A schematic representation of the filtration equipment. 1: The stirred, baffled tank. 2: filtration vessel. 3: Filter paper holder. 4: Valve. 5: Digital scale. 6: Computer. 7: liquid-in-glass thermometer. 8: airing valve.

3.1.3 Experimental conditions

First green liquor without any additional iron or aluminum was filtered. The pressure was kept constant at 1 bar. For the experiments with additions of iron two different filters were used as iron particles passed through the 1,6 μm filters and the change to 0,45 μm filters was made. At this point another filtration of green liquor without iron was performed to find the α_{av} value of green liquor for the filters with smaller pore size.

The green liquor was heated for all experiments in an attempt to make the conditions more similar to those in a pulp mill. However, for safety reasons the temperature was not raised to 90 °C as in the mill, but instead the green liquor was heated to 65 °C.

In order to keep the temperature constant during the filtration the stirred tank and filter chamber were pre-heated by running boiler water through the system before the warm green liquor is poured into the stirred tank. This method helped to keep the temperature of the filtrate between 45 °C at the beginning of the filtration and 40 °C at the end. The filtrations lasted between 10 and 20 minutes. The filtration of green liquor with 1190 mg iron per liter green liquor took much longer, over 90 minutes and the filtrate cooled to room temperature quickly.

This is a model system, where the metal ions are added to existing industrial green liquor instead of being burned in the recovery boiler and therefore included in the smelt and green liquor. The green liquor has also been allowed to cool down and was transported from the mill, which might effect the properties. The temperature at which the iron is added and the green liquor is filtered is also much lower than industrially, which may be a potential source of errors.

Iron sulfate heptahydrate ($FeSO_4 \cdot 7\,H_2O$) (20 g) was dissolved in water (100 ml) to form an iron sulfate solution (0.719 M). In each experiment a different amount of the iron sulfate solution was added to heated green liquor (700 ml, 65 °C) while stirring. Table 3.1 lists the different concentrations and additions made to the green liquor in the different experiments and the corresponding iron levels in the biosludge.

During the filtration trials the weight of the filtrate was continuously logged using a computer, which took measurements every second. The pressure was kept constant, 1 bar, using pressurized air. Once the filtration was completed the filter cake was weighed, dried and weighed again, the total salt content in the liquid was taken into consideration before c was calculated and the average specific filtration resistance was determined using equation 2.5. The filtration resistances for each concentration of iron or aluminum was compared and the effect of iron and aluminum on the filterability was assessed.

Table 3.1: Iron concentration, the amount of added iron sulfate, the corresponding iron level in the biosludge as well as the average filtration temperature.

Iron Concentration [mg/l]	96.8	119	167	1190
Iron Sulfate 0.72M added [ml]	1.69	2.07	3	20.7
Corresponding iron level in biosludge [w-% of dry solids]	7.5 %	9 %	13 %	88 %
Average filtration Temperature [°C]	48	42	42	25

In Appendix B the calculations of the different additions of iron and aluminum are presented. The assumption was made that 5 kg biosludge per ton pulp is burned in the recovery boiler. The total amount of moles of iron for the level of 7.5 w-% is the same as the amount of moles of aluminum at 3.6 w-% Al in the dry solids of the biosludge. The iron and aluminum which is used to precipitate phosphorus in the waste water treatment is added on a mole basis, where one mole of iron precipitates as much phosphorus as one mole of aluminum. Due to the large difference in molecular weight between iron and aluminum the same amount of moles will result in a much larger mass of iron than aluminum.

The corresponding experiments with aluminum were performed using aluminum chloride hexahydrate ($AlCl_3 \cdot 6\,H_2O$ (5 g) was dissolved in water (25 ml) to form an aluminum chloride solution (0.828 M). In each experiment a different amount of the aluminum chloride solution, shown in Table 3.2, was added to heated (65 °C) green liquor (700 ml) while stirring.

Table 3.2: Aluminum concentration, the amount of added aluminum chloride, the corresponding aluminum level in the biosludge as well as the average filtration temperature.

Aluminum Concentration [mg/l]	35.06	350.6
Aluminum Chloride 0.83 M added [ml]	1.1	11
Corresponding aluminum level in biosludge [w-% of dry solids]	3.6%	36 %
Average filtration Temperature [°C]	42	40

3.1.4 Analysis

The green liquor dregs which were retained on the filter paper were characterized using specific surface area. Specific surface area is measured with the BET method that uses the adsorption of nitrogen gas to measure the specific surface area of a particle. The instrument used is a Micromeritics Tristar 3000.

The iron and aluminum particle size distributions were analyzed using laser diffraction. The laser diffraction analyzer measures how the particles in the sample defract the light from the laser beam. If the particles are smaller than 20 μm the optical properties of the particles need to be known. It is therefore important to know the composition of the samples beforehand. The green liquor dregs were assumed to consist of mostly calcium oxide which is the component of highest concentration in the dregs. The samples were collected from the bottom of the bottles in which the unfiltered green liquor was stored, the green liquor dregs had sedimented on the bottom. The laser diffraction was measured using a Malvern Mastersizer 2000.

3.2 Leaching

Experiments were conducted in order to examine the leaching of cadmium from green liquor dregs and fly ash during acidic conditions.

3.2.1 Starting material

Leaching tests at constant pH were performed in order to study the leaching rate of cadmium from green liquor dregs and fly ash. The pH was kept constant at 4.0, which is a reasonable pH level of acidified soil (Swedish Environmental Protection Agency, 2007).

The fly ash and green liquor dregs came from the same pulp mill. The green liquor dregs consist of both green liquor dregs as well as the lime mud precoat which is used to aid in the separation of green liquor dregs from green liquor by means of filtration. The ashes and dregs were dried in an oven for at least 24 hours at 105°C and then weighed. The ashes and dregs were dried in order to make sure that there was no moisture in the samples. Four different concentrations of nitric acid (0.1 M, 0.5 M, 1 M and 3 M) were prepared and used in varying amounts to achieve the correct starting pH. HNO_3 was used as it simulates acid rain.

3.2.2 Equipment

The leaching tests are pH-stat tests, where the pH is kept constant by continuous automatic monitoring by a TitroLine Alpha titrator (Schott Instruments) HNO_3 (0.5 M) is used in the burette.

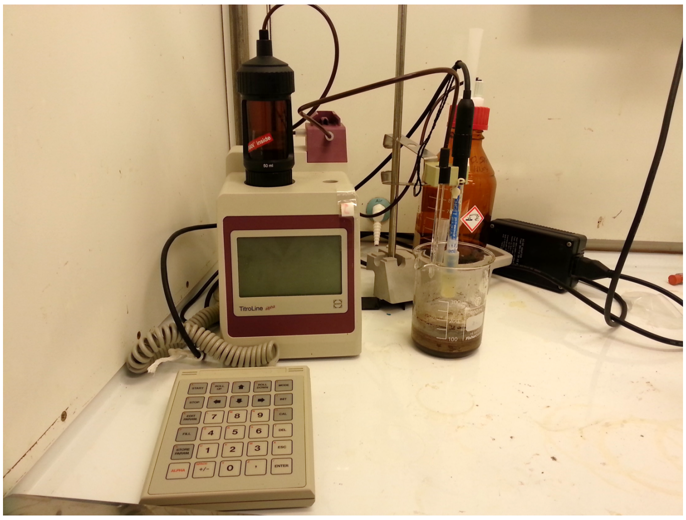


Figure 3.2: The TitroLine alpha titration equipment

3.2.3 Experimental conditions

The L/S ratio was not kept constant during the leaching experiments as acid was added as needed during the entire 80 hours of leaching. The L/S ratio is a measure of the volume of leachate over to solids and is given in l/kg. However, when each sample was taken the titrated amount of acid was noted in order to be able to find the maximum theoretical amount which can be leached. Since the suspension was well mixed and under constant stirring it can be assumed that the samples taken removed a constant amount of both solids and leachate and therefore the composition of the suspension would not change.

First fly ash was dried at 105°C and then the dried ash (10 g) was added to a covered beaker, with magnetic stirring, and nitric acid (100 ml) of different concentrations was added to achieve a starting pH of 4. The leaching experiment started with the

TitroLine Alpha set to pH-stat(pH 4), and the time was set to 90 hours. Samples (3 ml) were taken a few times daily to track the leaching rate. The well mixed samples were immediately filtered using syringe filters (Pall Acrodisc ® 0,45 μm PVDF membrane).

3.2.4 Analysis

The samples were analyzed using atomic absorption spectroscopy, (AAS), with flame and hollow cathode cadmium lamp operating at 228.8 nm. The instrument used was a Thermo Scientific iCE 3000 series AA Spectrometer. A stock solution of 1000 ppm cadmium was diluted in HNO_3 (0.1 M) in order to prepare the following standards:0.1 ppm, 0.5 ppm, 1 ppm and 2 ppm . The standards were then used to obtain a calibration curve. After the instrument had been calibrated the samples were analyzed, the standards were run again to check that the measurements did not deviate during the analysis.

4

Results and Discussion

In the following chapter the results of the filtration and leaching experiments will be presented and discussed. First the results from the characterization of the starting materials will be presented. Then the results from the filtration of green liquor with no addition and with additional iron and aluminum will be displayed. Thereafter, the results from the acidic leaching of green liquor dregs and fly ash will be introduced.

4.1 Characterization of green liquor and residue streams

In Table 4.1 the elemental composition of the solid residues and the green liquor(unfiltered) is presented. The metal contents were quantified by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) at Innventia AB.

Table 4.1: Concentration of elements in residue samples [g/kg dry solids] except those marked with * which are in [mg/kg DS]. Green liquor (GL), Green liquor dregs (GLD), Fly ash (FA), Biosludge (BS), Lime mud (LM) and Bottom ash (BA).

Sample	BS	GL	GLD	LM	BA	FA
Al	8,6	0,0	2,7	0,2	24	17
Ba	0,3	0,0	0,2	0,1	1,3	1,6
Ca	12	1,0	388	445	216	305
Cd *	15	N/A	6,3	<0,6	<0,6	12
Cu	0,1	0,0	0,1	0,0	0,0	0,1
Fe *	2,8	12,0	1,1	0,1	20	14
K	3,0	6,7	0,9	0,3	31	66
Mg	2,2	0,1	18	3,1	18	22
Mn	3,1	0,0	4,4	0,1	6,2	8,8
Na	13	69,7	19	8,9	11	18
P	9,0	0,0	4,9	6,8	9,4	14
S	19	22,0	4,9	0,1	1,0	31
Si	11	0,1	1,9	0,5	25	32
Zn	0,7	0,0	0,4	0,0	0,2	4,3

As can be seen in Table 4.1 the cadmium level in the fly ash and green liquor dregs is much higher than in lime mud and bottom ash, where the levels were not detectable in ICP-AES. The fly ash and green liquor dregs are therefore the only residues of interest for leaching experiments.

The green liquor composition is presented in Table 4.2 as concentration of NaOH, Na_2CO_3 and sulfidity as well as active alkali, total titratable alkali and effective alkali. This data comes from the online measurements at the pulp mill, where the samples were collected, using a Kaajani equipment and analyzed according to the SCAN-N standard 30:85.

Table 4.2: Green liquor sample composition data from Stora Enso measured using standard SCAN-N 30:85, Active alkali (AA), Total titratable alkali (TTA), Effective alkali (EA), Dry content of green liquor (not measured at Stora Enso)

NaOH [g/l]	Sulfidity %	Na2CO3 [g/l]	AA [g/l]	TTA [g/l]	EA [g/l]	Dry content [g DS/100 g GL]
5.2	29.6	108.5	53.1	161.5	29.1	23.5

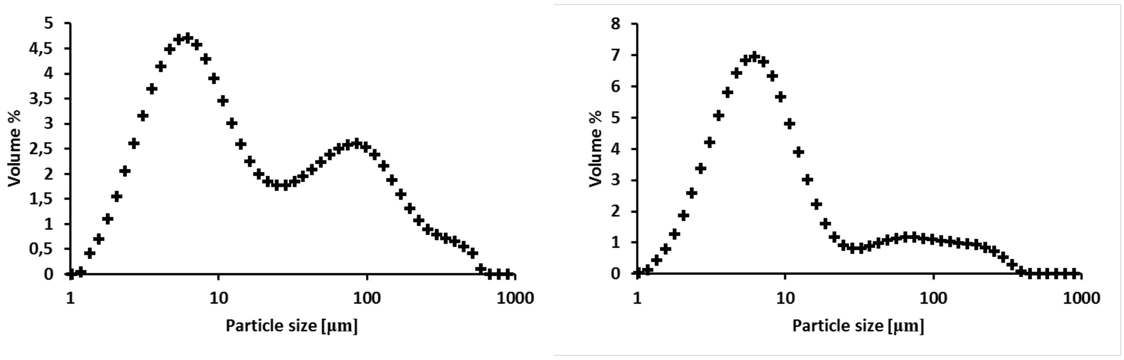
The data from Table 4.2 was used to calculate the concentration of Na_2S, which together with the concentration of NaOH and Na_2CO_3 was entered into a program developed by Theliander(1987) to calculate the viscosity and density of the green liquor at different temperatures, these are shown in Table 4.3.

Table 4.3: Density and viscosity of green liquor at 25°C, 40°C, 50°C and 70°C as calculated using data from Table 4.2

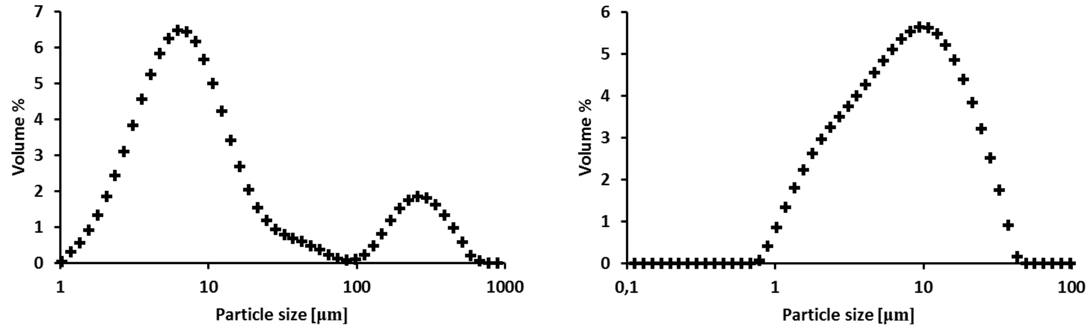
Temperature [°C]	25	40	50	70
Density [kg/m^3]	1154	1147	1142	1130
Viscosity [Pa s]	$1.88 \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$	$9.76 \cdot 10^{-4}$	$6.59 \cdot 10^{-4}$

The data in Table 4.3 was used to find the viscosity at the actual temperatures measured during the filtration experiments by interpolating between the different temperature intervals.

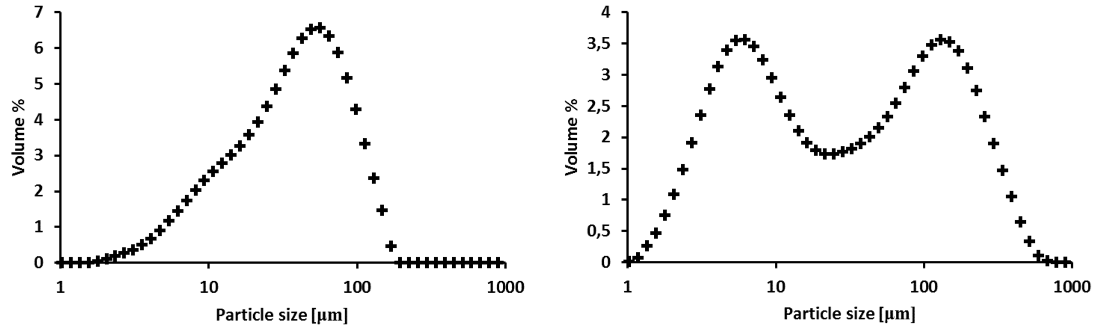
Figure 4.1 shows the result of the particle size characterization determined using laser diffraction of green liquor dregs from the unfiltered green liquor used in the experimental trials, and these are summarized in Table 4.4 . Figure 4.1e shows the particle size distribution of filtered green liquor to which a large quantity of iron sulfate solution was added at 65 °C. Figures 4.1a, 4.1f, 4.1c and 4.1b all have a bi-modal shape. The native green liquor, shown in Figure 4.1a, and green liquor with added aluminum, shown in Figure 4.1f, have the most similar shape however there are more particles having a large size in the green liquor with aluminum.



(a) Native green liquor **(b)** 96.8 mg Fe/l GL



(c) 167 mg Fe/l GL **(d)** 1190 mg Fe/l GL



(e) Iron particles in filtered GL **(f)** 350 mg Aluminium/l GL

Figure 4.1: Particle size distribution from laser diffraction measurements of green liquor dregs (a) with no addition of iron or aluminum. (b) with 350 mg Al/l (36 w-% Al in biosludge dry solids). (c) with 1190 mg Fe/l addition of iron (88 w-% Fe in biosludge dry solids). (d) Iron particles in filtered green liquor. (e) with 167 mg Fe/l addition of iron (13 w-% Fe in biosludge dry solids). (f) with 96.8 mg Fe/l addition of iron (7.5 w-% Fe in bioslugde dry solids).

Comparing Figure 4.1d with Figure 4.1a it can be seen that the particle size distribution has moved towards much smaller particles in the case of added iron. This can be seen even more clearly when looking at Table 4.4, the D_{50} value is lower for all three additions of iron compared to that of native green liquor. For the addition of 1190 mg Fe/l green liquor the trend of smaller particles is most evident, with a D_{50} value of only 7.4 μm compared 11.7 μm for native green liquor. The

D_{50} value indicates that 50% in volume of the particles are smaller than the value stated. When comparing the size distribution in Figure 4.1f, which is green liquor dregs with aluminum, to Figure 4.1d, liquor dregs with 1190 mg iron, it can be seen that there are more larger particles in the case of more aluminum. The trend shown in the figures is even more evident when comparing the D_{50} value of the aluminum particles which is much larger than the D_{50} of the 1190 mg iron value. The general shape of the particle size distribution for the smaller additions of iron, 4.1c and 4.1b, is quite similar to the native green liquor, 4.1a, for the first peak of the bimodal shape. However, the second peak is very small in Figure 4.1b which indicates that there are fewer large particles. The smaller peak at over 100 μm in Figure 4.1c is possibly due to the presence of an air bubble in the laser diffraction measurement as that peak is absent in the other additions of iron.

Table 4.4: The D_x values for the laser diffraction measurements shown as particle size distributions in Figure 4.1, where D_x indicates that x % in volume of the particles are smaller than the value stated. BET area is also shown for three of the green liquor dregs: the native dregs, 350 mg Al and 1190 mg Fe.

	D_{10} [μm]	D_{50} [μm]	D_{90}[μm]	BET Area [m^2/g]
Native green liquor	3.1	11.7	137.8	4.64
350 mg Al/l GL	3.6	29.2	215.2	4.63
1190 mg Fe/l GL	2.0	7.4	21.7	4.46
167 mg Fe/l GL	2.8	7.7	211.9	N/A
96.8 mg Fe/l GL	2.8	7.2	76.9	N/A
Iron particles in filtered GL	9.0	38.6	96.7	N/A

The BET results are quite similar for all three samples, this similarity may be due to the fact that the filter cakes were dried for an extended period of time, and then carefully ground with a pestel and mortar to break up the filter cake. The filter cake of green liquor dregs with additional iron had oxidized and become rust colored which may have an impact on the surface area.

4.2 Filtration of green liquor

In the following sections the results of filtrations of green liquor with no additions, addition of iron and addition of aluminum are presented and discussed. The data is presented in both figures and tables.

4.2.1 Filtration of green liquor without additions

Green liquor without addition of iron or aluminum was filtered in order to determine a baseline of the average specific filtration resistance. The average specific filtration resistance, α_{av} was found from the slope of the linear regressions in Figure 4.2.

The R^2 values of 0.97 and 0.98 indication that the linear regressions are a good approximation of the data.

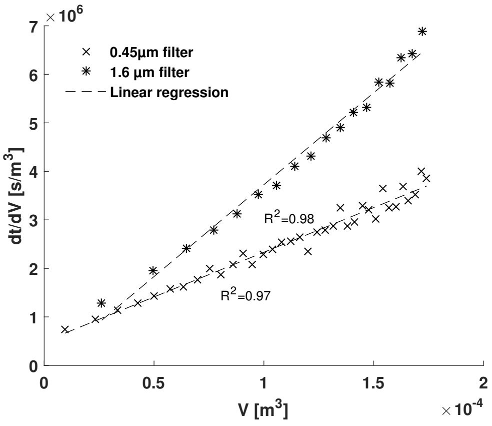


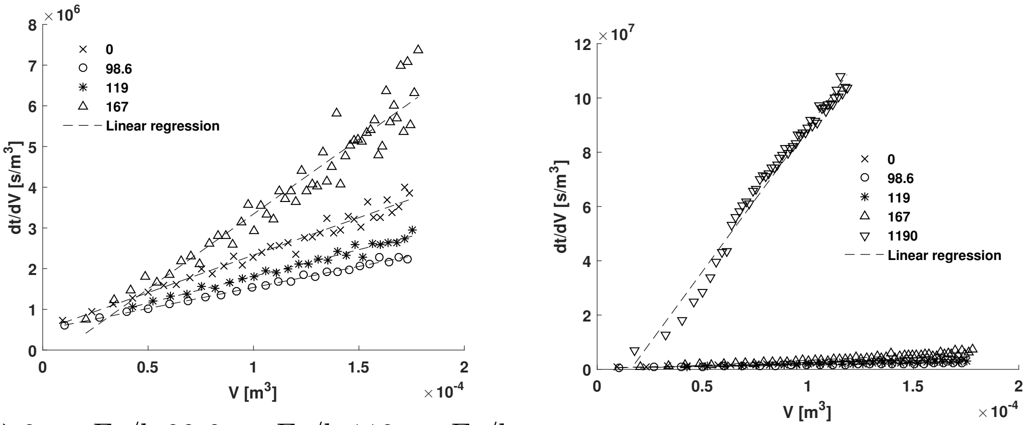
Figure 4.2: Filtration of green liquor without additional iron, with two different filter papers, 1.6 μm and 0.45 μm. For a case with the same value of c, a higher slope indicates a higher filtration resistance.

The value of c for the two different baseline filtrations with 0.45 μm filter and 1.6 μm filter was 3.4 and 3.1 respectively. The filtrate was clear and contained no visible particles for both of the filters used. The two values of α_{av} were determined to be $2.3 \cdot 10^{12}$ m/kg and $2.2 \cdot 10^{12}$ m/kg. The difference between the two α_{av} values is very small which indicates that the experimental trials were reproducable. These values are also within the interval that has been previously determined experimentally (Sedin & Theliander, 2004) (Mattsson & Richards, 2010).

4.2.2 Effect of iron addition

In the following section the results of the filtrations with additional iron will be presented. The data will be shown in both figures and tables. The results of the average specific filtration resistance, α_{av}, for the different additions of iron are shown in Table 4.5.

In Figure 4.3 the inverse volumetric flow rate, $\frac{dt}{dV}$, is plotted against filtrate volume, V, the slope of the linear regression gives $\frac{\mu \alpha_{av} c}{A^2 \Delta P}$ from equation 2.5. In order to show the similarities within the data two different plots of $\frac{dt}{dV}$ versus V are presented. Figure 4.3a shows the results of filtrations with no additional iron, 98.6 mg, 119 mg and 167 mg iron per liter of green liquor. Figure 4.3b also includes the results from the filtration experiments where 1190 mg iron per liter of green liquor was added. The average specific filtration resistance, α_{av}, is the only unknown in the formula and it can therefore be calculated.



(a) 0 mg Fe/l, 98.6 mg Fe/l, 119 mg Fe/l, 167 mg Fe/l

(b) As 4.3a also including 1190 mg Fe/l

Figure 4.3: Filtration of green liquor with added iron. A plot of dt/dV [s/m^3] versus volume [m^3]. (a) shows the plot of data from no addition of iron, 98.6, 119, and 167 mg iron per liter green liquor. (b) also includes the data from the addition of 1190 mg iron per liter green liquor.

The slope, $\frac{\mu \alpha_{av} c}{A^2 \Delta P}$, of each linear regression line in Figure 4.3 is used to calculate the α_{av} value for each concentration of iron shown in Table 4.5. Table 4.5 also shows the mass of solids per unit volume of filtrate as well as the calculated resistance of the filter media for each addition of iron. As can be seen in Figure 4.3a and 4.3b the difference in slope between the three different small additions of iron is quite small. The resulting α_{av}, shown in Table 4.5 is also quite similar for the three cases.

Table 4.5: The average specific filtration resistance, resistance of the filter media and the mass of solids per unit volume of filtrate for different additions of iron. The corresponding percentage of iron in the biosludge for the current amount added to chemical recovery process, is also listed.

Additional Iron Concentration [mg/l]	α_{av} [m/kg]	R$_m$	c [kg/m^3]	% Iron in Biosludge [kg Fe/kg DS]*100
0	$2.3 \cdot 10^{12}$	$7.42 \cdot 10^{10}$	3.4	0.28
0	$2.2 \cdot 10^{12}$	$-6.86 \cdot 10^{9}$	3.1	0.28
96.8	$1.4 \cdot 10^{12}$	$8.14 \cdot 10^{10}$	4.9	7.5
119	$1.3 \cdot 10^{12}$	$6.94 \cdot 10^{10}$	5.0	9
167	$3.8 \cdot 10^{12}$	$-4.72 \cdot 10^{10}$	5.5	13
1190	$3.0 \cdot 10^{13}$	$-1.49 \cdot 10^{12}$	14.1	88

In Table 4.5 the filter media resistance, R$_m$ and mass of solids per unit volume filtrate, c, are presented. The value of c increases with the increasing additions of iron. This indicates that solid material is precipitated, it is however not a direct measure of concentration. The R$_m$ value is negative for three of the experiments. When α_{av} is large small errors impact the value of R$_m$ greatly, which can be seen when looking at Equation 2.5. This can be one reason why the R_m value is negative when α_{av} is larger.

Figure 4.4 shows the different average specific filtration resistances plotted against the iron concentration for each level of iron. It can be seen in Figure 4.4 that the difference in filtration resistance between small additions of iron and no added iron is small. However, when ten times the potential level of iron is added the filtration resistance increases by an order of magnitude. No replicates were done for the additions of iron to green liquor, however the three lower levels of iron additions are somewhat similar and give results which do not vary greatly. These results indicate that the experiments are replicable.

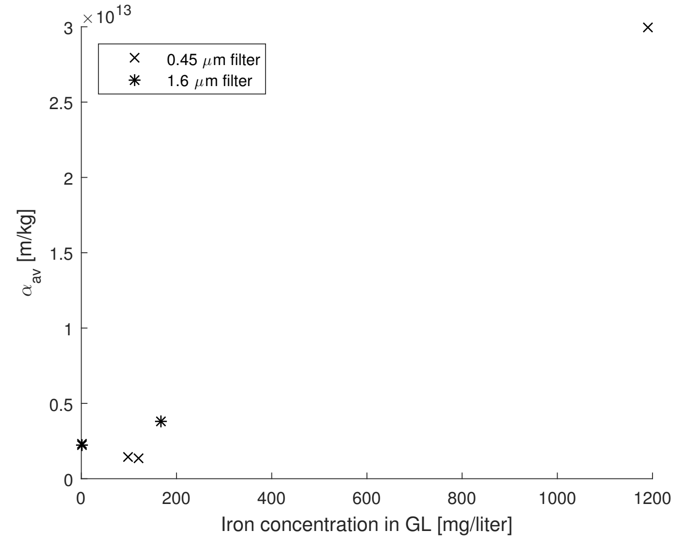


Figure 4.4: A plot of the average specific filtration resistance α_{av} against the iron concentration in the green liquor. * denotes 1.6 μm filter and x denotes 0.45 μm filter

After the first experiment with addition of iron, iron particles were observed in the filtrate, this led to a change in filter paper, from 1.6 μm to 0.45 μm. When the new filter paper was used less particles passed through the filter. This can be seen in Figure 4.5 where the unfiltered green liquor is shown next to filtrate which passed through 1.6 μm, 0.45 μm and 0.2 μm filters respectively. As can be seen in Figure 4.5 (b) has many particles under the size of 1.6 μm which passed through the filter easily. Enough particles were retained in the 0.45 μm filter which is the main reason it was selected. The smallest particles seen here in Figure 4.5 were not seen in the particle size distribution from the laser diffraction measurements in Figure 4.1d. There are evidently smaller iron particles present in the dregs than the laser diffraction can pick up on.

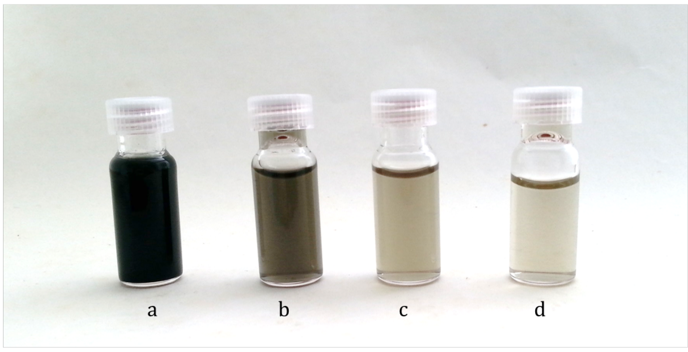


Figure 4.5: The green liquor with 167 mg/l additional iron (a) unfiltered. (b) filtrate filtered with 1.6 μm filters. (c) filtrate filtered with 0.45 μm filters. (d) filtrate filtered with 0.2 μm filters.

The industrial implications of having small particles which easily pass through the pores of the filter and filter cake could mean an incomplete separation of iron from the green liquor. Having an insufficient separation of iron could result in an accumulation of iron in the system which would effect the quality of the lime mud.

4.2.3 Effect of aluminum addition

The results of the experimental trials with additions of aluminum are shown in Table 4.6. The difference in the average specific filtration resistance between the different additions of aluminum is quite small. Compared to the results of Sedin and Theliander (2004) the difference is smaller than what they found with similar additions of aluminum. However, the formation of hydrotalcite which occurs when both aluminum and magnesium are present in the green liquor affects the filtration resistance. The ratio of magnesium to aluminum is a direct factor which influences the formation of hydrotalcite. The magnesium aluminum ratio in the green liquor used in this thesis is different from the concentration of magnesium which Sedin and Theliander used, making a direct comparison of the results difficult. The ratio of magnesium to aluminum in the filtration experiments in this thesis varied between 4.3 for no addition of aluminum, to 1.9 for the addition of 35 mg Al/l green liquor, to 0.3 for the addition of 350 mg Al/l green liquor. In the experiments of Sedin and Theliander the ratio of magnesium to aluminum was varied with levels at 1.6, 4.7 and 14.3. The trend in the results from Sedin and Theliander is that a decrease in the ratio gives a decrease in the filtration resistance. However, a large addition of both magnesium and aluminum which leaves the ratio unchanged increases the filtration resistance.

Table 4.6: The mass of solids per unit volume of filtrate, average specific filtration resistance and resistance of the filter media for different additions of aluminum

Additional aluminum Concentration [mg/l]	α_{av} [m/kg]	R_m	c [kg/m^3]	% Aluminum in Biosludge [kg Al/kg DS]*100
0	$2.3 \cdot 10^{12}$	$7{,}42 \cdot 10^{10}$	3.4	0.28
0	$2.2 \cdot 10^{12}$	$-6.86 \cdot 10^{9}$	3.1	0.28
35.06	$3.1 \cdot 10^{12}$	$2.45 \cdot 10^{10}$	3.2	3.6
350.6	$1.7 \cdot 10^{12}$	$6.39 \cdot 10^{10}$	4.0	36

In Figure 4.6 the results from the two experiments with aluminum are presented as a plot of the inverse volumetric flow rate against the filtered volume. The result from baseline trials are also included in the plot to show the relatively small difference in the slope between the different experiments.

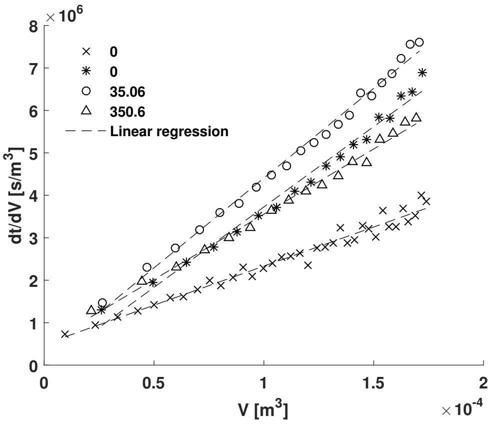


Figure 4.6: Filtration of green liquor with added aluminum. A plot of dt/dV [s/m^3] against volume [m^3].

The average specific filtration resistance is plotted against the addition of aluminum in Figure 4.7. As can be seen in Figure 4.7 the average specific filtration resistance α_{av} is not very affected by the addition of aluminum. Even at levels ten times higher than the expected aluminum level there was not a significant difference in the α_{av} value was found. The laser diffraction measurements in Figure 4.1 show that there are more large particles present when aluminum has been added to green liquor, compared to native green liquor. These larger particles seem to lead to a lower α_{av} value. Two different filters were used for these experiements, 1.6 μm and 0.45 μm filters. The structure of the filter cake can differ due to the difference in the filter media used, as the initial filtration rate varies depending on the resistance of the filter media. This can be one reason why the α_{av} value is higher when 35 mg aluminum per liter green liquor is added.

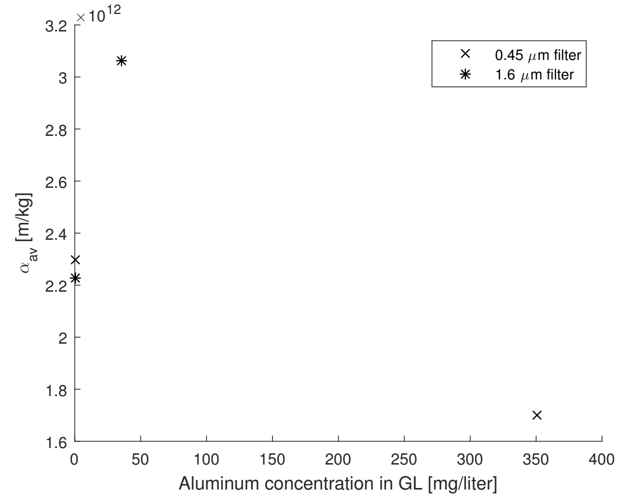


Figure 4.7: Average specific filtration resistance, α_{av}, plotted against the aluminum concentration in the green liquor

In the study of Sedin and Theliander (2004) they observed that the filtration resistance decreased with increasing addition of aluminum, and the trend seen in the two experiments with 0 mg Al/l and 350 mg Al/l in this thesis corresponds well with those observations. However, as stated previously a direct comparison with the results of Sedin and Theliander is difficult as the ratio between magnesium and aluminum is different for different green liquors. One possible cause why the average specific filtration resistance might be higher for the addition of 35 mg Al/l green liquor is that different filters were used for that filtration. The 1.6 μm filters were used instead of the 0.45 μm filters which were used for the other experiments.

4.2.4 Summation of filtration results

In Figure 4.8 both the results from the filtration of iron and aluminum are shown as a plot of average specific filtration resistance versus the additional metal concentration. It can be seen that there are no clear differences between adding small amounts of iron and aluminum. The results of the filtration with additional aluminum are dependent on the magnesium concentration, which is varies depending on the wood raw material. The main difference is however that a tenfold addition of aluminum has no effect on the filtration resistance whereas a tenfold addition of iron increases the filtration resistance by an order of magnitude. The additions of iron and aluminum are the same on a molar basis, as described in Chapter 3.1.3. The amount of aluminum added appears to be much smaller than the amount of iron added, but the amount of moles are the same for 35 mg Al and 96.8 mg Fe. The amount of moles are approximately the same for additions of 350 mg Al and 1190 mg Fe. The varying temperatures has been accounted for when calculating the average specific filtration resistance.

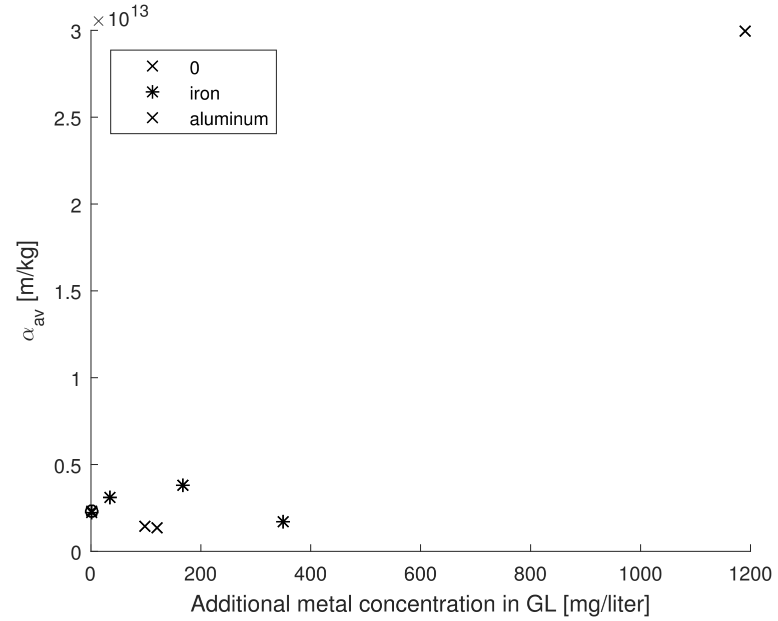


Figure 4.8: Average specific filtration resistance, α_{av}, plotted against the additional metal (iron and aluminum) concentration

4.3 Leaching

4.3.1 pH-stat leaching of fly ash

The first leaching experiment of fly ash with HNO_3 was only kept for 50 hours, the pH was held constant at 4. The second leaching experiment of fly ash with HNO_3 was kept at pH 4 for 150 hours. The cadmium concentration of the leachates from both experiments were analyzed with AAS. The concentration in the leachate was plotted against time in Figure 4.9. It can be seen that leached amount increases with time.

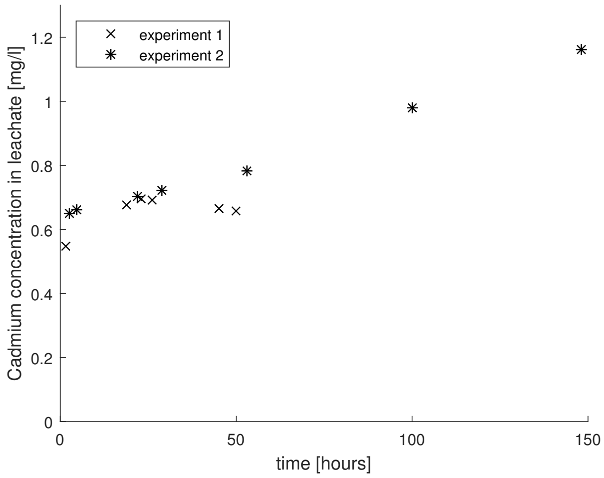


Figure 4.9: Fly ash leaching at pH 4. The cadmium concentration plotted against leach time

The results of the leaching experiments are shown in Tables 4.7 and 4.8.

Table 4.7: Cadmium concentration of leached fly ash (Experiment 1) with pH-stat titration pH 4 nitric acid.

Time [hours]	1.5	19	23	26	45	50
Titrated amount [ml]	62.89	92.17	93.43	95.25	98.59	100.37
Cd [μg/ml]	0.55	0.68	0.70	0.69	0.67	0.66

As can be seen from the results in Table 4.7 and Table 4.8 the cadmium concentration in the leachate increases over time. The leaching time was quite different for the two experiments, the second leaching lasted 100 hours longer than the first. The percentage leached cadmium is not presented as it in all cases exceeded 100%. The accuracy of the measurement methods are not known, but large uncertainties in both the amount of cadmium present in the starting material as well as the accuracy of the AAS results could be a reason to the total amounts leached reaching well over 100%. With such small quantities of cadmium a small error in the measurements can yield a much larger total error. Although the total amount of leached cadmium may be uncertain a trend can be seen that the cadmium is leached over time, this can be seen clearly in Figure 4.9.

Table 4.8: Cadmium concentration of leached fly ash (Experiment 2) with pH-stat titration pH 4 nitric acid.

Time [hours]	2.5	4.5	22	29	53	100	148
Titrated amount [ml]	99.56	108.97	119.83	120.91	122.83	124.04	125.00
Cd [μg/ml]	0.43	0.43	0.54	0.56	0.59	0.69	0.71

After leaching for 48 hours a layer of hydrophobic ash started to cover the surface of the leachate. The amount increased during the leaching experiment. The composition of this hydrophobic ash is unknown. It may also lead to uneven mixing of the suspension, which in turn impacts the leaching. It might be a source of errors when it comes to the amount of cadmium which can be leached.

4.3.2 pH-stat leaching of green liquor dregs

The leaching of green liquor dregs was aimed at pH 4.5, but due to unintentional over-titration the pH was constant at pH 3 from hour 26 of the experiment. The cadmium concentration in the leachate is plotted against the leach time in Figure 4.10. There it can be seen that the amount leached increases over time, which indicates that cadmium is in fact leached from green liquor dregs at pH 3.

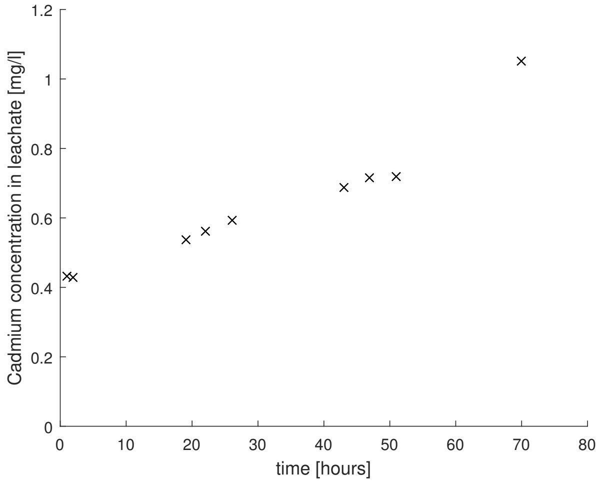


Figure 4.10: Cadmium concentration plotted against leach time for green liquor dregs leached at pH 3

The results of the leaching experiment are presented in Table 4.9.

Table 4.9: Cadmium concentration of leached green liquor dregs with pH-stat titration pH 3 nitric acid.

Time [hours]	1	2	19	22	26	43	47	51	70
Titrated amount [ml]	-	63	71.8	71.86	71.86	71.86	71.86	71.86	71.86
Cd [μg/ml]	0.43	0.43	0.54	0.56	0.59	0.69	0.71	0.72	1.05

The total amount of cadmium leached from the green liquor dregs exceeds the maximum amount possible considering the concentration of cadmium present in the starting material, shown in Table 4.1. There are a few possibilities as to why the concentration of cadmium is higher than theoretically possible. The green liquor dregs which are used in the leaching experiment are not homogeneous in size or composition, but are instead made up of both "pure" dregs and the filter precoat. The precoat that is used to filter the green liquor dregs is made up of lime mud. The lime mud has a cadmium level lower than 0.6 mg/kg dry solids as can be seen in Table 4.1 and a high lime mud content in the analyzed green liquor dregs sample might result in a lower cadmium concentration than in reality. A previous study of the leaching of cadmium from green liquor dregs had performed the same type of elemental analysis on green liquor dregs from three other pulp mills (Björkqvist, 2015). The results showed a higher concentration of cadmium in these samples than in the samples used in this thesis. The cadmium levels in Björkqvist's (2015) study were 11.2, 12.3 and 18.5 mg Cd/kg dry solids, on average 14 mg Cd/kg dry solids, as compared to the 6.3 mg Cd/kg dry solids found in the dregs used in these leaching experiments. If the assumption is made that the sample used to determine the cadmium level was not representative of the true level of cadmium and the previously documented levels are used instead the leached amount of cadmium will no longer be as much above the theoretically possible level. The important result is regardless of the total percentage of cadmium leached, that cadmium is in fact leached from green liquor dregs over time, which can be seen in Figure 4.10.

5

Conclusion

- The average specific filtration resistance, α_{av}, for green liquor with no addition at 44°C and 1 bar was found to be $2.3 \cdot 10^{12}$ m/kg.

- An addition of iron ions by addition of dissolved iron (II) sulfate heptahydrate at 65°C to the green liquor decreases the average particle size. This addition effects the average specific filtration resistance to a varying degreee depending on the added amount. A large addition of Fe^{2+}, 1190 mg Fe^{2+} per liter green liquor, increased the filtration resistance by an order of magnitude to $3.0 \cdot 10^{13}$ m/kg. A more realistic level of addition of iron, 98.6 mg Fe^{2+} per liter green liquor, from process point of view did however not effect the filtration resistance significantly.

- Adding aluminum ions by addition of dissolved aluminum chloride hexahydrate at 65°C to green liquor shifted the particle size distribution toward larger particles. A large addition of aluminum, 350 mg aluminum per liter green liquor, to green liquor decreases the average specific filtration resistance. A small addition of aluminum, 35 mg aluminum per liter green liquor, to green liquor gave a slight increase of the filtration resistance for the green liquor studied in this thesis. A difficulty in comparing the results is that two different filter papers were used.

- Preliminary results of the leaching study indicate that cadmium is leached from both the fly ash at a pH 4 and green liquor dregs at a pH of 3, this indicates that this could be an issue when utilizing the residue and further studies are required.

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A

Appendix A

```
clear all;
close all; clc;
A= importdata('Fe1');
w= A(1:length(A), 10);
J=find(w>0,1, 'first');
w=w(J-1:length(A));
t= A(J-1:length(A),1);
t= (t-t(1,1))/1000;
total_time=t/60;
time_max=max(total_time)

D=[t w];
time(1:length(D),1)=D(1:length(D),1)./60;
time(1:length(D),2)=D(1:length(D),2);

diameter=4.6E-2;
radius=diameter/2;              %[m]   Radius of filter paper
area=(pi()*radius^2);       %[m2]   Area of filter paper
deltaP=1E5;                 %[bar]  Pressure drop
mu=0.00119424538;             %[Pas]  Viscosity
rho=1.1459634e+03;               %[kg/m3] Density of green liquor at 50
degrees

w=w*1E-3;                   %[kg]   Converts w från g till kg
V=w/rho;                    %[m3]   Volume of filtrate [kg / (kg/m3)]



%Filter cake calculations
filter=0.2023E-3+0.4827E-3;          % The weight of the filters [g]
glass=47.8922E-3;                    % The glass that the filters rested on
[g]
cake_wet=53.8619E-3;                 % Filter cake before drying [g]
cake_dry=50.0711E-3;                 % Filter cake after drying [g]
dry_content=0.235261303;             % Dry content of green liquor
motherliquor=cake_wet-cake_dry;      % Amount of mother liquor left in the
filter cake [g]
dry_solids=motherliquor*dry_content;% Weight of dry solids left in the
filter cake from the mother liquor[g]
cake_solids=cake_dry-dry_solids;     % Weight of the filter cake without dry
solids from mother liquor  [g]
```

```
cake=cake_solids-glass-filter;       % Weight of the filter cake without
filter and weighing glass

c=cake/max(V);                       % mass of solids per unit filtrate
volume [kg/m3]

I=find(V>=180E-6,1, 'first');        % This cuts the data at a volume of 180
ml
t=t(1:I);
V=V(1:I);


%A=[1:155];

step=10;

k=floor(length(V)/step);

B1=zeros(k,1);

for j=0:1:k-1

    for i=1:step
        B1(j+1)=B1(j+1)+V(i+(j*step),1);
        V1(1+j)=V(1+(j*step));
        V2(1+j)=V(step+(j*step));
    end

    averageV(j+1)=B1(j+1)/step;

end
averageV=averageV';

V1=V1';
V2=V2';

dV_average=V2-V1;


step=10;

k=floor(length(t)/step);

B2=zeros(k,1);

for j=0:1:k-1

    for i=1:step
        B2(j+1)=B2(j+1)+t(i+(j*step),1);
        t1(1+j)=t(1+(j*step));
        t2(1+j)=t(step+(j*step));
    end

    average_t(j+1)=B2(j+1)/step;

end
average_t=average_t';
```

```
t1=t1';
t2=t2';

dt_average=t2-t1;                     % Average of the start and end time
in each step


for i=1:k-1                          % En loop which gives dt of the average
time och dV of the average volume

average_dt(i)=average_t(i+1)-average_t(i);
average_dV(i)=averageV(i+1)-averageV(i);
end

average_dt=average_dt';
average_dV=average_dV';

average_dtdV=average_dt./average_dV;      % The average dt/dV from the
average dt and dV



figure (1)
hold on
plot(averageV(1:k-1), average_dtdV,'k^')     % Plots the average dtdV vs
average volume

X = [ones(length(averageV)-1,1) averageV(1:k-1)];
b = X\average_dtdV
yCalc2 = X*b;
Rsq1 = 1 - sum((average_dtdV - yCalc2).^2)/sum((average_dtdV -
mean(average_dtdV)).^2)
plot(averageV(1:k-1),yCalc2,'k--')
legend('Data','Linear Regression', 'Location', 'southeast');
legend('boxoff')
xlabel('V [m^3]')
ylabel('dt/dV [s/m^{3}]')
title('V vs dt/dV')
axis([0.0E-4 1.8E-4 0.0E6 8E6])

text(1E-4,2E6, ['R^{2}=',num2str(Rsq1)])

alpha=b(2)*area^2*deltaP/(mu*c)

Rm=b(1)*area*deltaP/mu
```

B

Appendix B

The assumptions made for the levels of iron in the biosludge, which are shown in Table 3.1, is that all of the iron present in the biosludge will contribute to the iron level in the green liquor.

The difference in iron content between the actual biosludge and the potentially much higher level of iron is used to calculate how much iron should be added to each green liquor sample, using the formulas listed below as B.1 and B.2.

The plant A where the samples come from burns approximately 6 kg biosludge per ton pulp, whereas plant B burns 5 kg biosludge per ton pulp.

$$\frac{g\ \ \text{Fe}}{kg\,\text{biosludge}} \cdot \frac{kg\,\text{biosludge}}{ton\,\text{pulp}} = \frac{g\,\text{Fe}}{ton\,\text{pulp}} \tag{B.1}$$

$$\left(\frac{m^3\,\text{Green liquor}}{ton\,\text{pulp}}\right)^{-1} \cdot \frac{g\,\text{Fe}}{ton\,\text{pulp}} = \frac{g\,\text{Fe}}{m^3\,\text{Green liquor}} \tag{B.2}$$