CHALMERS
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Mass balances of carbonate and oxalate in a Kraft pulp mill

Master's thesis at Stora Enso and Chalmers University of Technology

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ABSTRACT

The Kraft pulping process is the most used pulping process in Sweden, and one problem that may arise in this process is the scaling of insoluble salts. Salts can be formed from different ions, for example carbonate and oxalate anions combined with a cation e.g. calcium. This thesis has investigated the possible formation of carbonate and oxalate ions throughout a Swedish softwood Kraft pulp mill producing fully bleached pulp with the bleaching sequence D-Q-PO.

Carbonate and oxalate ions are presented to the Kraft pulping process via the wood and the cooking chemicals, but it is also of interest to investigate if there is a formation of these ions during the process. To study this, sampling of both pulp and liquor throughout the mill was performed.

The samples were analysed with atomic absorption spectroscopy for sodium, calcium and potassium ion content, with ion chromatography for oxalate ion content, and with TOC for carbonate ion content. Dry content and density were also determined for the samples.

Mass balances were established over the Kraft pulp mill, using data extracted from the mill's data handling system. With the calculated mass flows, balances of carbonate and oxalate throughout the mill were calculated. These were then evaluated to see if there was a formation occurring in the process.

The results found in this thesis indicate that there is a formation of carbonate in the digester, the oxygen bleaching step, and the PO bleaching step. Formation of oxalate seems to be occurring in the digester, the oxygen bleaching step, and the D and PO bleaching steps.

Metal ion profiles of sodium, calcium and potassium were established over the fibre line. As expected, a decreasing trend could be seen throughout the mill for pulp samples as well as filtrates and carryovers for sodium and potassium. For calcium, there was a decreasing trend for pulp samples, but the liquor samples had an almost constant content of calcium indicating that calcium is difficult to wash out from the process.

Some results, especially the formation of carbonates, seem somewhat high. This could be the result of aging effects in the samples, which could be caused by absorption of carbon dioxide. Due to this, and the general uncertainties in the mass balance calculations, no exact numeric value on the formation could be presented. The results could still be seen as an indication of where there is a formation of both carbonate and oxalate ions in the Kraft pulp mill, and further investigations should be made in order to validate these results.

Keywords: Kraft pulping, mass balances, carbonate ions, oxalate ions

SAMMANFATTNING

Kraftprocessen är den mest använda metoden för att producera pappersmassa i Sverige. Ett problem som kan uppstå i processen är bildandet och utfällning av olösliga salt, så kallad inkrusterbildning. Salter kan bildas av flera olika joner, däribland anjonerna karbonat- och oxalatjoner kombinerat med exempelvis kalcium som katjon. Detta examensarbete behandlar den eventuella bildningen av karbonat- och oxalatjoner i de olika stegen hos ett svenskt massabruk som producerar fullt blekt pappersmassa i en bleksekvens bestående av D-Q-PO.

Karbonat- och oxalatjoner kommer in i massaprocessen med vedråvaran och kokkemikalierna, men det är också intressant att studera om det finns någon bildning av dessa joner under processen. För att undersöka detta togs prover av både lut och massa ut från hela massabruket.

Proverna analyserade sedan med atomabsorptionsspektrometri för att bestämma halten av natrium, kalcium och kalium, jonkromatografi för att bestämma oxalatinnehållet och med TOC för att bestämma karbonatinnehållet. Även torrhalt och densitet bestämdes för proverna.

Massbalanser upprättades över massabruket med hjälp av processdata från bruket. Med hjälp av de beräknade massflödena kunde sedan balanser för karbonater och oxalater beräknas över alla processteg. Dessa utvärderades sedan för att se om bildning ägde rum.

Resultaten från denna studie indikerar att det bildas karbonatjoner över kokaren, syrgasblekningen och PO-bleksteget. Oxalatjoner verkar bildas vid kokaren, syrgasblekningen samt D- och PO-bleksteget.

Grafer för metalljoninnehållet över fiberlinjen upprättades för natrium, kalium och kalcium. En minskande trend kunde ses för både natrium och kalium, både i massaprover så väl som i filtrat och överbäring. För kalcium var det en minskande trend för massaproverna, medan halterna för filtrat och överbäringen var nästan konstanta. Detta antyder att kalcium är svårt att tvätta ut helt från processen.

Några resultat, speciellt för bildning av karbonater, verkar lite höga. Detta skulle kunna bero på att proverna har åldrats på grund av problem med förvaringen (antagligen absorption av koldioxid). Detta, samt generella osäkerheter vid bestämningen av massbalanserna, gör att inget exakt värde för bildningen kan anges. Resultaten kan fortfarande ses som en indikation på var det bildas karbonat- respektive oxalatjoner i massaprocessen. Fortsatta studier krävs för djupare förståelse av bildningen av dessa joner.

Nyckelord: Kraftprocessen, massbalanser, karbonatjoner, oxalatjoner

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1 INTRODUCTION

The pulp and paper industry is one of the largest industries in Sweden, exporting products worth around 130 billion SEK annually (Skogsindustrierna, 2015). The most abundant pulping method used in Sweden is the Kraft pulping process, where Na_2S and NaOH are used as cooking chemicals to liberate the cellulose fibers of wood into pulp (Gellerstedt, 2004).

Non-process elements are elements that exist in the different streams of the pulp mill but don’t take place in the reactions, and is often abbreviated NPE:s. Examples of NPE:s are calcium, potassium, magnesium and chloride (Ulmgren, 1997). Due to the increased environmental concern the pulp mills are working with a high degree of system closure, which means that effluent streams are kept at a minimum. This leads to a higher accumulation of non-process elements, which can cause different problems in the pulp mill (Ulmgren, 1997).

Other substances presented to the process with the wood are negatively charged ions, such as carbonate and oxalate (Ulmgren, 2005) (Saltberg, 2009). Together with the non-process elements these can form insoluble salts that, for example, precipitates as scales in the pulp process causing different problems, such as heat transfer limitations.

Except from the carbonate and oxalate presented with the wood, it is also of interest to investigate whether there is a formation of these ions during the process. With more knowledge about the behaviour of these ions, problems caused by them could be minimised. This thesis will evaluate if such a formation occurs in a Swedish softwood Kraft pulp mill producing fully bleached pulp by using mass balances over the pulp mill.

1.1 OBJECTIVE AND LIMITATIONS

The purpose of this master thesis was to investigate the behaviour and possible formation of carbonate and oxalate ions in the different steps of the Kraft pulp mill. This is of interest since these ions can cause several different process disturbances, such as scaling in tubes.

The work included sampling from one Swedish softwood Kraft pulp mill producing fully bleached pulp. Analyses for sodium, calcium, and potassium, carbonate and oxalate ions were performed on the samples. Mass flow balances were established over the mills different unit steps and these were used to evaluate the behaviour of carbonate and oxalate ions through the pulp mill.

Originally the aim was to compare the formation of carbonate and oxalate ions between one Swedish softwood Kraft pulp mill and one eucalyptus mill. Due to different problems, for example with shipping of the eucalyptus Kraft pulp mill samples to Sweden, the time span of the thesis wasn’t enough to establish balances over the eucalyptus mill. Since most of the analyses were performed on the eucalyptus samples, the eucalyptus Kraft pulp mill is to some extent included in this thesis, even though neither results nor discussion can be presented for this mill. The last chapter of this thesis will discuss future work that can take its starting point in this work.

1.2 THESIS OUTLINE

The thesis starts with a brief background in chapter 2.Background, including the basic concepts of the Kraft process and the problems that can arise in it. The experimental work and methods used for determination of Na, Ca, K, carbonate and oxalate are described in chapter 3.Experimental . How the general mass balances for the Swedish softwood Kraft pulp mill were established is described in chapter 4.Mass balances, and how the content of different ions in streams were calculated are described in chapter 5.Calculations. The results are presented and discussed in chapter 6.Results and Discussion, and conclusions are made in chapter 7.Conclusions. Finally, possible future work is discussed in chapter 8.Further studies. In Appendix A1-A3 different laboratory analysis values can be found.

2 BACKGROUND

This section will start with a brief description of the raw material to the pulping process, wood. After that follows a description of the different process units in Kraft pulping, and a brief description of what non-process elements are and what problems they can cause.

2.1 WOOD

Wood is usually categorized in two different categories, hardwood and softwood. Examples of softwoods are spruce and pine, and hardwood examples are birch, oak and eucalyptus (Henriksson, Brännvall, & Lennholm, The trees, 2004). The raw material used in this study was Swedish softwood, and it is therefore interesting to look at the composition of these species more closely.

The main constituents of wood are cellulose, hemicelluloses, lignin, extractives and inorganics. For softwood, the relative composition of these can be seen in Table 1 (Theliander, Paulsson, & Brelid, 2002).

Table 1. Components of softwood.

What	Content [%]
Cellulose	42 ±3
Hemicelluose	27 ±2
Lignin	28 ±3
Extractives	3 ±1
Inorganics	0.1-0.2

Cellulose is a linear chain polymer carbohydrate consisting of glucose units with a high degree of polymerization, up to 10 000 (Theliander, Paulsson, & Brelid, 2002). The long fibers are insoluble in water and together with the hemicelluloses they build up the supporting structure of the wood (Lennholm & Blomqvist, 2004). Hemicellulose is a collection name for different types of carbohydrates with a lower degree of polymerization than the cellulose. In hemicelluloses the main monomers are, except for glucoses, also mannose, galactose, xylose and arabinose (Theliander, Paulsson, & Brelid, 2002).

Lignin is a complex polymer which can be said to be the glue which keeps the different components together in the wood. Except from the gluing function, other functions of the lignin in the wood are that it makes the cell wall hydrophobic, it gives stiffness to the cell walls and it is a protection against microbial degradation (Henriksson, 2004).

Extractives are also a collection of different compounds, with the common denominator that they have a not too high molecular mass and that they could be extracted from the wood with different neutral solvents. Generally the highest content of extractives and inorganics can be found in the bark of the tree (Björklund Jansson & Nilvebrant, 2004). Examples of inorganics are sodium, calcium, potassium, silicon, phosphorous, iron etc. The content of Na, Ca and K can be seen in Table 2 (Theliander, Paulsson, & Brelid, 2002). Other compounds entering the process with the wood are for example carbonate and oxalate ions (Ulmgren, 2005) (Saltberg, 2009).

Table 2. Examples of inorganic content in softwood.

Compound	Na	Ca	K
Content in wood [mg/kg]	6	700	450

2.2 THE KRAFT PROCESS

Pulp can be produced by several different methods, for example mechanical pulping, thermomechanical pulping and chemical pulping. They all have the common overall aim of liberating the cellulose fibers from the wood matrix (Theliander, Paulsson, & Brelid, 2002). The Kraft process is a type of chemical pulping, and a schematic description of this process can be seen in Figure 1. After the figure, more details of the different process units will be discussed.

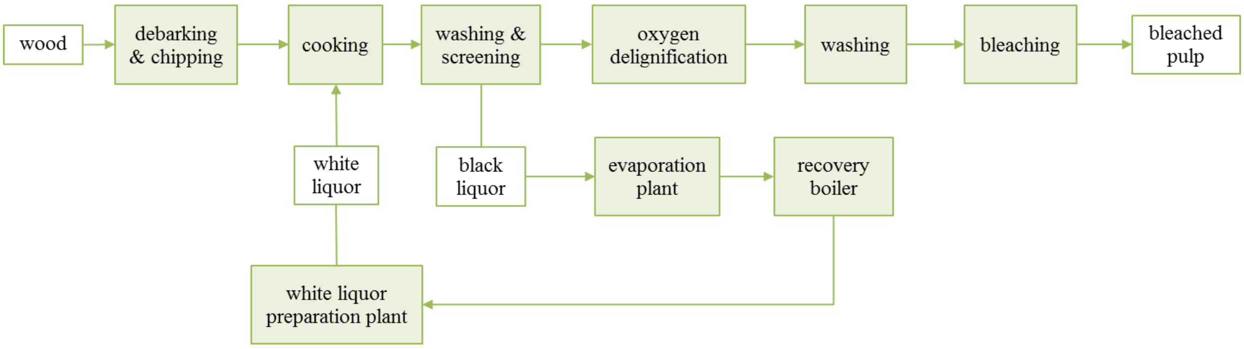

Figure 1. Schematic figure over the Kraft pulping process.

2.2.1 WOOD HANDLING

The wood enters the mill as logs, and the first step is to debark and chip these in to wood chips. The debarking is an important step since the bark contains a significant amount of the non-process elements of the wood, as discussed in the previous section. Wood chips need to be in equal shape in order for the cooking to be even in the following digester, so all fibers are equally liberated.

2.2.2 COOKING

Cooking can be either batch-wise or continuous, and here the continuous cooking will be described. Wood chips are pretreated with steam to get rid of air in the chips and then impregnated with cooking liquor to mix the reactants (Theliander, Paulsson, & Brelid, 2002). The wood chips liquor mixture is then sent into the top of a continuous digester where the pressure is elevated. The top part of the digester is called the cooking zone and most of the reactions take place here (Brännvall, 2004).

The cooking liquor is called white liquor, and the active cooking chemicals hydroxide ions and sulfide ions, presented as sodium hydroxide and sodium sulfide. To liberate the fibers, the lignin that acts as the glue for the wood fibers is decomposed into smaller fragments which are soluble in water. The chemistry of the pulping is a complex process, but the most important reaction in the delignification of wood is the cleavage of the β-O-4 structures in the lignin (Gellerstedt, 2004). Simultaneously as the delignification reactions, depolymerisation reactions of the cellulose fibers also occurs. Due to that, not all lignin is dissolved in the black liquor in the digester, since there would then be a too high degree of depolymerisation of the cellulosic fibers.

The lignin fragments are then dissolved in the cooking liquor. The liquor extracted from the digester is called black liquor (due to its colour) or weak liquor (Ziesig, 2014). After the cooking zone, excess liquor is extracted from the digester and a washing zone starts. Part of the weak liquor is then recirculated to the digester, and the rest is sent to the evaporation plant to recover the chemicals and the energy from the lignin dissolved in the weak liquor.

At the end of the digester the pressure is dropped leading to evaporation of the liquid inside the wood chips, causing the loosely connected wood chips to fall apart and the cellulosic fibers are deliberated (Theliander, Paulsson, & Brelid, 2002). In order to separate the fibers more throughout, mechanical defibrators are placed directly after the continuous digester (Brännvall, 2004).

2.2.3 WASHING AND SCREENING

After the digester the pulp is washed and screened. The washing aims to replace the lignin rich black liquor containing the pulp with a cleaner washing liquor, i.e. to get rid of the lignin. The purpose of the screening is to get rid of larger pieces of wood not properly digested in the cook. To obtain an effective screening the pulp is diluted in order to be easily screened. (Theliander, Paulsson, & Brelid, 2002)
An example of a washing and screening sequence can be seen in Figure 2.

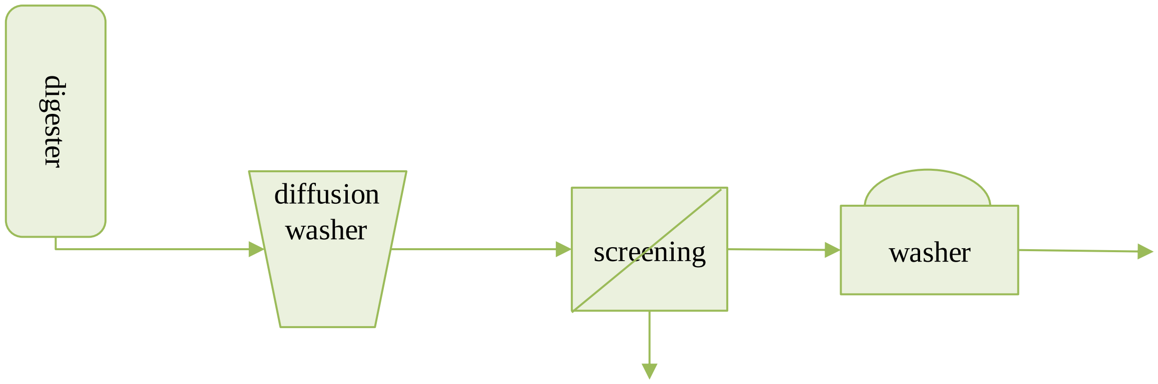

Figure 2. Example of a washing sequence after the digester.

The diffusion washers could be both atmospheric and pressurized. The washing equipment after the screening could typically be a displacement washer. An example of an atmospheric diffuser can be seen in Figure 3 (Miliander, 2009).

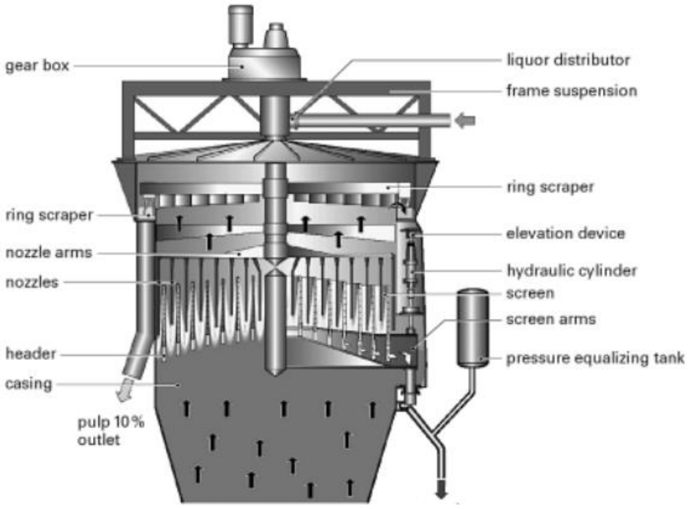

Figure 3. An atmospheric diffuser.

In a diffuser washer, the pulp is let in at the top and the washing liquor at the bottom. The pulp is cleaned mainly by displacement of liquor with the washing liquor (Miliander, 2009).

The washing liquor is sent counter current compared to the fibre line in the process. This is in order to minimize the use of water in the pulp mill and reduce the impact on the environment. The high degree of system closure can cause an accumulation of non-process elements, which can cause different problems in the process (Ulmgren, 1997). This is further discussed in the next section.

Approximately 90% of the lignin is dissolved by the cooking, which means that the pulp still contains residual lignin after washing. This gives the pulp a dark brown colour, and the pulp could be used to produce unbleached products such as cardboard. When a brighter product is desired, the pulp is further treated with different bleaching methods. Pulp is also washed after the next step, the oxygen delignification. The theory and washing equipment for this washing step corresponds to what have been described in this subsection and will not be described again.

2.2.4 OXYGEN DELIGNIFICATION AND BLEACHING

There are two different methods of bleaching pulps, one way is to oxidize, decompose and remove the residual lignin in the fibers, and one way is to not decompose the lignin but instead oxidize chromophores in the lignin. The first method is the one used for chemical pulping, and the decomposition of lignin takes place in several stages, together forming a bleaching sequence (Germgård, 2004). The bleaching stages all have abbreviations depending on what chemicals are added. In the pulp mill studied in this thesis the bleaching sequence D0-Q-PO was used.

Oxygen delignification is a prebleaching step that is used in most modern pulp mills before the bleaching sequence since it reduces the amount of bleaching chemicals needed to be added later on. In this step the lignin is degraded by addition of oxygen. The filtrate from this sequence is often used as washing liquor in the washing after the digester (Germgård, 2004).

When chlorine dioxide is added to the pulp the bleaching stage is called D, and it is performed at acidic conditions. The Q stage is a chelating stage which by addition of either EDTA or

DTPA binds to the metal ions in the pulp stream and they are thus washed out. This is done to prepare for the next step, the PO step which is bleaching with oxygen and hydrogen peroxide. This since bleaching with hydrogen peroxide is affected by the metal ion content (Theliander, Paulsson, & Brelid, 2002).

2.2.5 BLACK LIQUOR EVAPORATION AND CHEMICAL RECOVERY

The black liquor that is obtained from the cooking tower is called weak black liquor, and has a dry content of between 15-20%. In order to be able to recover the cooking chemicals and the energy in the black liquor as lignin, most of the water in the black liquor must be removed which is done in the evaporation plant where the dry content is elevated to about 70-80% dry content, and the liquor is now called strong black liquor. The strong black liquor is burned in a recovery boiler and the resulting smelt is then converted to white liquor (Theliander, 2004).

2.3 NON-PROCESS ELEMENTS

Non-process elements (NPE:s) are elements occurring in the pulp mill without having any purpose for the process. These elements are introduced to the process via the wood, the process waters or the cooking chemicals. Sometimes a non-process element can be a process chemical in another part of the process (Ziesig, 2014).

Some examples of non-process elements and the negative effects they may have on the pulp mill are described by Ulmgren (1997) and can be seen in Table 3.

Table 3. Examples of non-process elements

Elements	Negative effects
Al, Si, Ca, Ba	scales, deposits
K, Cl, Mg	corrosion
K, Cl	plugging in recovery boiler
P, Mg, Al, Si	inerts in lime cycle
Mn, Fe, Cu etc.	effects on TCF-bleaching
N, P, Cd, Pb etc.	impact on the environment

Since the metals to a great extent are dissolved in the black liquor, most of them will end up in the recovery cycle where they are accumulated (Saltberg, 2009). Another large fraction will follow the fibre line and will end up in the final pulp (Ulmgren, 1997).

In order to avoid the accumulation of NPE:s in the recovery cycle, something called kidneys are introduced to the process. These have the purpose to remove NPE:s, and examples of these are the green liquor dregs, lime mud and recovery boiler dust (Saltberg, 2009).

3 EXPERIMENTAL

The experimental work included planning, sampling, and analysing of samples. Analyses were made for sodium, calcium, and potassium ion content as well as for oxalate and carbonate ion content. Also dry content and density were measured. The different methods used for these determinations are described in the following sections.

3.1 SAMPLING

Samples were obtained from two different Kraft pulp mills, one using Swedish softwood as raw material and the other one using eucalyptus. The difference in sampling between the two mills was that sampling points for the eucalyptus plant were decided before the start of this thesis work and staff from the mill took the samples. For the Swedish softwood mill planning of and participation in sampling was included in the work.

3.1.1 SWEDISH SOFTWOOD KRAFT PULP MILL

The Swedish softwood Kraft pulp mill studied produces both bleached and unbleached pulp, but it is the bleached pulp that is considered in this thesis. After debarking and chipping wood chips are sent to a continuous digester. The blown pulp is washed in a pressure diffuser before the pulp is bleached in an oxygen delignification step. The pulp is then washed again in a pressure diffuser and a double diffuser before it is bleached with a D-Q-PO-sequence.

The location of the sampling points was decided in consultation with the supervisors and engineers from the mill. Sampling was carried out with help of the plant's staff. Pulp samples were taken in two different ways, both as they were and by pressing the pulp stream and keeping the resulting liquor. This liquor is hereinafter called the carryover to that pulp stream. The samples were stored refrigerated, except from the wood chips which were stored openly at room temperature. All sampling points can be seen in Appendix A1: Dry content and density.

3.1.2 EUCALYPTUS KRAFT PULP MILL

The samples from the eucalyptus plant were prepared by the plant's staff and were stored refrigerated before they were shipped to Sweden. The samples were kept refrigerated even here. Samples from each sampling point was taken at four different times resulting in quadruplets of samples, except for the dried pulp samples which were taken as triplets. When analysing a sample, equal amounts of samples from the four different times were mixed. The analyses were thus carried out on a mean mixture of the samples, in order to get a more representative result.

3.2 METAL ION CONTENT

Metal ion content in the samples was determined in order to be able to compare the results to previous work, and to be able to determine the validity of the carbonate and oxalate balances. The ions that were determined were sodium (Na), calcium (Ca) and potassium (K). To determine the content in process samples, atomic absorption spectroscopy (AAS) was used after the samples had been pretreated with wet combustion.

3.2.1 WET COMBUSTION

In order to dissolve the metal ions the samples were pretreated with wet combustion. About 1.5 g of sample was weighed in a cylindrical container and 5 ml of 70 % nitric acid was added to each sample. The container was sealed and put into a microwave oven and heated to 80°C during 25 minutes. After the sample had cooled down the solution was transferred to a 50 ml volumetric flask. 5 ml of CsCl solution with 10 000 ppm was added in order to get a concentration of 1 000 ppm after the sample was diluted with distilled water to 50 ml. Cesium is added to suppress ionization of potassium and sodium in the air acetylene flame used for detection (SCAN N37:98, 1998) (Varian, 1989).

Before wet combustion of the wood chips, they were grounded in a mill to a fine powder. The wet combustion was then carried out as described above.

3.2.2 ATOMIC ABSORPTION SPECTROSCOPY

In atomic absorption spectroscopy, the sample is injected to a flame where the electrons in the metal ions are transferred to an excited state. When this happens, the sample absorbs light of a wavelength specific to the element analysed. The amount light absorbed is measured and can be used to calculate how much of the metal ion the sample contains, by comparing with calibration from samples of known concentration (Harris D. C., 2010).

Methods for detecting sodium, calcium and potassium ions were developed for an atomic absorption spectrometer of brand Thermo Scientific, iCE 3 000 series, equipped with hollow cathode lamps for each element to be analysed. The detection technique used in all three methods was flame absorption spectroscopy, the measurement mode was set to absorption and the calibration method used was *Quadratic least square fit*. Parameters that were different for the three methods can be seen in Table 4.

Table 4. Method parameters for AAS.

Substance	Wavelength [nm]	Flame type	Fuel flow [l/min]	Bandpass [nm]
Na	330.3	Air/acetylene	1.1	0.5
Ca	239.9	Air/nitruos oxide	3.6	0.2
K	404.4	Air/acetylene	1.2	0.5

For each compound a standard stock solution of 1 000 ppm was prepared. The stock solution for sodium was prepared by dissolving 2.542 g of NaCl in distilled water in a volumetric flask and diluting it to 1 000 ml. For the calcium solution, 2.497 g of $CaCO_3$ was dissolved and diluted, and for potassium, 1.907 g of KCl. The standard stock solutions were then diluted to standard solutions according to Table 5 used to establish a calibration curve for the determination. CsCl was added to the standards so that each standard contained 1 000 ppm CsCl.

Table 5. Standards used for AAS.

	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5
Na	5 ppm	10 ppm	50 ppm	100 ppm	200 ppm
Ca	5 ppm	10 ppm	50 ppm	100 ppm	200 ppm
K	5 ppm	10 ppm	50 ppm	100 ppm	200 ppm

A blank sample was prepared for setting zero absorbance by diluting 0.1429 ml of 70% HNO_3 to 100 ml with distilled water in a volumetric flask.

After the calibration was made, the sample was injected to the AAS. If the measured value for metal ion content didn't fit to the calibration curve it was further diluted and measured again. To calculate the concentration of metal ions in the sample, equation (1) was used.

$$X = \frac{f}{m}C \qquad (1)$$

In this equation, X is the concentration of metal ions as mg/kg sample, f is the dilution factor, m the mass weighed for wet combustion and C is the concentration in the diluted sample measured with AAS.

3.3 CARBONATE ION CONTENT

The carbonate content was measured for all process liquors. The liquors were diluted in order to get results in the region of the calibration curve. The analysis was performed according to SCAN method N32:98 by the staff at the Swedish mill's laboratory.

The result from the analysis was the total inorganic carbon of the diluted sample, TIC. The carbonate ion concentration in the liquid was then calculated with equation (2) (SCAN N32:98, 1998).

$$X = C \times D \times 5 \qquad (2)$$

Here, X is concentration of carbonate ions in mg/kg sample, C is the concentration of total inorganic carbon in ppm given by the analysis, D is the dilution factor and 5 is a numerical factor in order to convert from carbon to carbonate ions.

3.4 OXALATE ION CONTENT

The oxalate content of samples was measured according to the method described by Reimann et al (2000).

An eluent was prepared with 0.3816 g of Na_2CO_3 diluted to 1 000 ml with milli-Q water in a volumetric flask. A regenerant was prepared by mixing 3 ml H_2SO_4 with 1 000 ml milli-Q water in a volumetric flask.

A standard stock solution of 1 000 ppm oxalate was prepared by dissolving 1.5223 g $Na_2C_2O_4$ in 1 000 ml Milli-Q water in a volumetric flask. Standards used for establishing a calibration curve were 3, 10, 30, 150 and 400 ppm. Since several articles reported that the diluted oxalate standards were stable for only one day the dilution of standards were performed just before they were run (SCAN N39:05, 2005) & (Menon & Mahle, 1983).

The samples were pretreated differently depending on if it was process liquor, a pulp sample or wood chips. For 50 ml of liquor, approximately 10 g of strongly acidic cation exchange resin (Amberlite IR-120 (H^+)) was added in order to achieve pH lower than 2. If pH was not low enough a small amount of HCl of 10% concentration was added. The sample was put in a sealed plastic bottle and placed in a shaking water bath at 70 °C for 30 minutes.

For pulp samples, pulp corresponding to 1.5 g dry matter was added to 100 ml of Milli-Q water and disintegrated in a kitchen mixer. 10 g of acidic cation exchange resin (Amberlite IR-120 (H^+)) was added to about 50 ml of the suspension. If pH was not below 2, a small amount of HCl was added. The sample was put in a sealed plastic bottle in shaking water bath at 70°C for 30 minutes.

For wood chips, about 0.3 g of finely grounded wood powder was mixed with 15 ml Milli-Q water, 5 ml acidic cation exchange resin (Amberlite IR-120 (H^+)) and 3 drops of 10% HCl. The solution was put in a sealed plastic bottle in a shaking water bath at 70°C for 3 hours.

After the samples were pre-treated they were filtered and injected to ion chromatograph 850 Professional IC from Metrohm with a Metrosup A Supp7 column.

3.5 DRY CONTENT

The dry content in all of the samples was measured with a moisture analyzer (Sartorius MA30). The sample was heated to 130°C until all liquid had evaporated and the dry content was calculated automatically from the weight of the sample before and after the heating.

3.6 DENSITY

The density of the black liquor streams were estimated from Figure 4, that shows the dependence of density based on the dry content of the stream.

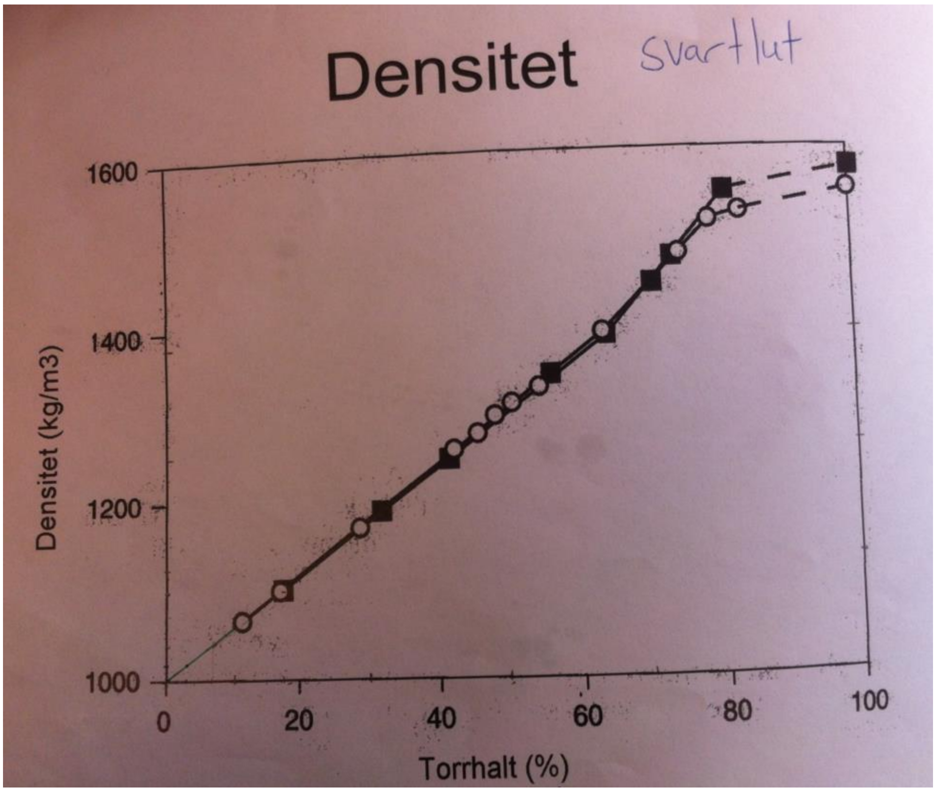

Figure 4. Graph for determination of black liquor density.

As can be seen in Figure 4, the graph only contains values down to a dry content of 16 %, but since it is rather linear for the lower part values were extrapolated for streams with lower dry content. The white liquor density was estimated to 1 150 kg/m^3.

The density of pulp streams were measured by weighing 100 ml of the pulp sample into a beaker of known weight. The weight of the pulp sample could then be calculated and divided with the volume and the density was obtained. The results were then compared with pulp density results from Harris et al (1974) to check the validity of the pulp densities.

4 MASS BALANCES

In the project's time span there was only enough time to establish mass balances over the Swedish softwood pulp mill. Because of that this chapter will only describe how mass balances for this mill were made.

Mass balances are a good tool when working with chemical processes since they give a clear picture of what happens in the process. A typical way of working with mass balances is to establish a control volume over the interesting area, with inlet and outlet streams. (Welty, Wicks, Wilson, & Rorrer, 2008) An example control volume with two inlet streams and one outlet stream can be seen in Figure 5.

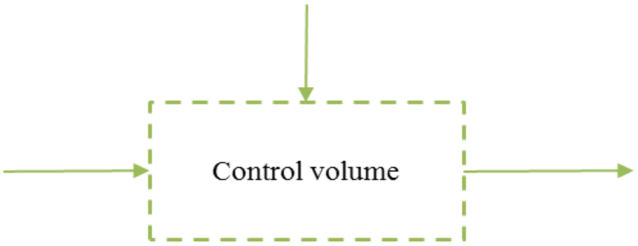

Figure 5. Example of a control volume.

The law of conservation of mass says that mass can't be created or destroyed (Welty, Wicks, Wilson, & Rorrer, 2008). This means that the total mass of the system will be constant and a mass balance over the system can be established according to equation (3).

$$in - out = accumulation \tag{3}$$

The Kraft pulp mill is operated continuously, and under steady process conditions it is assumed that it also operates at steady state. This means that there is no accumulation in the different unit steps, and equation (4) can be simplified to

$$in - out = 0 \tag{4}$$

It is not only the total mass balance that is of interest for the mill, but also balances of the different compounds, and in this thesis balances of carbonate and oxalate ions have been investigated. When considering species, there can also be a reaction taking place with the compound inside the control volume (Sedin & Richards, 2011). This means that the equation (4) becomes instead like equation (5) for the specific compound.

$$in - out \ \pm produced/reacted = 0 \tag{5}$$

The first step was to establish ordinary mass flow balances over the pulp mill. These were obtained by simplifying the different unit operations into boxes represented in a block diagram with in and out streams. The streams were calculated both in ton/h and in dry ton/hour, dry ton meaning the content of dry matter in the stream. Another common way to name dry ton per hour is Bdt, bone dry ton per hour. How dry content was measured is described in section 3.5 Dry content. This was done to be able to see how correct the balance was in two ways instead of just one. In order to establish mass balances, values of mass flows for the pulp mill were needed.

Process values were obtained from the mill's data handling program with the help of a process engineer as a mean value between 1st of March to the 29th of April. The sampling took place in between those dates, and it was considered to be good to have process data for a longer period of time to get stable values.

The majority of the flow values were given in volumetric flow, and they needed to be converted to metric ton per hour. Densities of the different streams were obtained as described in section 3.6 Density and can be seen in Appendix A1: .

Some streams were also given as air dry ton per hour, Adt/h. This means that they are reported as if the dry matter of the stream is 90 % of the total stream. The real stream has another dry content, measured according to 3.5 Dry content and that can be seen in Appendix A1: . To get the actual mass flow the value was recalculated according to equation (6).

$$\dot{m}_{ton} = \frac{0.9 * \dot{m}_{Adt}}{DC} \tag{6}$$

In this equation, DC is the dry content of the stream, $\dot{m}_{ton}$ is the mass flow in ton/h and $\dot{m}_{Adt}$ is the flow in Adt/h.

After the flow data was extracted from the pulp mill and recalculated, there were still some missing flow values of streams. In order to be able to establish mass balances some assumptions had to be done, and those are described unit step by unit step in the following subsections.

After general mass balances were established for all unit steps, balances were made for the carbonate and oxalate ions.

4.1 DIGESTER

The first step in the process, after the wood handling which is not considered in this thesis, is the digester. The inlet streams are wood chips, black liquor, white liquor and steam, and the outlet streams are blown pulp and weak liquor. For the wood chips inlet stream and the weak liquor outlet stream some calculations were needed to get the mass flows. The value for the white liquor flow extracted from the data log system was too low, and the flow was instead estimated with help from engineers at the mill.

The value available for wood chips was the production from the digester. This value had to be divided with the digester yield and the moisture content of the wood in order to get the total mass flow of wood chips in to the digester. The moisture content was estimated to 50% and the digester yield to 47%, typical values normally used by the pulp mill.

The value available for the weak liquor out of the digester was a downstream value, after the liquor had gone through a series of flashes to thicken it. In order to get the flow out of the digester, the mass fraction X that was evaporated in the flashes was calculated. This was done by the expression shown in equation (7), which is derived from a heat balance over the flashes.

$$X = \frac{cp_{hot} \times (T_{hot} - T_{cold})}{\Delta H_{vap,cold}} \tag{7}$$

It was assumed that the evaporated liquid consisted of pure water. The heat of evaporation for water at 110 °C was taken from table in Elliot & Lira (2009). The specific heat for the weak liquor stream was estimated with the help from a process engineer at the pulp mill. A schematic picture of the flash can be seen in Figure 6.

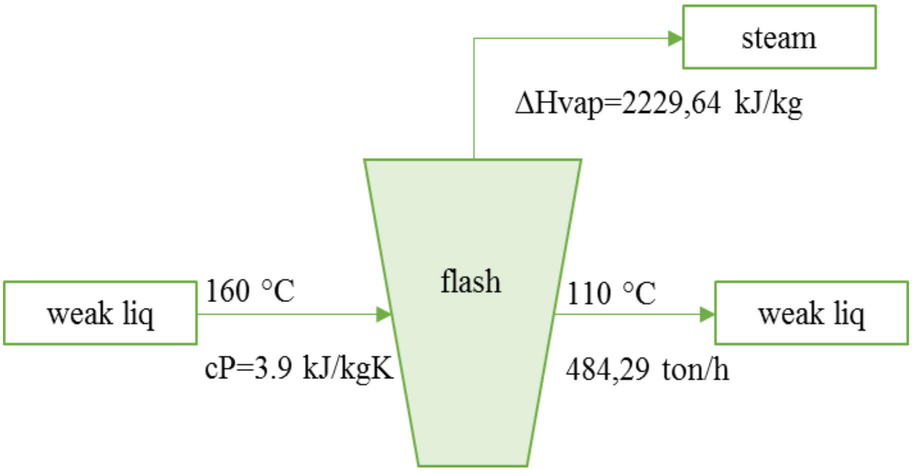

Figure 6. Schematic picture over evaporation of water from black liquor in flashes.

When the mass fraction evaporated was calculated, the value for the weak liquor out of the digester could be calculated by dividing the thickened weak liquor with 1-X.

The resulting block diagram of the digester with mass flows can be seen in Figure 7.

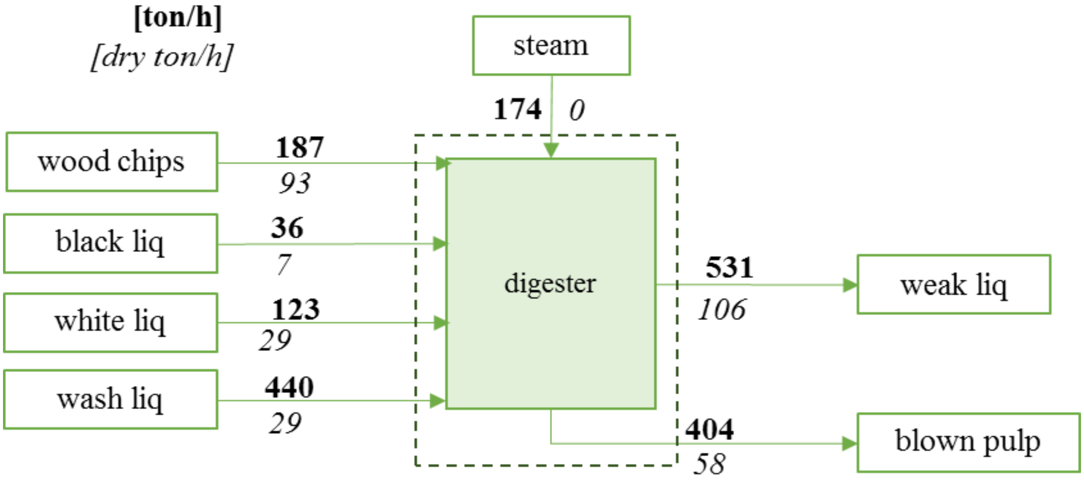

Figure 7. Mass balance over the digester.

Analyse results were available for all streams in and out of the digester except for the steam which was assumed to consist of pure water. The weak liquor out of the digester has the same composition as the black liquor in to the digester, so sample was only taken of the black liquor. Mass flows for the inlet and outlet streams can also be seen in Table 6.

Table 6. Mass flows of streams in and out from digester.

In	[ton/h]	[dry ton/h]	Out	[ton/h]	[dry ton/h]
wood chips	187	93	weak liq	531	106
black liq	36	7	blown pulp	404	58
white liq	123	29			
wash liq	440	29			
steam	174	0			
total	**960**	**159**		**935**	**164**

The difference between the inlet and outlet streams, and thus the error in the mass balance estimation is 2.7% for the total mass. This is considered to be a good result, since there are so many uncertainties in the process data measurements.

4.2 WASHING

After the digester the blown pulp is sent to a washing step where washing liquor is sent into a pressure diffuser counter current to the pulp. The system boundary is set to also include a dilution tank where wash liquor dilutes the washed pulp. This is to prepare the pulp for the screening step that comes afterward. The block diagram for the washing step can be seen in Figure 8, where the system boundary is shown by the dashed line.

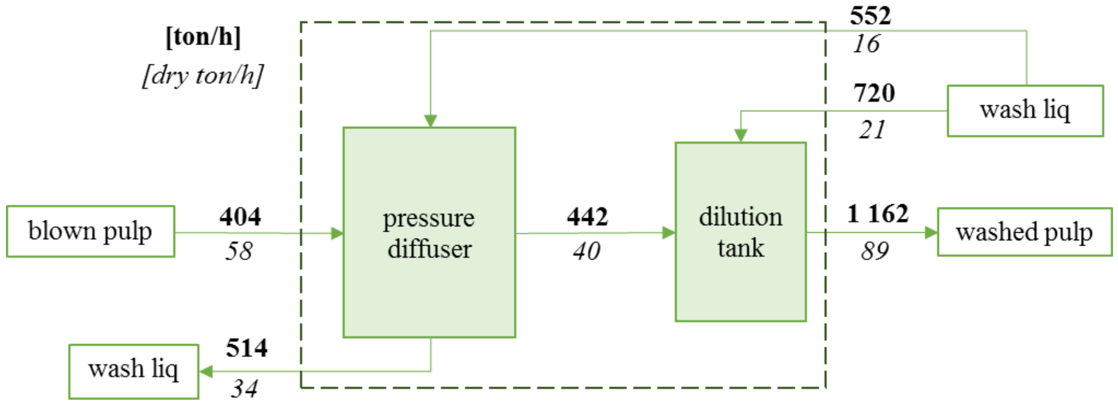

Figure 8. Mass balance over the washing step after the digester.

Analyses were made for the blown pulp, the wash liquor in and out from the pressure diffuser, and for the washed pulp out from the blow tank. To complete the mass balance, the flow of wash liquor in to the dilution tank was calculated from the in and out pulp streams to the dilution tank. The flow of pulp out from the diffuser, both total and the flow of dry content, was calculated from the difference of the inlet blown pulp and wash liquor and the outlet wash liquor. The dilution liquor into the dilution tank is in reality only partly the same as the wash liquor in to the pressure diffuser, but for simplicity it is assumed that they have the same composition.

The values of the inlet and outlet streams can be seen in Table 7.

Table 7. Mass flows of streams in and out from washing after digester.

In	[ton/h]	[dry ton/h]	Out	[ton/h]	[dry ton/h]
blown pulp	404	58	washed pulp	1 162	89
wash liq in PD	552	16	wash liq out	514	34
wash liq in dilution	720	21			
Total	**1 676**	**95**		**1 676**	**123**

The total mass flows in and out of the washing step are exactly the same since four of them are used to calculate the fifth one. Instead, the dry matter flows can be compared. The outlet value of the dry matter stream is 29% larger than the inlet, but it is still considered to be acceptable.

4.3 OXYGEN BLEACHING

After the pulp stream has been washed it is screened to get rid of knots and larger wood pieces which have not been properly digested. Over this screening step no mass balance was established since no interesting reactions should take place there. The next part considered is instead the oxygen delignification step, consisting of a press where excess liquor is removed before an oxygen bleaching stage, and this can be seen in Figure 9.

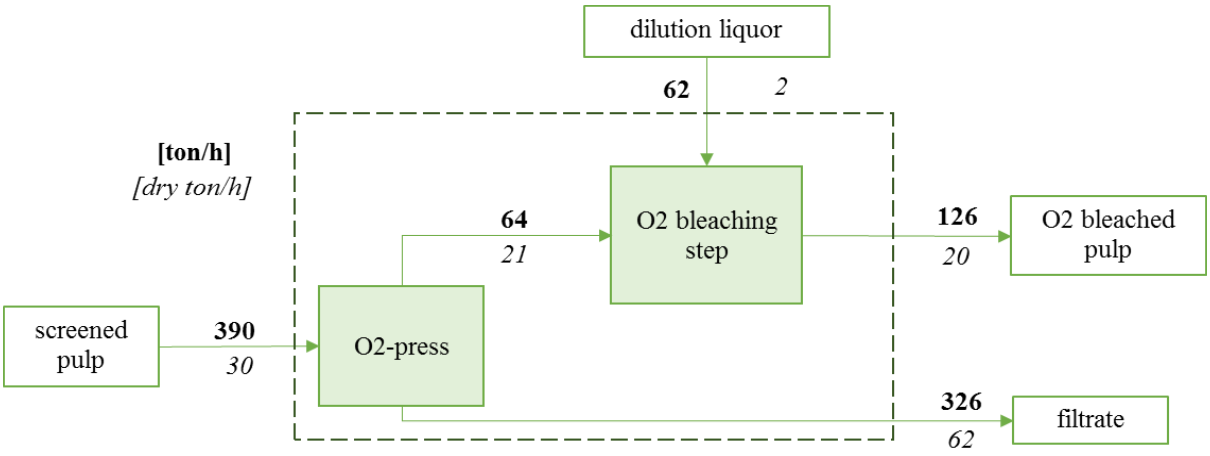

Figure 9. Mass balance over the oxygen bleaching step.

Inlet streams are the screened pulp and dilution liquor to the oxygen bleaching step, and outlet streams are filtrate from the O_2-press and the oxygen bleached pulp.

Analyses were made for the pressed pulp out from the O_2-press, the filtrate from the O_2-press and the O-bleached pulp. In order to complete the mass balance it was assumed that the screened pulp has the same dry content and density as the pulp out from the washing step, so the pulp into the oxygen bleaching has the same composition as the pulp from the previous washing. The filtrate out from the O2-press was calculated from the pressed pulp and the pulp into the press. The pressed pulp was given in air dry ton per hour (Adt/h) and was recalculated as described previously in this chapter. The dilution liquor in to the bleaching step was assumed to be of the same composition as the wash liquor in to the washing step after the digester, and its mass value was calculated from the difference between the inlet and outlet pulp to the oxygen bleaching step. The flows in ton per hour and dry ton per hour can be seen in Table 8.

Table 8. Mass flows of streams in and out from oxygen bleaching.

In	[ton/h]	[dry ton/h]	Out	[ton/h]	[dry ton/h]
screened pulp	390	30	O-bleached pulp	126	20
diultion liquor	62	2	filtrate O2-press	326	9
total	**452**	**32**		**452**	**29**

As for the first washing step, the total mass flows are the same since all values but one were used to calculate the last stream. The flow of dry matter in is 10% larger than the inlet, so the balance is considered as rather correct.

It can be noticed that the dry matter flow in to the oxygen bleaching is much smaller than out from the washing. This is since the pulp stream is divided into two parts after the screening, one bleached and one unbleached line.

4.4 WASHING

Another washing step takes place after the oxygen delignification. The pulp is sent in to a washing sequence consisting of a pressure diffuser and a double diffuser where washing liquor flows countercurrent to the pulp. The block diagram can be seen in Figure 10.

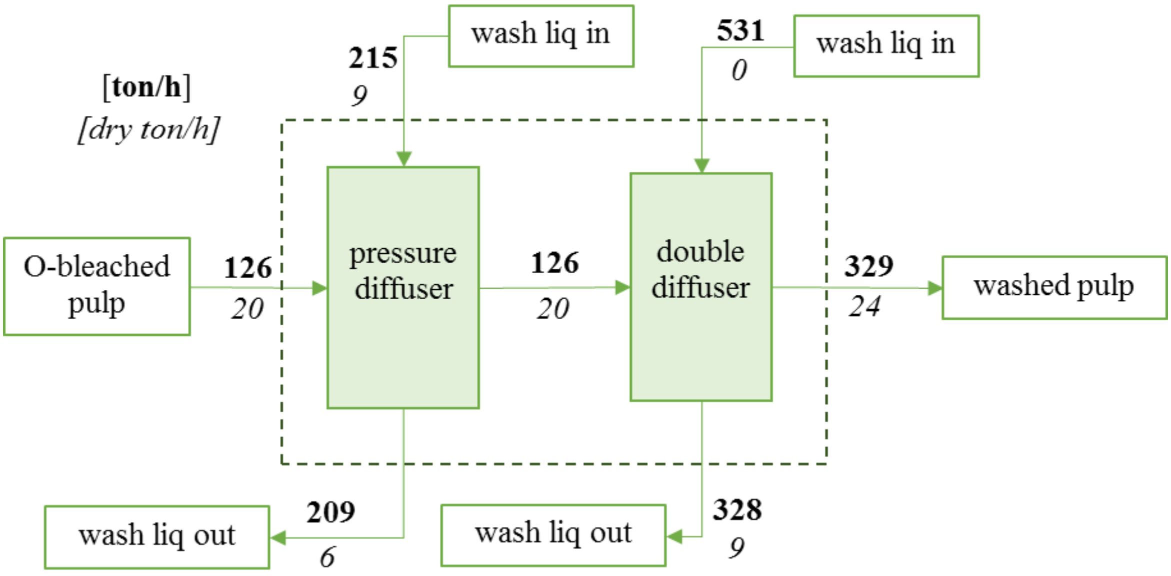

Figure 10. Mass balance over the washing sequence after the oxygen bleaching.

To complete the mass balance it was assumed that the pulp flow to the double diffuser was constant in dry content and density from the pulp in to the pressure diffuser. The flow of wash liquor out from the double diffuser was calculated by the difference of pulp in and out from the double diffuser and the wash liquor to the double diffuser. The wash liquor in to the pressure diffuser was assumed to be the same as the wash liquor out from the double diffuser. The wash liquor out from the pressure diffuser was assumed to have the same composition as the wash liquor in to the washing step after the digester. Analyses were made for the wash liquor in and out of the diffusers, the oxygen bleached pulp and the washed pulp.

The values of the streams can be seen in Table 9.

Table 9. Mass flows of streams in and out from washing after oxygen delignification.

In	**[ton/h]**	**[dry ton/h]**	**Out**	**[ton/h]**	**[dry ton/h]**
O-bleached pulp	126	20	washed pulp	329	24
wash liq in PD	215	6	wash liq out PD	209	6
wash liq in DD	531	0	wash liq out DD	328	9
total	**872**	**25**		**867**	**39**

The dry matter flows differ to some extent, the outlet is 56% larger than the inlet, but the total mass flows are close. Since some assumptions were made for the washing liquor composition, this is considered to be an acceptable result for the mass balance.

4.5 BLEACHING

After washing, the pulp is dewatered in a press to prepare it for bleaching. Bleaching of pulp is performed with the bleaching sequence D-Q-PO. Each bleaching step has an inlet pulp stream, an inlet stream of dilution liquor and after the bleaching step it is pressed to get rid of excess liquor. The mass balance for the bleaching sequence is divided into three parts, which all contains one bleaching step and the associated press.

It is assumed that the diluted pulp out from all bleaching stages have the same density as the pulp in to the bleaching, which was available for measurement. It was also assumed that the dilution liquor in to a stage has the same composition as the filtrate from the press associated to the bleaching, meaning that the dilution liquor flow is countercurrent to the pulp. Mass flow values for the pressed pulps were given in Adt and were recalculated as described in section Mass balances. The values for the total mass flow of filtrate out from presses and dilution liquor in to bleaching stages were calculated from the pulp streams in and out to the unit.

The first step is the D-stage, and the balance includes, except from the D-tower and the D-press, also the dewatering press before the stage. The block diagram can be seen in Figure 11.

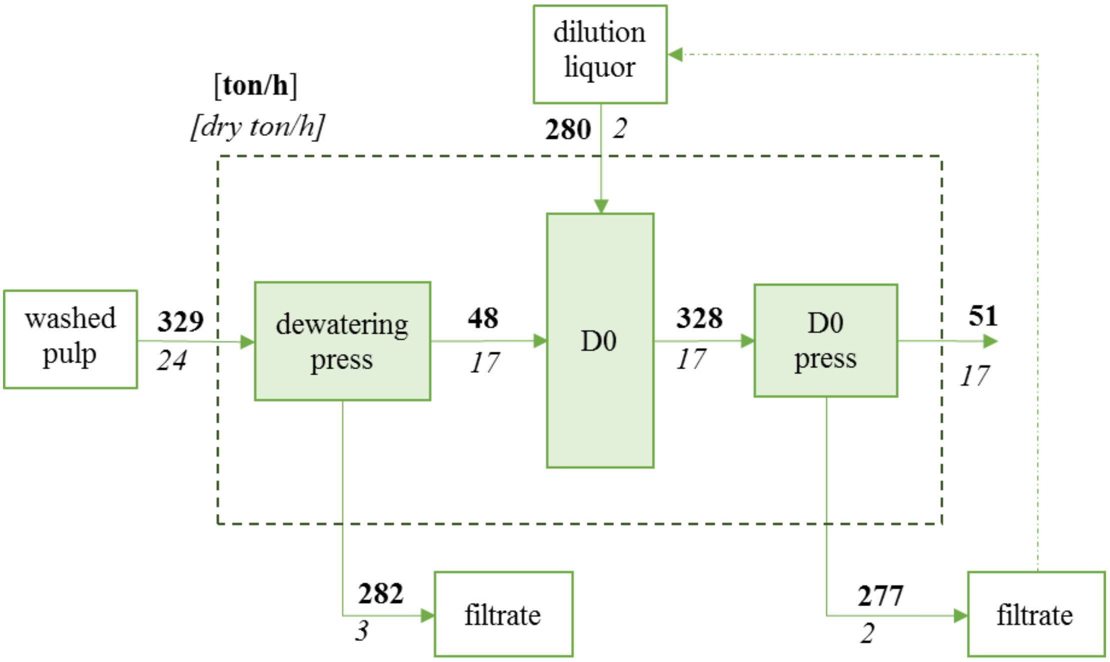

Figure 11. Mass balance over D0 bleaching.

Mass flow values for both total and dry matter of the streams can be seen in Table 10.

Table 10. Mass flows of streams in and out from D0-stage.

In	[ton/h]	[dry ton/h]	Out	[ton/h]	[dry ton/h]
washed pulp	329	24	filtrate dewatering press	282	3
dilution D0-stage	280	1	filtrate D0-press	277	2
			pulp D0-press	51	17
total	**609**	**25**		**609**	**22**

The next step is Q-stage, including the press after the bleaching tower. The block diagram can be seen to the left in Figure 12.

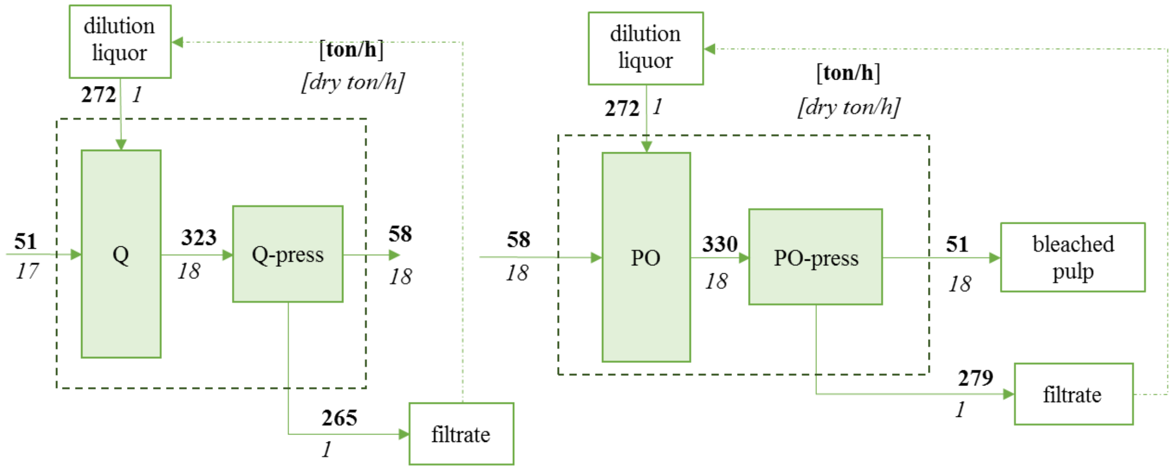

Figure 12. Mass balances over the Q and the PO bleaching steps.

Values for mass flows can also be seen in Table 11.

Table 11. Mass flows of streams in and out from Q-stage.

In	[ton/h]	[dry ton/h]	Out	[ton/h]	[dry ton/h]
pulp D-press	51	17	pulp from Q-press	58	18
dilution Q-stage	272	1	filtrate Q-press	265	1
total	**323**	**18**		**323**	**19**

The last bleaching step, which produces the final fully bleached pulp, is the PO beaching step. This can be seen to the right in Figure 12. The mass flows can also be seen in Table 12.

Table 12. Mass flows of streams in and out from PO-stage.

In	[ton/h]	[dry ton/h]	Out	[ton/h]	[dry ton/h]
pulp from Q-press	58	18	pulp from PO-press	51	18
dilution PO-stage	272	0	filtrate PO-press	279	1
total	**330**	**18**		**330**	**20**

The total mass flows in and out from the different bleaching steps are equal to one another due to how the calculations and assumptions were made. The dry matter flows for the different streams are however similar for all three bleaching stages and does not differ more than 13% in magnitude between inlet and outlet for all bleaching stages, which indicates that the mass balances are valid.

4.6 BLACK LIQUOR EVAPORATION

The weak liquor out from the digester is sent to a black liquor evaporation plant, where its dry content is changed from about 20 to 75%. After evaporation the strong black liquor is burned in order to recover both the cooking chemicals and the energy from the lignin dissolved in the black liquor.

The weak liquor out from the digester is sent through a series of flashes and mixed with intermediate strong liquor before it enters the evaporator train, but since the weak liquor in to effect 5 was a sample point, what happens before that is not considered. The evaporator train contains of 7 effects for the Kraft pulp, and two effects for CTMP liquor. The CTMP liquor enters into effect 1, see Figure 13. Samples were taken between effect 7 and 4, effect 3 and 2, after effect 2 both before and after mixing with ash, and after effect 1. The CTMP liquor in to effect 1 was also analysed. The mass flows of the evaporator train can be seen in Figure 13.

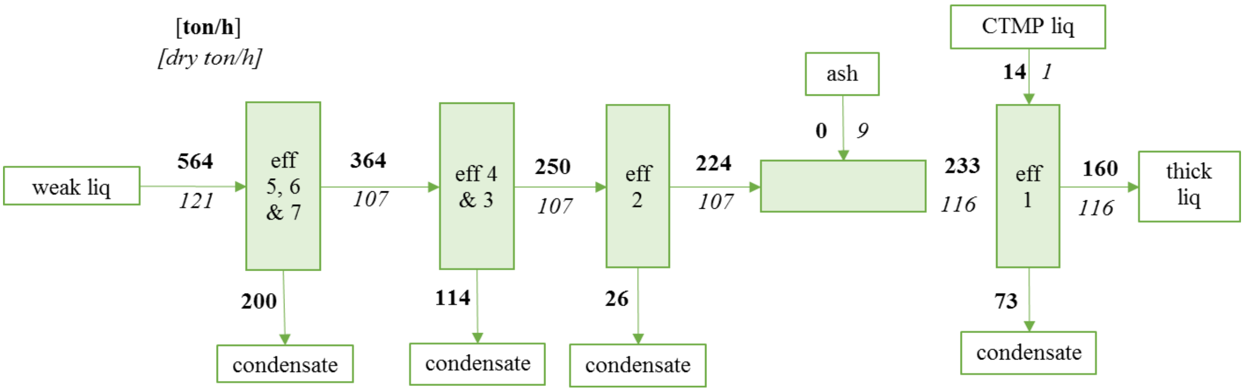

Figure 13. Mass flows in the black liquor evaporation plant.

It was assumed that the condensates out from the different evaporator effects are the difference between the liquor in to the effect and the liquor out of the effect. Flow values were only available for the liquor in to effect 5 and in to evaporator effect 4. After that it was assumed that the dry matter was constant during the evaporation, and the measured dry content was used to calculate the flow value. After effect 2 it was assumed that the liquid content was constant and that the ash only consisted of dry matter, and the ash flow could then be calculated. The values of the streams can be seen in Table 13.

Table 13. Mass flows of streams in black liquor evaporation.

Stream	**[ton/h]**	**[dry ton/h]**
weak liquor in to eff 5	564	121
condensate out eff 5,6 & 7	200	0
liquor in to eff 4	364	107
condensate out eff 4 & 3	114	0
liquor in to eff 2	250	107
condensate out eff 2	26	0
intermediate strong liquor	224	107
ash	9	9
liquor in to eff 1	233	116
CTMP liquor in to eff 1	14	1
thick liquor out from evaporation plant	160	116
condensate out eff 1	73	0

5 CALCULATIONS

The calculations used to determine the content of metal ions throughout the fibre line, and the content of carbonate respectively oxalate content in process streams will be described in this section.

5.1 METAL ION PROFILES

It is of interest to follow how the positive counter ions behave through the fibre line in the pulp mill. The metal ions are presented to the process from the wood and the cooking chemicals, and since scaling problems occur when carbonate and oxalate react with metals it is also wanted to wash out the metals from the process.

Metal ion profiles for sodium, calcium and potassium are established by plotting the concentrations of metal ions throughout the pulp mill against the sampling points for both pulp samples but also filtrates and carryovers. Both filtrates and carryovers are liquid samples corresponding to a pulp stream, and in this thesis the definition of a filtrate is the liquor pressed out from the pulp in a press, and the carryover is the liquor present in the pulp sample.

The concentration of metal ions is presented in two different ways for pulp and liquor samples. For the pulp stream the concentration is calculated as gram metal per bone dry ton of pulp, and for the carry over or filtrate corresponding to the different pulp streams as milligrams per litre. The different sampling points used for the graphic representation can be seen in Table 14.

Table 14. Sampling points for pulp streams used for metal ion profiles.

Pulp stream	Acronym	Filtrates and carry over	Acronym
wood chips	WC	carryover blown pulp	cBP
blown pulp	BP	carryover washed pulp	cWP1
washed pulp	WP1	filtrate from O2-press	fOOP
pulp out from oxygen bleaching	OOP	carryover pulp to bleaching	cPB
washed pulp to bleaching	PB	filtrate dewatering press	fDWP
pulp from dewatering press	DWP	filtrate D-press	fDP
pulp from D press	DP	filtrate Q-press	fQP
pulp from Q press	QP	filtrate PO-press	fPOP
pulp from PO press	POP		

For pulp streams, the concentration in g/Bdt was calculated by multiplying the value in g metal per kg sample of metal ion as measured by AAS (see section 3.2.2 Atomic absorption spectroscopy) with the mass flow of the stream, and then dividing it with the dry matter of that stream. Total mass flows and dry matter flows are the ones determined and described in the section Mass balances.

The concentration of filtrates and carryovers is plotted in mg/l. The values for these were obtained by multiplying the density of the sample in kg/l with the measured concentration of the sample in mg per kg sample. Values of metal concentrations can be found in Appendix A2: Metal ion content and densities in Appendix A1: .

The resulting graphs together with discussions of the appearances of the metal ion profiles can be found in section 6.1 Metal ion profiles.

5.2 CARBONATE CONTENT OF STREAMS

The carbonate ion content was determined in mg/l for all process liquors, as described in section 3.3 Carbonate ion content. The measured values can be seen in Appendix A3: Carbonate and oxalate content. In order to check if the measured values were reasonable some comparison to values found in literature was done. For black and white liquor, reference values were presented in the test method (SCAN N32:98, 1998) and the measured ones correspond well with these. The carbonate content in the pulp after oxygen bleaching was a bit higher compared with earlier results from the lab. A discussion of possible reasons to this will follow in section 6.2 Carbonate ion balances.

When calculating the carbonate content of the streams, it was assumed that all carbonate present in the stream was in the liquid phase and thus no carbonate was bound to the fibre. This could be a source of error, and it should be kept in mind when analysing the results.

The mass flow of carbonate was calculated according to equation (8).

$$\dot{m}_{carbonate} = \frac{\dot{m}_{liquid} * X}{1\,000} \qquad (8)$$

In this equation, $\dot{m}_{carbonate}$ is the flow of carbonate in kg per hour, X is the carbonate content in mg/kg from the analysis, $\dot{m}_{liquid}$ is the liquid part of the total mass flow of the stream in ton per hour calculated by subtracting the dry matter from the total stream, and the division with 1 000 is to get the unit in kg.

Calculation of carbonate content was done for each stream, and the results can be seen in section 6.2 Carbonate ion balances.

5.3 OXALATE CONTENT OF STREAMS

The measured oxalate concentrations can be seen in Appendix A3: Carbonate and oxalate content, given in mg per kg sample.

The oxalate content of the wood chips was calculated to 0.4 kg per ton of dry wood. It was compared with values of oxalic content of hardwood and pine reported by Ulmgren and Rådeström (2002), who reported values between 0.2-0.7 per tonne of 100 % dry wood, so the measured value is in agreement with earlier reported results.

The oxalate content of the different streams was calculated as mg per Bdt, but this was done a bit differently for pulp streams with low dry content and for pulp streams after presses, where the dry content was higher. In the next few paragraphs it will be described how.

For the pulp streams with low dry content, meaning blown pulp, the washed pulp after the digester and the pulp out from oxygen bleaching, the oxalate content was calculated in two steps. The oxalate content in both the total stream respectively in the carryover sample was calculated first, and then the difference between them gave how much that was bound to the fibre. The total oxalate content was then calculated by adding the oxalate content bound in the fibre with the oxalate in the carryover, giving a total concentration.

A wet pulp stream that goes in to a press is afterwards divided in one pulp stream and one filtrate stream. The presses considered in the fibre line were the O_2 press and the different presses of the bleaching plant. For pulp samples out from these presses, it was assumed that all oxalate was in the pure fibers. The oxalate concentration was then recalculated to mg per kg dry solid by dividing the measured value in mg/kg sample with the dry content. This corresponds to an oxalate concentration in mg per Bdt, with the assumption that no oxalate is in the carryover. This makes a small error, but in comprehension with the uncertainty in the general mass balances this is negligible.

For filtrates out from presses, the flow was recalculated to m^3/Bdt by dividing the volumetric flow with the production of dry ton pulp out from each press. This flow was then multiplied with the oxalate content of that stream, in mg/l. That value was obtained by multiplying the oxalate content in mg/kg sample with the sample density. This method was also used when calculating oxalate content of process liquors, where the whole sample was in liquid phase, e.g. black liquor and wash liquor.

Results from the oxalate content calculations can be seen in section 6.3 Oxalate ion balances.

6 RESULTS AND DISCUSSION

Results for metal ion profiles for sodium, calcium and potassium for the fibre line, together with balances for first carbonate and then oxalate ions are presented and discussed in this section.

6.1 METAL ION PROFILES

The metal ion content profile through the pulp mill for sodium can be seen in Figure 14, for calcium in Figure 16 and for potassium in Figure 17. The acronyms representing the x-axis are the acronyms presented in section 5.1 Metal ion profiles, and represent the sampling points. The left graph in each figure contains the profile for the pulp samples, and the right one the profile for filtrates and carry over. Discussions of the profiles follow after each figure.

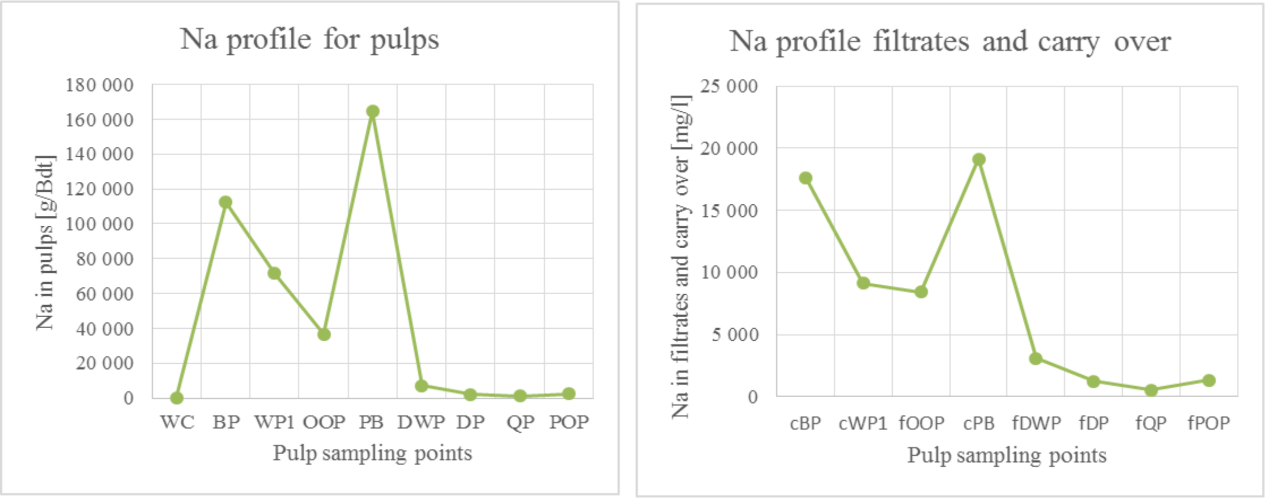

Figure 14. Sodium ion profiles through the pulp mill, pulp samples to the left and liquors to the right.

For sodium there is a decreasing trend throughout the pulp mill, except for pulp stream in to bleaching. What has happened since the step before is a washing sequence, so the sodium is probably presented to the pulp with the washing liquor. The washing liquor is sent counter current to the pulp throughout the pulp mill, so it is expected that the washing liquor in this early stage of the process contains sodium. This since it has been used to wash the pulp later on in the process first. Even though, the sodium content of the pulp in to bleaching seems a bit high compared to previous findings, and it could also depend on that the dry content of the pulp there is lower than for the other pulp streams, and that it has an impact on the calculations.

The first value of the sodium pulp profile is much lower than the next ones. This is explained by that it is the wood chips value, and after that cooking liquor is added. The active cooking chemicals in kraft pulping are NaOH and Na_2S, so it is expected that the sodium content is rapidly increased in this stage.

The sodium profile for the bleaching sequence can be seen in a more close up version in Figure 15. There it can be seen that, as expected, the concentration goes up in the PO stage.

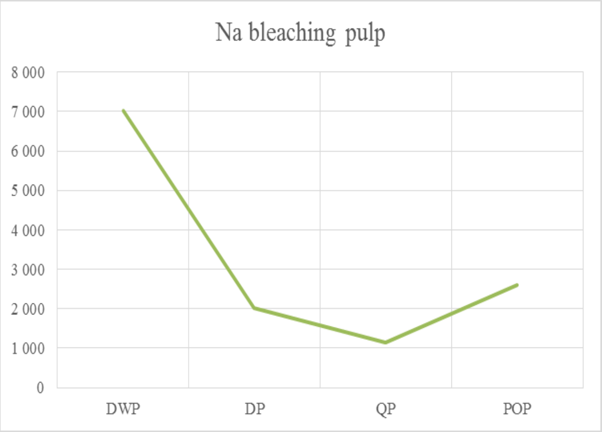

Figure 15. Metal ion profile for Na in bleaching plant.

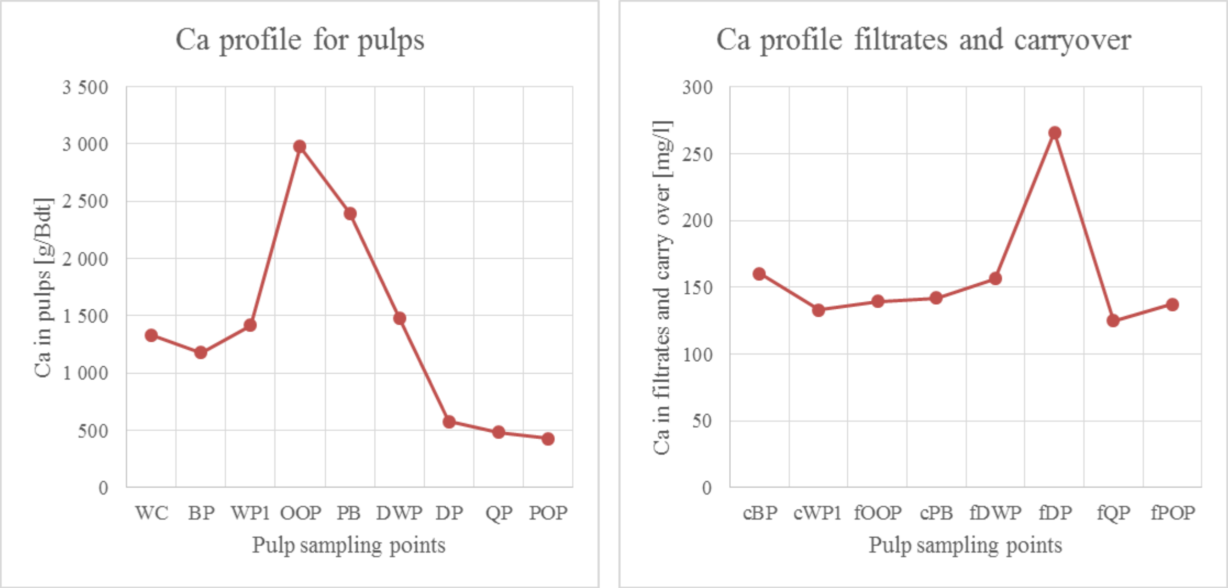

Figure 16. Calcium ion profiles through the pulp mill, pulp samples to the left and liquors to the right.

Calcium is the only one of the three evaluated metal ions that can be said to have a significant intake with the wood chips. The calcium content of the wood chips is in the same order of magnitude as for the blown pulp, and in comparison both sodium and potassium increases significantly when the process liquors are introduced.

The profile of calcium for the filtrates and carryovers is rather constant, except for the pulp after the D0 bleaching. This indicates that the calcium cannot be washed out, and it will stay in the process liquor. Since calcium salts are of importance in scaling, this is an important observation.

For the pulp samples, there is an increase of calcium in the oxygen bleached pulp. Otherwise there is a decreasing trend, which means that the calcium is washed out from the final pulp.

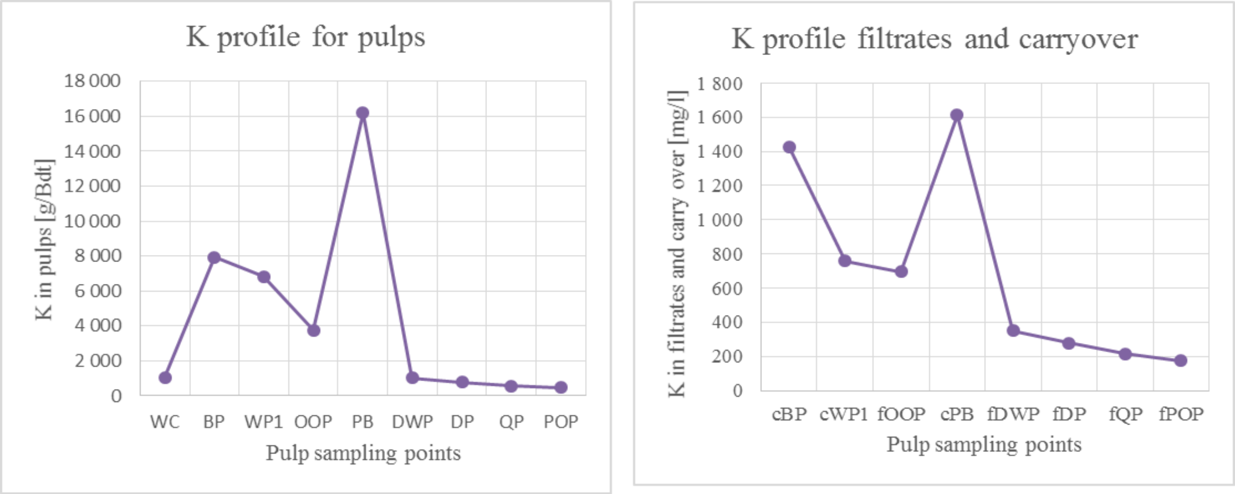

Figure 17. Potassium ion profiles through the pulp mill, pulp samples to the left and liquors to the right.

The trend for the potassium ions is similar to that for sodium. There is not so much potassium introduced with the wood compared to what is introduced with cooking liquors in the digester, but it is still more compared with sodium.

6.2 CARBONATE ION BALANCES

Carbonate content of the streams together with balances over each process step in the process are presented and discussed in this section. The carbonate content of streams is presented as kg carbonate per hour. If needed, the results could be transformed to kg carbonate per BDT (bone dry ton) by dividing the carbonate content with the dry content of the outlet stream in each process step, those values can be found in section Mass balances. The calculations made in this step are done to see trends in carbonate formation, and that can be seen with these values as well.

Carbonate content was only measured for process liquors, meaning that it is assumed that all carbonate present in the stream is in the liquid phase. This might contribute to errors in the measurements of carbonate.

6.2.1 DIGESTER

The carbonate content of inlet and outlet streams can be seen graphically in Figure 18 and in Table 15.

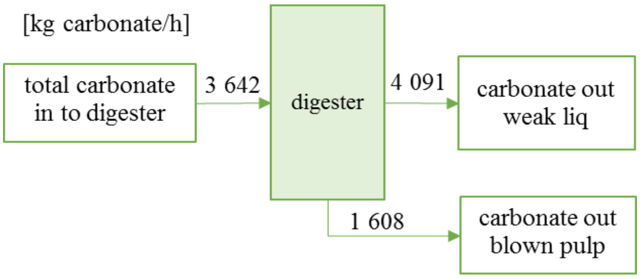

Figure 18. Carbonate balance over the digester.

Table 15. Carbonate content in digester streams.

	Total in [kg/h]	Total out [kg/h]	Difference[kg/h]
Digester	3 642	5 699	2 057

According to this result it appears as if there is a net production of carbonate in the digester. There are a lot of possible error sources in the mass balance calculation over the digester, but the outlet content of carbonate is 56% larger than the carbonate presented with the inlet streams. This should be larger than the error of margins, and it can be concluded that there is a production of carbonate in the digester. The formation over the digester is calculated to 46.8 kg carbonate/Bdt.

Most of the carbonate out from the digester can be found in the weak liquor stream. This implies that there will be more problems with carbonate related process disturbances in the black liquor evaporation plant than in the fibre line.

6.2.2 WASHING AFTER DIGESTER

The carbonate content of inlet and outlet streams can be seen graphically in Figure 19 and as total in and out with the difference between them in Table 16.

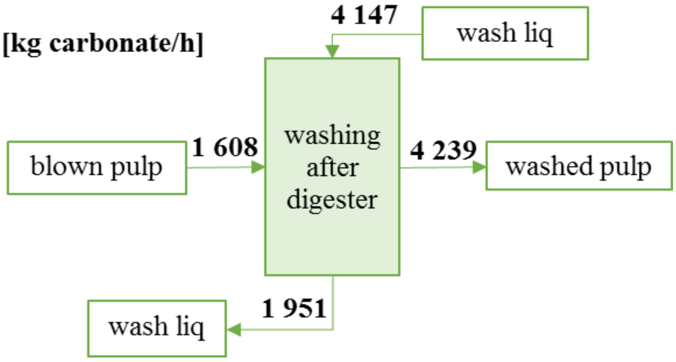

Figure 19. Carbonate content in washing streams.

Table 16. Carbonate content in washing streams.

	Total in [kg/h]	Total out [kg/h]	Difference [kg/h]
Washing	5 755	6 190	435

Since this is a washing step there should not be any reactions involving carbonate here. The carbonate out from the pressure diffuser is 8 % larger than the inlet value, and this is probably within measurement and mass balance errors. It seems as if the carbonate is just reallocated from the washing liquor to the pulp stream, and that is an expected and good result.

After washing, the pulp stream contains more carbonate than before. The carbonate comes from the washing liquor, which means that this step does not wash with respect to carbonate. The washing step still has a function and washes out other compounds.

6.2.3 O_2 BLEACHING

The carbonate content of inlet and outlet streams can be seen graphically in Figure 20 and in Table 17.

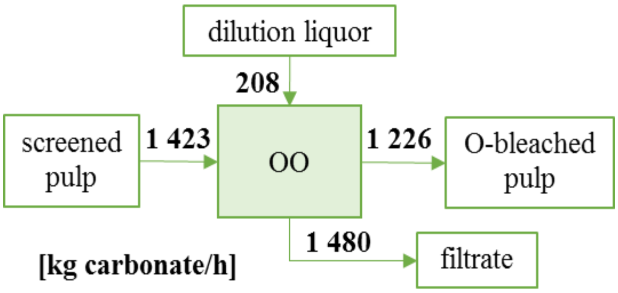

Figure 20. Carbonate content in oxygen bleaching.

Table 17. Carbonate content in O_2-streams.

	Total in [kg/h]	Total out [kg/h]	Difference [kg/h]
O_2	1 631	2 706	1 075

It might be noted that the inlet pulp stream contains less carbonate than the outlet from the previous washing step. This is to be expected, since the pulp stream is divided to one unbleached and one to be bleached pulp stream after the washing, and this stream is thus smaller.

The carbonate content of the outlet streams are 66% larger than the inlet. This seems to be more than can be described by the error margin and it implies that there is a formation of carbonate in the oxygen delignification step. The formation of carbonate can be calculated to 460 kg carbonate/Bdt.

Even though the trend shows that there should be a formation of carbonate taking place, the carbonate values for the pulp streams seem a bit high. This could depend on that it took some time from sampling to the time of analysis, and that the sample in the meantime continued to react. There could have been some aging of the samples, causing further reactions that increased the content of carbonate in the samples. This could be an explanation to the seemingly high values, but no further studies were done on this subject.

One possible way to reducing effects of aging of the pulp sample could be to also include the next washing step in the balance over the oxygen delignification and thus increase the system limit, but this has not been considered in this report.

6.2.4 WASHING AFTER O_2-BLEACHING

The carbonate content of streams in the second washing sequence can be seen in Figure 21 and in Table 18.

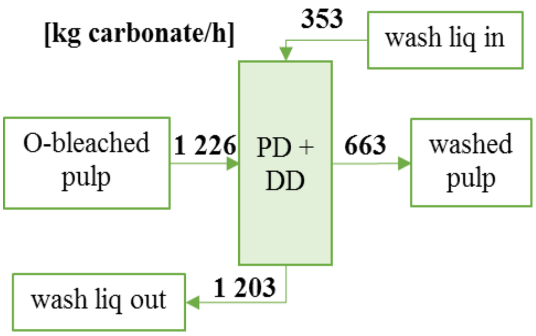

Figure 21. Carbonate content in washing after O_2

Table 18. Carbonate content of streams in washing after O_2.

	Total in [kg/h]	Total out [kg/h]	Difference [kg/h]
Washing	1 579	1 866	287

For the second washing sequence the same reasoning as for the first could be used, meaning that no carbonate should be formed in this step. The outlet carbonate stream is 18% larger than the inlet, which is larger than for the other washing step. However, it is still not so large that it can be excluded that the difference is within the error margin, and it cannot be said that carbonate is formed in the washing step.

6.2.5 BLEACHING SEQUENCE

The carbonate content in the different streams of the bleaching sequence can be seen in figure Figure 22.

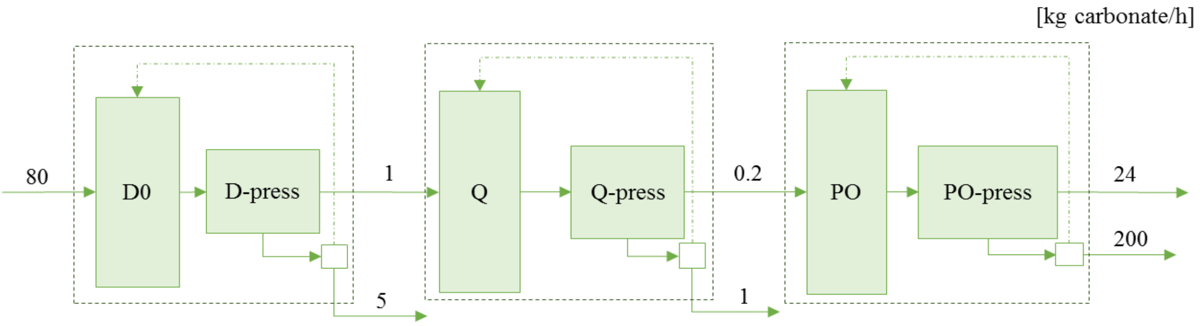

Figure 22. Carbonate content for the bleaching sequence.

The balance over each step with total inlet and outlet content for D0, Q and PO bleaching steps can also be seen in Table 19. The results of the balances are discussed below for each step.

Table 19. Carbonate content for bleaching stages.

	Total in [kg/h]	Total out [kg/h]	Difference [kg/h]
D0 bleach	80	6	-74
Q	1	1	0
PO	0.2	225	224

The outlet pulp stream from the *D0 bleaching step* contains close to no carbonate, which makes the carbonate balance over the step has a negative production. This means that carbonate is consumed, and that can be explained by the fact that D0 is an acidic stage. When adding acid to a sample containing carbonates, the carbonate is converted to carbon dioxide which is in a gaseous phase and thus it is released from the pulp stream.

In the *Q bleaching step* the carbonate content is unchanged, even though most of the carbonate is washed out in the press after the bleaching step. There is not a large amount of carbonate in the pulp stream in to the last bleaching stage. This is also within the expected result, since the chelating agent is not supposed to react with the carbonate.

Over the last step, *the PO bleaching*, there seems to be a formation of carbonate of about 9.7 kg/Bdt. The formation may be a bit higher compared to previous findings, and this could as in the case for the oxygen bleaching be a result of aging of samples. The trend that it is formed should be correct, but how much cannot with certainty be determined by these results.

6.2.6 EVAPORATION

The values that were obtained can be seen in Figure 23 and in Table 20.

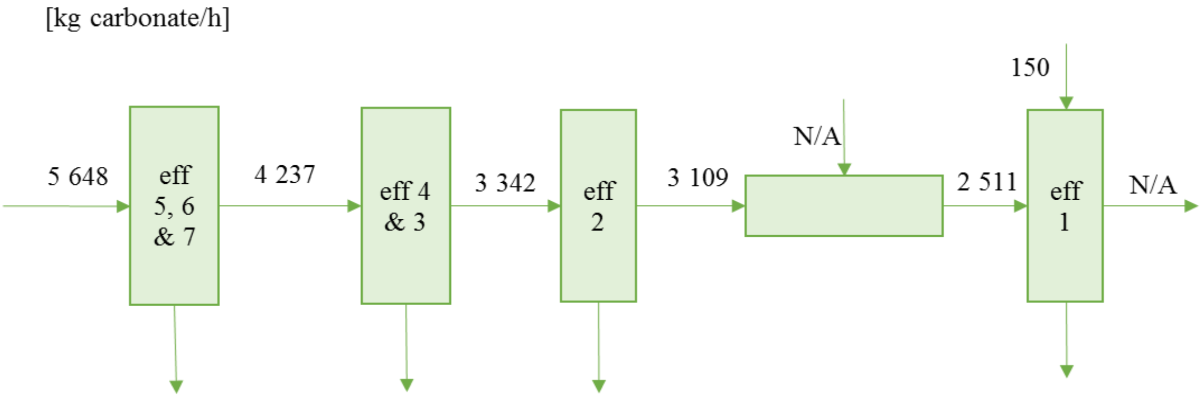

Figure 23. Carbonate content of evaporation streams.

Table 20. Carbonate content during black liquor evaporation.

Stream	Carbonate [kg/h]
weak liquor in to eff 5	5 648
liquor in to eff 4	4 237
liquor in to eff 2	3 342
intermediate strong liquor	3 109
ash	N/A
liquor in to eff 1	2 511
CTMP liquor in to eff 1	150
Strong liquor out	N/A

For the ash and the strong liquor, no analyse results were available, and the carbonate content is shown as not available (N/A) in Table 20. According to the calculations performed, the carbonate content is decreased for each step in the evaporation train.

The evaporation results are not the most reliable. No analysis was able to be performed on the strong black liquor, and there was not so many process data available for intermediate liquors, which means that a lot of assumptions have been made to establish the mass balances. This indicates that the results of the mass balances for carbonate in the black liquor evaporation maybe not is valid, and in order to get a reliable result this part of the work should be rerun.

6.3 OXALATE ION BALANCES

Oxalate balances over the digester, the oxygen bleaching step and the bleaching sequence are presented and discussed in this section.

6.3.1 DIGESTER

The calculated content of oxalate in the inlet and outlet streams of the digester can be seen in Figure 24. The total oxalate content in and out, together with the difference between the two, can be seen in Table 21.

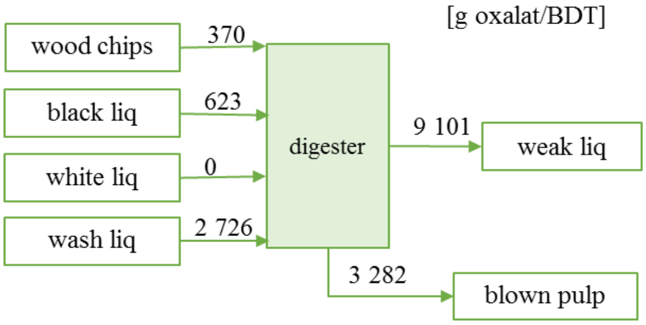

Figure 24. Oxalate content of digester streams.

Table 21. Oxalate content of digester streams.

	Total in [g/BDT]	Total out [g/BDT]	Difference [g/BDT]
Digester	3 719	12 384	8 665

The oxalate content in the outlet streams is more than twice as much as that for the inlet streams. This indicates that there is a formation of oxalate in this step of 8.7 kg oxalate/Bdt.

The oxalate content of the black liquor and the weak liquor was somewhat difficult to measure, but for this sample a result was obtained. More discussion of the difficulties with determining black liquor oxalate content can be found in the section 6.2.6 Evaporation. Since three quarters of the oxalate goes out with the weak liquor, the numeric value of formed oxalate could be discussed. The oxalate content of the blown pulp is in parity with the total inlet. The ion chromatography of the weak liquor showed that there was oxalate in the sample, even if it might be unsure if the value is absolutely correct. This indicates that there is a formation of oxalate over the digester, regardless of the fact that the measurements might not be exactly correct.

The mechanisms behind the formation of oxalate in the pulping process have not been looked at to any further extent in this study, but previous studies states that the formation could depend on the alkalinity in the process. The kinetics of the formation follows the relation showed in equation 9 (Yu, 2005), (Yu, Rae, & Ni, 2004).

$$r \propto [OOH^-] \qquad (9)$$

6.3.2 O_2 BLEACHING

The oxalate content of inlet and outlet streams can be seen graphically in Figure 25 and in Table 22.

Table 22. Oxalate content of O_2 bleaching streams.

	Total in [g/BDT]	Total out [g/BDT]	Difference [g/BDT]
O_2	8 185	13 231	5 046

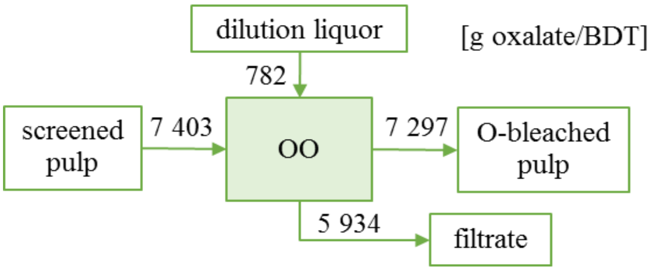

Figure 25. Oxalate content of O_2 bleaching streams.

The outlet oxalate is about 60% more than the inlet, indicating that there is a formation of oxalate, about 5 kg/Bdt, during the oxygen bleaching. The formed oxalate seems however a bit high, and a discussion about why this could be follows after the oxalate balance over the bleaching sequence. Another source of error could be the low dry content of the pulp in to bleaching.

When peroxide is present, the formation of oxalate is also depending on the presence of chromophores from the lignin. According to He et al (2007) chromophores can react with peroxide and then be further oxidized into oxalate.

6.3.3 BLEACHING

The oxalate content in the streams of the bleaching sequence can be seen in figure Figure 26 and in

Table 23.

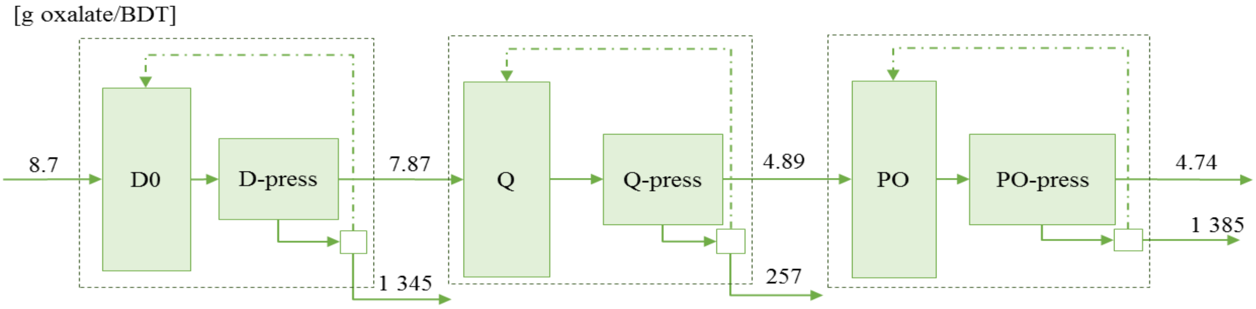

Figure 26. Oxalate content of streams in the bleaching sequence.

Table 23. Oxalate content of bleaching streams.

	Total in [g/BDT]	Total out [g/BDT]	Difference [g/BDT]
D0	8.7	1 353	1 344
Q	7.9	252	254
PO	4.9	1 390	1 385

From these results, it seems as if there is a formation of oxalate occurring in the D and PO stages, the formation being 1.3 kg oxalate per ton pulp in the D stage and 1.4 kg for the PO stage. For the Q stage, there is a larger amount of oxalate out than in, but the difference is not so large and there are so many possible errors in the calculations that it cannot be said to be significant.

Some previous work has been done on oxalic acid formation in the bleaching sequence. Krakowski & Marton (Krasowski & Marton, 1983) states that about 0.8-1 kg oxalic acid per ton pulp is produced in the bleaching sequences CEDED. In the work by Ulmgren & Rådeström (2002) the formation of oxalate in is said to be about 0.5 kg per ton for D and PO stages. Compared to these values, the ones measured in this thesis is a bit higher. In another article from Ulmgren & Rådeström (2002) describes formation of oxalate when storing filtrates from a D bleaching stage at high temperature. It is also stated that when stored refrigerated, no significant amounts of oxalate are formed. The samples that were analysed in this work were stored at room temperature during transport, and it could be so that the samples continued to form oxalates during storage. This could possibly explain why the values of formation, not only in the bleaching sequence but also for the oxygen bleaching, are higher than expected. The conclusion to draw from the balances over the bleaching is that there probably is a formation of oxalic acid in the D0 and PO stage, but to see the exact amount formed the analysis should be rerun with fresh samples.

6.3.4 EVAPORATION

No good results were obtained from the ion chromatography analysis for the different strong black liquors. This is probably a consequence of the high dry content in the streams. For the ion chromatographs ability to detect oxalate the sample pH had to be lowered below 2, and for evaporation samples a large amount of hydrochloric acid was needed to reach the desired pH. This led to that the base line of the chromatogram was disturbed by a large chloride peak, and it was impossible to tell what the content of oxalate was in the sample.

When using the method as described by Reimann et al (2000), dilution of black liquors with a high dry content should be done in order to get a valid result. This was not fully investigated, but the trend when analysing was that it was easier to get results when the dry content was somewhere below 10-20%.

7 CONCLUSIONS

From this thesis work it can be concluded that there is a possible formation both oxalate and carbonate in the digester and the oxygen delignification. In the bleaching sequence, carbonate is formed during PO bleaching and oxalate is formed during D0 and PO bleaching. How much that is formed is somewhat uncertain, since there a suspicion of aging of the samples.

The results from this study can thus be seen more as indications of reactions that could take place in the different steps of the Kraft process than as definite values of how much that is formed. In order to investigate the amounts formed more work are needed, and possible future works are discussed in section Further studies.

8 FURTHER STUDIES

This thesis has investigated the behaviour of carbonate and oxalate ions in one Swedish softwood Kraft pulp mill. It has given some indications on how oxalate and carbonate behave in the different process steps, but the results have several possible error sources. In order to be more certain of the validity of the results, the analysis should be rerun in order to avoid possible aging effects of the samples. Deeper studies for each process step should also be conducted, to give a more quantitative understanding on how the formation occurs.

The metal ion profiles could be used in order to further investigate the mass balances of carbonate and oxalate ions. This has not been done in this thesis, and is proposed as a further study.

For the future it is also of great interest how these ions behave in Kraft pulp mills using eucalyptus as raw material, since eucalyptus pulping is not as well documented as softwood pulping. Future work should thus also include establishing mass balances over the eucalyptus Kraft pulp mill in the same way as for the softwood pulp mill.

One eucalyptus kraft pulp mill was contacted for this thesis, and samples were shipped to Sweden. Analysis of metal ion content and carbonate content have been performed for the eucalyptus kraft pulp mill samples, but the oxalate content needs to be experimentally determined. The handling of the samples was not perfect, and these samples are also thought to have aged and it is not certain that the measured results from this work can be used.

The results of the two different mills should be compared with each other, to see where they differ in behaviour. If there are differences in behaviour between these two mills it could indicate that the eucalyptus Kraft pulp mills needs to be treated differently than the softwood mills.

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APPENDIX A: PROPERTIES OF PULP MILL SAMPLES

A1: DRY CONTENT AND DENSITY

Dry content and density of Swedish softwood mill samples.

No	Stream	Dry content (%)	Density (kg/m^3)
1	Wood chips	92.70	
2	Black liquor in to digester	20.03	1 115
3	White liquor in to digester	23.66	1 150
4	Wash liquor in to digester	6.61	1 040
5a	Circulation liquor C5	17.53	1 100
5b	Circulation liquor C6	17.26	1 100
5c	Circulation liquor C8	9.08	1 065
6a	Blown pulp	14.24	946
6b	Carry over blown pulp	8.83	1 050
7	Wash liquor in to pressure diffuser	2.94	
8a	Pulp after blow tank (diluted)	7.70	989
8b	Carryover after blow tank	3.84	
9	Pulp O2-press	33.14	
10	Carryover O2-press	2.85	
11a	Pulp after O-stage	15.70	740
11b	Carryover O-stage	6.28	
12	Wash liquor in to double diffuser	0.00	1 000
13	Wash liquor out from double diffuser	2.62	
15a	Pulp in to bleach plant	7.34	1 003
15b	Carryover pulp in to bleach plant	1.22	
16	Filtrate dewatering press	1.18	1 000
17	Pulp from dewatering press	35.85	313
18	Filtrate D-press	0.58	1 000
19	Pulp out from D-press	33.72	355
20	Filtrate Q-press	0.24	1 000
21	Pulp out from Q-press	31.41	354
22	Filtrate PO-press	0.50	1 000
23	Pulp out from PO-press	35.94	376
24	Black liquor in to evaporation plant	21.42	1 120
25	Intermediate strong liquor	29.47	1 175
26	Liquor before eff2	42.91	1 255
27	Liquor after eff2	47.80	1 285
28	Liquor before eff1	49.73	1 300
29	Strong liquor	73.00	1 470
30	CTMP liquor	4.17	1 030

A2: METAL ION CONTENT

Metal ion content of Swedish softwood mill samples measured by AAS.

No	Sample	Na [mg/kg sample]	Ca [mg/kg sample]	K [mg/kg sample]
1	Wood chips	98	666	523
2	Black liquor into digester	42 131	123	3 472
3	White liquor into digester	94 391	83	7 727
4	Wash liquor in to digester	13 687	117	1 063
5a	Circulation liquor C5	51 041	107	4 176
5b	Circulation liquor C6	43 361	92	3 616
5c	Circulation liquor C8	19 511	103	1 600
6a	Blown pulp	15 994	168	1 132
6b	Carry over blown pulp	16 732	153	1 359
7	Wash liquor in to diffuser	8 229	92	672
8a	Pulp after blow tank	5 502	109	526
8b	Carryover after blow tank	8 841	129	738
9	Pulp after O2-press	5 775	467	589
10	Carryover O2-press	8 262	137	682
11a	Pulp after O-bleaching	12 066	176	1 190
11b	Carryover O-bleaching	18 406	136	1 550
12	Wash liquor in DD	777	118	234
13	Wash liquor out DD	8 100	130	649
15a	Pulp into bleaching plant	3 520	127	269
15b	Carryover pulp into bleaching	3 359	133	381
16	Filtrate dewatering press	3 077	156	351
17	Pulp dewatering press	2 515	531	367
18	Filtrate D-press	1 232	266	278
19	Pulp D-press	685	195	260
20	Filtrate Q-press	522	125	216
21	Pulp Q-press	362	151	181
22	Filtrate PO-press	1 325	137	174
23	Pulp PO-press	939	155	171
24	Black liquor in to evaporation plant	47 712	170	3 636
25	Intermediate strong liquor	55 352	177	5 583
26	Liquor before eff2	91 683	189	7 361
27	Liquor after eff2	100 132	199	8 574
28	Liquor before eff1	94 911	196	8 574
29	Strong liquor			
30	CTMP liquor	10 970	247	1 033

A3: CARBONATE AND OXALATE CONTENT

Measured content of carbonate and oxalate in process samples.

No	Sample	Carbonate [mg/l]	Oxalate [mg/kg sample]
1	Wood chips	N/A	161
2	Black liquor into digester	9 640	753
3	White liquor into digester	18 010	0
4	Wash liquor in to digester	4 065	272
5a	Circulation liquor C5	12 745	N/A
5b	Circulation liquor C6	10 595	N/A
5c	Circulation liquor C8	6 245	341
6a	Blown pulp	N/A	117
6b	Carry over blown pulp	4 638	166
7	Wash liquor in to diffuser	3 360	245
8a	Pulp after blow tank	N/A	188
8b	Carryover after blow tank	3 953	253
9	Pulp after O2-press	N/A	250
10	Carryover O2-press	4 675	354
11a	Pulp after O-bleaching	N/A	733
11b	Carryover O-bleaching	11 535	30
12	Wash liquor in DD	664	47
13	Wash liquor out DD	4 713	364
15a	Pulp into bleaching plant	N/A	137
15b	Carryover pulp into bleaching	2 172	296
16	Filtrate dewatering press	2 092	184
17	Pulp dewatering press	N/A	3
18	Filtrate D-press	19	83
19	Pulp D-press	N/A	3
20	Filtrate Q-press	4	18
21	Pulp Q-press	N/A	2
22	Filtrate PO-press	721	91
23	Pulp PO-press	N/A	2
24	Black liquor in to evaporation plant	12 755	N/A
25	Intermediate strong liquor	16 505	N/A
26	Liquor before eff2	23 420	N/A
27	Liquor after eff2	26 540	N/A
28	Liquor before eff1	21 440	N/A
29	Strong liquor	N/A	N/A
30	CTMP liquor	11 445	58