

Mapping of sodium/sulphur-balances A study on losses in a kraft pulp mill

Master of Science Thesis

MARKUS PERSSON

Department of Chemical and Biological Engineering Division of Forest Products and Chemical Engineering Chalmers University of Technology Göteborg, Sweden, 2015

Mapping of sodium/sulphur-balances A study on losses in a kraft pulp mill

Markus Persson

Department of Chemical and Biological Engineering Chalmers University of Technology Göteborg, Sweden 2015

Mapping of sodium/sulphur-balances A study on losses in a kraft pulp mill Markus Persson

© Markus Persson, 2015.

Department of Chemical and Biological Engineering Chalmers University of Technology SE-412 96 Göteborg Sweden

[Digitaltrycknu] Göteborg, Sweden 2015

Mapping of sodium/sulphur-balances A study on losses in a kraft pulp mill

Markus Persson

Department of Chemical and Biological Engineering Chalmers University of Technology

Abstract

Sulphate pulp is produced by treating wood chips with alkaline chemicals at elevated temperature in the so called cooking process in a pulp mill. The active cooking chemicals are sodium hydroxide (NaOH) and sodium sulphide (Na₂S). After the cooking the pulp goes to the bleaching plant for further treatment and the cooking liquor, called black liquor goes to recovery system. The sodium/sulphur-balance is important because it affects the properties of the pulp.

The losses of sodium and sulphur are to the atmosphere by flue gases from recovery boiler and by effluent, green liquor sludge, lime mud, fibre sludge, tall oil and ash. These losses have to be replaced by make-up chemicals.

For continuous production of pulp it is important that the stock of liquors is kept at a reasonable level therefore the sodium/sulphur-balances in the liquors is important. This master's thesis aims to investigate where and the size of the losses of sodium/sulphur are. The master's thesis has been accomplished as a case study at Södra Cell Värö during 20 weeks as the final part in the master's programme Applied physics.

The mapping of sodium/sulphur has been compiled by listing all streams that enter the mill and leaving the mill. From this a more detailed balance was developed where it was possible to determine from which part of the mill the losses were largest. The project started with a literature study to get more knowledge on how sodium/ sulphur enter and leave the mill. According to literature sulphur is lost at evaporation plant and gas emissions and other losses. Sodium is lost by liquor at liquor tanks and evaporation plant and other losses. Sodium-to-sulphur ratio of the losses is 3 or more on molar basis.

The result of the study performed at Södra Cell Värö indicates that the prime contribution to the loss of both sodium and sulphur is the effluent from bleaching plant. Sulphur can leave the mill independent of sodium while sodium losses are associated with sulphur. This means that sulphur leaves the mill for example in the form of sulphur dioxide.

The losses of sodium and sulphur can be reduced by reduce the amount of sulphuric acid in the ash purging because the ash purging was performed during the autumn of 2013 without sulphuric acid and the concentration of chlorine and potassium were lowered, replace magnesium sulphate by magnesium hydroxide or install a chlorine dioxide plant. It would also be possible to change the wash water to stage 1 in the bleaching plant to stage 2 and this would decrease the losses of sodium.

Mapping of sodium/sulphur-balances A study on losses in a kraft pulp mill

Markus Persson Department of Chemical and Biological Engineering Chalmers University of Technology

Sammanfattning

När pappersmassa tillverkas blandas flis och vitlut i en kokare och värms med ånga. Vitlutens aktiva komponenter är NaOH och Na₂S, natrium ingår enbart som motjon. De aktiva komponenterna reagerar med ligninet i flisen som löses upp i syfte att frilägga fibrerna. Massan går sedan vidare för vidare behandling i blekeriet och kokluten, den så kallade svartluten, går vidare till återvinningssystemet för att återvinna vitlutens aktiva komponenter och värmet i de organiska komponenterna. Natrium/svavel-balans är viktig därför att den påverkar massans egenskaper. Förluster av natrium och svavel sker till atmosfären och till avloppen. Dessa förluster ersätts med makeup kemikalier.

För att kunna producera massa kontinuerligt är det viktigt att lutstocken, som är fabrikens lager av lutar, inte tar slut eller blir överfull. Detta projekt har därför fokuserat på att bestämma hur stora förlusterna av natrium och svavel är och var de uppstår.

Kartläggningen av natrium och svavel har gjorts genom att lista alla strömmar som kommer in till fabriken och de som lämnar fabriken. Utifrån detta gjordes en mer specifik kartläggning, genom vilken det var möjligt att bestämma var de största förlusterna uppstår. Projektet startade med en litteraturstudie för att få mer kunskap om hur natrium/svavel kommer in till bruket respektive lämnar bruket. Litteraturstudien visade att svavel förloras med luten och gasemissioner från återvinningssystemet och andra förluster. Natrium förloras med lutar vid luttankar och indunstningen och andra förluster. Natrium-till-svavel förlustkvoten har visats vara 3 eller mer på molärbasis.

Studien på Södra Cell Värö visar att största delen av natrium och svavel förloras till avloppen, svavel kan förloras oberoende av natrium medan natriumförluster är associerad med svavel.

Förlusterna av natrium och svavel kan minskas genom att reducera mängden svavelsyra som används i asklakningen då asklakningen kördes utan svavelsyra under hösten 2013 med goda resultat med avseende på att minska koncentrationerna på K och Cl, ersätta magnesiumsulfat med magnesiumhydroxid eller installera en klordioxidanläggning.

List of abbreviations

V1: Effluent from bleaching plant, mainly BB1 and BB3

V2: Effluent from bleaching plant

V3: Effluent from recovery boiler, digesting, evaporation and causticizing

V4: Effluent from oxygen delignification, recovery boiler and ash purging

V6: Total effluent

V7: Effluent from waste water treatment

V11: Effluent from chemical and causticizing plant

V12f: Leach water from landfill

V16: Effluent from debarking plant

BB1: Filtrate from the first bleaching stage

BB2: Filtrate from the second bleaching stage

BB3: Filtrate from the third bleaching stage

Adt: Air dry ton pulp

TRS: Total reduced sulphur

GLS: Green liquor sludge

DF: Dry fraction

WS: Wet substance



Figure 1. Flow sheet of the waste water treatment. Reference Jenny Svensson 2012.



Figure 2. Flow sheet of the waste water treatment. Reference Jenny Svensson 2012.

Acknowledgements

The author would like to thank my examiner Hans Theliander, supervisors from Södra Cell Värö Andreas Martinsson and Linda Rudén for very good help concerning this thesis.

I would also like to thank Knut Omholt, Marianne Tärnberg and Lennart Stolpe.

Markus Persson Göteborg, October 2015

Table of Contents

1. Introduction	1
2. Background	3
2.1 Chemical composition of wood	3
2.2 Sulphidity	3
2.3 Digesting	4
2.4 Evaporation	4
2.5 Tall oil digesting	4
2.6 Recovery boiler	5
2.7 Ash purging	5
2.8 Lime kiln and causticizing	6
2.9 Oxygen delignification	6
2.10 Bleaching	6
2.11 Water cleaning	9
2.12 Chlorine dioxide plant	9
3. Methodology	11
3.1 Sample analysis measurements of sodium	11
3.2 Sample analysis measurements of sulphur	11
3.3 Estimation of error sources	12
4. Results	14
4.1 The whole mill	16
4.2 Recovery system	18
4.3 Tall oil digesting	19
4.4 Water cleaning	20
4.5 Waste water treatment	21
4.6 Digesting and oxygen delignification plant	24
4.7 NaOH, MgSO4 and H ₂ SO4	25
4.8 Complementing analysis measurements of sodium/sulphur	26
4.9 Losses of sodium/sulphur	29
4.9.1 Losses in bleaching plant	29
5. Discussion	32
6. Conclusions	33
7. Proposals to improve the sodium/sulphur-balance	34
References	
Appendix 1	
Appendix 2	
Appendix 3	
Appendix 4	54
**	

Appendix 5	
Appendix 6	
Appendix 7	
Appendix 8	69

1. Introduction

When chemical pulp is produced chemicals and steam are added in order to dissolve the lignin and separate the fibers. Sulphate pulp is produced by treating wood chips with chemicals in the so called cooking process. The chemicals are added in the form of a water solution, the white liquor. The active components in the cooking chemicals are sodium hydroxide (NaOH) and sodium sulphide (Na₂S). The ratio between Na and S, is expressed as the Na/S ratio. The properties of the pulp are affected by this ratio, thus it is important to control it.

Today a pulp mill normally has low losses of cooking chemicals to air and to the waste water. Sulphur leaves the mill in form of air emissions, lime mud, green liquor sludge, ash, tall oil, effluent stream and fibre sludge. However, no matter how closed the mill is, it will always have losses of sodium and sulphur, the losses must be replaced by makeup chemicals.

The losses of sulphur to the atmosphere are typically in the form of H₂S and SO₂ and the size of the losses vary from mill to mill and over time. Sulphur containing gases are characterized as total reduced sulphur (TRS) and oxidized gases. TRS are hydrogen sulphide (H₂S), methyl mercaptan (CH₃SH), dimethyl sulphide (CH₃SCH₃) and dimethyl disulphide (CH₃S*SCH₃). Oxidized gases are mainly sulphur dioxide and sulphur trioxide. TRS are generated where liquor is evaporated. Typical values of sulphur losses from lime kiln flue gas is 0.02 kg/Adt and from recovery boiler flue gas 0.5 kg/Adt. [1]

Sodium is lost from the mill by the effluent, lime mud, green liquor sludge and fibre sludge.

Typically values of the ratio between sodium and sulphur losses are 3 or more on molar basis.

Comparatively little research has been accomplished in this area, therefore this thesis can be seen as a help or a guide for further studies. This master's thesis is a case study at Södra Cell Värö.

System boundary for the thesis is the whole mill, which means it starts with wood and chemicals entering and ends with flue gases, sludge and effluent. Only a brief investigation of each process stage will be discussed.

Hopmans and Earl have written a paper how sodium/sulphur make-up balance can be improved. Many bleached kraft pulp mills use the by-product from the chlorine dioxide plant called sodium sesquisulphate as make-up chemical. A better alternative would be neutral salt cake which add 33% more sodium for the same amount of sulphur. Neutral saltcake cannot be produced from the chlorine dioxide plant. In their paper they have written how neutral saltcake be produced from sodium sesquisulphate. [2]

Another study has showed that the effluent from the bleaching plant can be recycled to the recovery system resulting in an excess of sodium and/or sulphur in the chemical balance of the mill. One important operational problem when recycling this effluent is accumulation of NPEs. Case study has showed that removal of sodium and sulphur, primarily discarding a portion of recovery boiler precipitator. [3]

A third study was done during the autumn of 2013 at Stora Enso Skoghall where the author used WinGEMS 5.3 to model a dynamic sodium/sulphur balance. The model was built with one fibre line and control the sulphidity in the white liquor by purging electrostatic precipitator ash from recovery boiler. Also a static model was done in this thesis. The result from the static model was small differences between the model and the result from the mill.

Unbleached and bleached pulp were simulated in dynamic simulation on one fibre line and the result was a variation of sulphidity over time. [4]

The purpose with this thesis was to investigate the sodium and sulphur balances at the Värö mill by answering following questions:

- Where do sodium and sulphur enter mill and where do they leave the system?
- The size of the losses?
- What parts of the process have the highest losses?

2. Background

2.1 Chemical composition of wood

At Södra Cell Värö only softwood pulp is produced. Softwood consists mainly of cellulose, hemicellulose and lignin and a rough distribution of these components can be seen in table 1 below [5].

Substance	Approximate mass fraction [%]
Cellulose	42
Hemicellulose	27
Lignin	28
Ashes	0.1

Table 1. Chemical composition of softwood.

Some of the inorganic elements of the wood are listed in table 2 [6].

T 11 1	т .	1 4	•	0 1
Table)	Inorganic	substances	1n	softwood
<i>1u0ic 2</i> .	morgume	Substances	111	50110000.

Substance	Na	К	Si	Al	Fe	Mn	Ca
Concentration [mg/kg]	6	450	25	10	8	100	400

From table 2 it can be concluded that wood contains only a small part of sodium, thus it is not a big sodium source.

2.2 Sulphidity

The fraction of sodium sulphide in the cooking liquid, white liquor, is called sulphidity and is defined as:

$$\text{Sulphidity}(\%) = \frac{2n_{Na_2S}}{2n_{Na_2S} + n_{NaOH}} \tag{1}$$

The sulphidity defines the properties of the pulp and it is desired to keep it on 37% [7]. This is the reason why it is so important to know the balance of Na/S.

2.3 Digesting

Before chips and chemicals are mixed in a digester the wood is debarked followed by being cut up into wood chips. The digesting can be divided into 4 stages: steaming, impregnation, delignification and blowing. Digesting at the Södra Cell Värö mill is accomplished in 10 batch digesters where the chips are steamed and white liquor is added. Direct steam is only added to the steaming stage and for the other stages steam is used as heating medium in heat exchanger [8].

The wood consists mainly of cellulose, hemicellulose and lignin. The lignin in the wood holds the fibres together and during the digesting the lignin between the fibres is dissolved and the fibres are separated, thereby producing the pulp [5]. The active compounds in white liquor are NaOH and Na₂S. NaOH and Na₂S are dissolved into hydroxide ions and hydrogen sulphide ions, these ions are active in the decomposition of lignin [9]. If the cook is allowed to proceed for a too long period of time, the yield decreases due to that cellulose and hemicellulose are decomposed [10]. After all sequences in the digester, pulp and a solution called black liquor are obtained. The black liquor contains the used cooking chemicals and the dissolved organic substances, mainly lignin residues. The black liquor and pulp are separated in the pulp washing process. At this stage the black liquor is called thin black liquor. It goes to evaporation and the pulp goes to bleaching. At this position in the process thin black liquor holds a dry fraction of approximate 17%. To reuse the chemicals and to recover the energy of the wood substance, thin black liquor is treated in a recovery system [12].

2.4 Evaporation

The first step in the recovery system is evaporation where the dry fraction of the black liquor is increased considerably from 17% to 75%. In Södra Cell Värö this is accomplished in 7 evaporation effects. The steam induced in each effect is used to heat the next effect - which means fresh steam is only applied to the first effect. This is possible by successive decrease the pressure in the system. When water evaporates from the thin black liquor a very viscous medium called thick black liquor is obtained. The thick black liquor contains a high degree of energy and is used as fuel in the recovery boiler [13].

2.5 Tall oil digesting

One of the components in the wood is extractives which have to be removed. During the digesting sodium and various extractive components react to form various sodium soap. These sodium soaps are dissolved to single molecules in the cooking liquid. The soap could cause the liquor to foam. At some critical concentration of soap molecules, micelles are formed. The micelles rise to the surface, due to that they have lower density then the liquor, and form a layer on top of the liquor. The soap layer is separated from the liquor and goes to tall oil cooking plant.

Tall oil is produced from the soap by adding sulphuric acid and heat the mixture in a reactor. The oil is then separated from acid in a centrifuge. Sodium hydroxide neutralize the acid which then goes to the black liquor [14].

2.6 Recovery boiler

The thick black liquor is combusted in the recovery boiler and the purpose of this is to recover the chemical bounded energy in the organic material and the sodium and sulphur in the form of sodium sulphide and sodium carbonate. The end products are flue gases and a salt smelt. The heat from combustion is used to produce steam. The recovery boiler consists mainly of 4 parts: fireplace, convection surfaces, electric precipitation filters and mix tank. Make-up chemicals are added in the mix tank together with strong black liquor and fly ash. As oxidant in the combustion of the black liquor, air is used and it is added in different levels of the recovery boiler. Atmosphere in the lower part of the combustion chamber is reducing and in the upper part it is oxidizing. The mixture is pre heated before liquor guns spray it into the fire place in the form of drops.

The drops will undergo drying and pyrolysis when they fall to the bottom of the fireplace and the char formed will be partly or completely combusted. The inorganic part of the drop form sodium sulphide and sodium carbonate and the rest fall to the bed where oxidized sulphur compounds are reduced to sulphides. Reduction agent is thus carbon which exits the char bed as carbon monoxide or carbon dioxide [15].

Sulphur oxide is formed via several reaction paths e.g.: direct oxidation of the sulphur bound to the organic material, oxidation of sodium sulphide [16]:

The salt smelt produced is tapped from the bottom of recovery boiler and is then transported to the smelt dissolver, where it is dissolved in weak white liquor. The solution produced is called green liquor and contains sodium carbonate and sodium sulphide. To recover hydroxide ions further treatments are needed. Green liquor is sent to a clarifier where undissolved particles are separated after which the green liquor goes to caustizing plant. The undissolved particles leave the mill with the green liquor sludge therefore some sodium/sulphur are lost by this stream [15].

2.7 Ash purging

In recent years pulp mills have closed their recovery cycles to decrease chemical losses. Concentrations of Cl and K in liquor have then increased. The increase of these two elements has caused problems with corrosion in recovery boiler. Cl and K are enriched in precipitator ash because NaCl and KCl vaporise from char bed in furnace and from burned black liquor particles.

A method to remove these species from recovery boiler is ash leaching.

Water, ash and sulphuric acid are added to leaching tank where a slurry is formed. The slurry consists of a solid/liquid mixture. The solid phase is mainly sodium sulphate and the liquid is water, containing dissolved Cl and K. The slurry is removed from bottom of the leaching tank and goes to a centrifuge where the solids are separated from the liquid. The solids are sent to the mix tank and the liquid containing Cl and K go to a reject tank and then as effluent [17].

2.8 Lime kiln and causticizing

The clarified green liquor flows to the causticizing where calcium oxide is added. Water in the green liquor reacts with calcium oxide:

$$CaO(s) + H_2O(aq) \rightarrow Ca(OH)_2(s) + Heat$$
 (3)

Calcium hydroxide then reacts with carbonate ions in the green liquor and forms hydroxide ions and calcium carbonate:

$$Ca(OH)_{2}(s) + CO_{3}^{-2}(aq) \Leftrightarrow CaCO_{3}(s) + 2OH^{-}(aq)$$

$$\tag{4}$$

Not only sodium hydroxide and sodium sulphide have a recovery system but also calcium.

Often a part of the lime mud or calcium carbonate is removed from the system to reduce NPEs, this is also an outgoing material stream of sodium/sulphur. The loss of lime mud is compensated by adding calcium oxide or calcium carbonate and this contains also sodium and sulphur.

Calcium carbonate is separated from white liquor by filtration and is then burned in the lime kiln to regenerate calcium oxide: [18]

$$CaCO_3(s) + Heat \Leftrightarrow CaO(s) + CO_2(s)$$
 (5)

2.9 Oxygen delignification

After the cooking but before the actual bleaching oxygen delignification is used and its filtrate is recirculated as wash water to brown stock wash. There are many advantageous to install oxygen delignification: it contributes to reduced pollution and decreased consumption of bleaching chemicals. Sodium hydroxide is added before oxygen delignification to increase pH to 10-11 and a small amount of magnesium sulphate is used. Magnesium acts as a protector to cellulose. Elements as iron and manganese are trapped by magnesium hydroxide formed and therefore they cannot initiate the oxidative degradation of cellulose.

This positive effect by adding magnesium ions is shown by that the viscosity of pulp, for a given kappa number, is increased. The kappa number is a measure on lignin fraction of the pulp. It is also possible to keep viscosity constant and get a lower kappa number by using oxygen delignification [19].

The following reactions occur when magnesium sulphate is added:

$$MgSO_4 \to Mg^{2+} + SO_4^{2-} \tag{6}$$

(7)

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$$

From the reactions above it can be seen that hydroxide ions are consumed and solid magnesium hydroxide is formed.

Instead of using magnesium sulphate it might be possible to use the cheaper magnesium hydroxide. When magnesium hydroxide is used no hydroxide ions are consumed and thus it will not has an impact on the degree of delignification. The change in kappa

number over the oxygen delignification plant is a measure of consumption of hydroxide ions. Experiments have shown that the kappa number is lower when using magnesium hydroxide instead of magnesium sulphate, this means that magnesium sulphate has consumed hydroxide ions. The difference in kappa number is approximately 1 unit. The disadvantageous to add magnesium hydroxide instead of magnesium sulphate is shown by the viscosity. The viscosity is a rough measure on the length of the pulp fibres is lowered when magnesium hydroxide is used [20]. Typically values of chemicals at oxygen delignification [21]:

NaOH: 1.2-1.6 kg/Adt/delta kappa number

MgSO4: 0.5-1.0 kg Mg /Adt

2.10 Bleaching

Many different methods can be used to bleach kraft pulp. Each bleaching stage has got a single letter representing how the pulp is bleached. The symbols for different bleaching stages can be seen in the table 3 [21]. The bleaching plant at Södra Cell Värö is using a 4-stage process. The first and the third stage is a Q-stage and the second and the fourth is a PO-stage. This sequence can be denoted QOPQPO, see table 3.

A bleaching stage contains:

- A pulp pump
- · A mixer where bleaching chemicals are added
- · A reaction tower where reactions occur
- A transport pump
- · A washing device



Figure 3. Flow sheet of the bleaching plant at the Värö mill. Reference Jenny Svensson 2012.

Bleaching stage	Bleaching stage Symbol		Symbol
Treatment with acid	nent with acid A Chelating stage		Q
Chlorine	С	Peracetic acid	Т
Chlorine dioxide	D	Treatment with water	W
Alkaline extraction	Е	Enzyme stage	Х
Hydrogen peroxide	Р	Dithionite	Y
Oxygen	0	Ozone	Ζ

Table 3. Symbols for different bleaching stages.

The aim of bleaching pulp is to remove the last parts of lignin. The bleaching increases the brightness of the pulp [23].

By examining the composition of wood it can be seen that it contains different metals. Some of them are harmful for the process and equipment, e.g. calcium creates scaling. Other harmful metals are manganese, iron and copper.

The aim of the first stage (Q) is thus to remove these metals from pulp. Manganese, iron and copper are very important to remove because they act as catalysts in degradation reactions with hydrogen peroxide. Hydroperoxyl- and hydroxyl radicals are created when hydrogen peroxide is decomposed and they are very aggressive for the pulp. In the Q stage chelating agents are added which bind the metals in harmless complexes. Magnesium sulphate is added after wash filter. The function of magnesium is that its ions create magnesium hydroxide in alkaline solution which bind with manganese, iron and copper ions. The pulp is pumped from a pulp tower in oxygen delignification to the reactor in bleaching and before the pump sulphuric acid is added to adjust pH to approximate 5,5. The pulp is then fed to bottom of the reaction tower. After tower pulp becomes washed in a wash filter [24].

Next stage in the process is to delignify pulp by a combination of hydrogen peroxide and oxygen. This stage is denoted OP. Many reactions can occur when bleaching with hydrogen peroxide. The bleaching can be adjusted to be delignifying or not delignifying. By adjusting the pH with sodium hydroxide the reactions are controlled. Chemicals are mixed in a mixer then reactions occur in a tower. After the reactor pulp is washed and again magnesium sulphate is added in the transport screw. Filtrate from this step goes to the wash press in oxygen delignification plant [25].

The third stage is another Q-stage where harmful metals are removed by changing pH with sulphuric acid. Magnesium sulphate is added to transport screw after the wash press in previous stage [24].

Last stage in bleaching plant is a PO-stage which is very similar to the second stage but here two reactors are used. Bleaching chemicals are oxygen and hydrogen peroxide and magnesium sulphate is fed to transport screw. Also sodium hydroxide is added to control the delignification reactions [27].

2.11 Water cleaning

The raw water that is used in the mill has to be cleaned from solid particles before it can be used. Different stages in the mill have different requirements for the water, therefore it has to be cleaned either mechanically or chemically.

The first step in the cleaning is to remove big particles, for example branches and ice. This is accomplished in a coarse separator. The water goes then to mechanical cleaning. In the mechanical cleaning the water flows through a sieve cloth in order to remove smaller particles like leafs. After this stage the water can be used in the mill as cooling and washing water. Some stages in the mill need purer water and this is obtained by adding chemicals to the mechanically cleaned water. The water still contains colloidal particles, and these particles are harmful for the equipment. They are removed by adding aluminium sulphate. At a certain pH aluminium ions react with hydroxide ions, forming flocks that can catch colloidal particles. These flocks rise to the surface in the flocculation plant where they becomes separated. When aluminium reacts with hydroxide the pH is lowered and this is adjusted by adding sodium hydroxide [27]. Some stages in the mill need extremely pure water, the water has to be totally deionized. This is performed in two filters, cat ion filter and an ion filter. The water is feeded to the top of the cat ion filter and then it pass through a mass with hydrogen ion. The water is then feeded to the an ion filter where the water pass through a mass with hydroxide ions. In the first filter all the cat ions in the water are replaced by hydrogen ions and in the second filter all the an ions are replaced by hydroxide ions. When all the ions are consumed the filters are cleaned by acid/alkali and the ions goes to the effluent [29].

2.12 Chlorine dioxide plant

Södra Cell Värö does not utilise chlorine dioxide when bleaching pulp. For factories using chlorine dioxide sodium salt cake can be produced from chlorine dioxide plant. This salt cake can then be used as a part of make-up chemicals in the recovery cycle. One of the most used chlorine dioxide plant is Eka SVP-lite and this is operating with high acidity. The by-product of this process is sodium sesquisulphate. This salt cake is a good source of both sodium and sulphur but far from ideal. Typically values of kraft mill are that sodium losses are three times or more higher than the losses of sulphur. The sodium-to-sulphur ratio in sodium sesquisulphate is about 1.5 on molar basis. This means that sodium sesquisulphate can only recover the sulphur losses. Additional sodium sesquisulphate would add more sodium but too much sulphur which affect the sulfidity.

Due to its high acid content, sodium sesquisulphate cannot be safely dissolved directly into black liquor, because of danger of hydrogen sulphide formation.

Sodium sesquisulphate also contains chlorine, which is undesirable in the kraft recovery cycle, because it causes corrosion and gives problems in the recovery boiler.

A better alternative would be sodium sulphate because it adds 2 mole of sodium to the kraft recovery cycle per mole of sulphur recovered. This would decrease the need for purchased make-up caustic for the kraft liquor cycle. Sodium sulphate can be produced directly in the chlorine dioxide process if the temperature is increased and the acidity is below 5,5 N but this would negatively affect the production of chlorine dioxide. So normally the chlorine dioxide plant produces chlorine dioxide and the by-product sodium sesquisulphate. Sodium sesquisulphate is then separated from the liquor, sodium hydroxide is added to sodium sesquisulphate, and sodium sulphate is formed. The solution is then added to the black liquor as make-up sodium and sulphur to the kraft liquor cycle [30]. In a few years Södra Cell Värö will install a chlorine dioxide plant to bleach pulp.

3. Methodology

The first step in this project in order to make a map of sodium/sulphur in the mill, was to list all inlet and outlet material streams containing sodium/sulphur. At this point the mill was considered as a black box. From this list irrelevant material streams were removed.

Next step in developing the map was to do a more specific flow sheet in order to calculate the losses. This is shown in figure 4 for sulphur and figure 5 for sodium. All process streams have been taken from a process control system at Södra showing process in real time and saved historical data. The major part of the flow rates were obtained from the process control system and internal reports of raw material usage in the mill. The analysis values that were used for this thesis were taken from reports of 2012. The average of the online measurements were calculated of all 2012 and not only the operating time. Some process points had not been analysed and needed to be measure to complete the map. The decision was to make a series of 5 measurements of these points. The results of concentrations and flow rates can be seen in chapter 4.

3.1 Sample analysis measurements of sodium

Sodium was analysed by flame photometry. Solid materials were analysed by dissolve it by HNO_3 and H_2O_2 in a microwave oven in accordance with Värö analysis method 1:24 *metals in mass* with the modifications of the amount of added chemicals to match difference of concentrations of metals and sulphur in the sample. The samples were then analysed with the Värö analysis method 9:1 *Sodium, potassium and lithium evaluation with flame photometry*.

A flame photometer consists of a liquid sample, flame, lens, filter and a detector. The sample is sprayed into a flame where it is evaporated and decomposed into its single elements. Some of the elements are excited to higher energy levels. When it falls back to ground state light with characteristic wavelength is emitted. The light passes then through a lens and a filter before it comes to a detector [33].

3.2 Sample analysis measurements of sulphur

Sulphur was analysed by ion exchange chromatography or by titration. According to Värö analysis method 1:24 *degree of reduction evaluation* on liquor sulphur was analysed in green and white liquor. In this method the total sulphur content was analyzed. This method is a modified version of SCAN-N 5:83. Solid materials were analyzed by dissolving the sample

by HNO₃ and oxidate the sulphur by H₂O₂ in a microwave oven in accordance with Värö Analysis method 1:24 *metals in mass* with the modifications of the amount of added chemicals to match the difference of concentrations of the metals and sulfur in the sample before analyzed in the ion exchange chromatograph. Sulfur in lime mud was analyzed in accordance with Värö Analysis method 3:6 *sulphur in calcium oxide* in ion chromatography by first oxidate the sulfur with H₂O₂. Sulfur in waste water was

analyzed by 8:5 *sulphur in waste water* in ion chromatography by first oxidate the sulfur with H₂O₂. The fresh water was analyzed without oxidation in the ion chromatography.

The ion exchange chromatography consists of a sample, eluent that extracts a material from another, two columns connected in series, separator column that separates the ions and suppressor column that remove the excess eluent and a conductivity cell that measure the conductivity of the sample. A low capacity surface active resin is packed in the separator column. A high capacity gel type exchanger is packed in the suppressor column.

The sample and the eluent are added to the separator column where the analyte binds to the resin and then washed out by the eluent. In the suppressor column the eluent is separated from the analyte. The analyte is detected by measure its conductivity in the conductivity cell [34].

3.3 Estimation of error sources

Error sources that can affect the result are online measurements and the number of sample measurements. Some of the sample were analysed autumn of 2013 and the flow rates were taken from 2012 and this can affect the results even if the operation was identical. The complementing measurements of sodium/sulphur were analysed only 5 times autumn of 2013 and this is not so many times, this can impact the result if this samples were not representative.



Figure 4. Flow sheet of sulphur of the Värö mill process.



Figure 5. Flow sheet of sodium of the Värö mill process.

4. Results

Detailed calculations can be found in appendices.

The analysis values of 2012 were collected from different reports and laboratory values and can be seen below. This values was converted to kg/Adt. Also a series of complementing analysis measurements were carried out in autumn of 2013. 5 measurements of each sample were analysed and the results can be seen in section 4.8. A complete map of sulphur is shown in figure 6 and in figure 7 for sodium.



Figure 6. Flow sheet of sulphur with numbers.



Figure 7. Flow sheet of sodium with numbers.

4.1 The whole mill

In to the mill	Na [kg/Adt]	S [kg/Adt]		
Wood	0.01	-		
NaOH	14.1	-		
Fresh water	0.88	0.31		
Alvamix	2.29	0.57		
Sodium formate	0.69	4.05*10^-4		
Calcium oxide	3.7×10^-3	2.3*10^-3		
Oil	-	0.1		
Synthetic gas	-	2.5*10^-2		
MgSO ₄	-	1.01		
AlSO ₄	-	0.26		
H ₂ SO ₄	-	6.7		
Total	18.0	8.98		
Out of the mill				
Tall oil	1.8×10^-2	-		
Pulp	0.64	2.2*10^-3		
Green liquor sludge	0.38	0.14		
Lime mud	0.5	24.6*10^-3		
Fibre sludge	1×10^-2	2*10^-2		
Effluent V6	17.5	12.6		
Flue mases (SO_2)	- /			
The gases (SO ₂)	-	3.2*10^-2		
Flue gases (H ₂ S)	-	3.2*10^-2 9*10^-3		
Flue gases (H2S) Strong gases	- -	3.2*10^-2 9*10^-3 9*10^-2		
Flue gases (H ₂ S) Strong gases Weak gases	- - -	3.2*10^-2 9*10^-3 9*10^-2 5*10^-2		
Flue gases (H ₂ S) Strong gases Weak gases Ash	- - - -	3.2*10^-2 9*10^-3 9*10^-2 5*10^-2 1.84*10^-4		

Table 4. Mass balances of the whole mill of sodium and sulphur.

The total mass balances are good with respect to sodium and less accurate to sulphur. The reason for this can be ascribed the online measurement of sulphur of effluent (V6). The online measurements are less accurate. The calculation of sulphuric acid was done with reported purchased amount of sulphuric acid. When it was done with online measurements the sum of ingoing mass of sulphur differed a lot from outgoing mass.

Table 4 shows all ingoing and outgoing material streams of sulphur and sodium. It can be seen that ingoing differs from outgoing for sulphur and it is good with respect to sodium. It can also be seen that a small amount of sodium enters the mill by the wood, fresh water and chemicals [6]. Pulp, green liquor sludge and lime mud cause small losses of sodium. Sodium also leaves the mill in tall oil but mainly sodium is lost via the effluent (17.5kg/Adt).

Sulphur enters the mill by different chemicals and fresh water. It leaves the mill mainly by effluent and a minor part by sludges, lime mud and flue gases.

Ash purging is another part of the mill that loses a lot of sulphur. The liquid containing Cl and K goes to the effluent (V4) and it also contains some sulphur. From the calculations of ash purging it can be seen that the loss of sulphur is 1.79 kg/Adt from ash purging.

4.2 Recovery system

Ingoing material streams	Na [kg/Adt]	S [kg/Adt]		
Makeup chemicals	2.98	0.57		
Black liquor	229	57.0		
Sodium hydroxide	0.05	-		
Sulphuric acid	-	0.1		
Bio sludge	-	1.1*10^-3		
Acid from tall oil digesting	3.99	1.91		
Total	236	59.6		
Outgoing material streams				
White liquor	266	73		
Green liquor sludge	0.38	0.14		
Lime mud	0.5	2.4*10^-3		
Soap	6.34	0.55		
Gases	-	0.09		
Ash	-	0.18*10^-3		
Total	273	73.8		

Table 5. Mass balances of recovery system.

From the table above it can be concluded that there are a big difference between the sum of outgoing and ingoing material streams for sulphur. This can be ascribed to the white liquor. Sulphur leave the recovery system in the form of white liquor and enter the system in the form of black liquor and it is a big difference between these two streams. Because there are no big losses of sulphur in the recovery system it is expected that these two streams would contain approximate the same amount of sulphur. If white liquor and black liquor are removed the balances over recovery system of sodium and sulphur are good. One another explanation to the difference can be that black liquor is recirculated to the digesters and this has not taken into account.

4.3 Tall oil digesting

Ingoing material streams	Na [kg/Adt]	S [kg/Adt]		
Sodium hydroxide	0.01	-		
Sulphuric acid	-	1.79		
Soap	6.34	0.55		
Total	6.35	2.34		
Outgoing material streams				
Tall oil	1.8*10^-2	-		
Acid	3.99	1.91		
Total	4.01	1.91		

Table 6. Mass balances of tall oil digesting plant.

The balances on tall oil digesting is good with respect to sulphur and approximate good with respect to sodium. Sodium hydroxide is used to neutralise the acid that is going back to the evaporation plant. From table 6 it can be seen that tall oil and sodium hydroxide are small mass streams of sodium. The result of chemical analysis was no sulphur in tall oil but the sum of outgoing sulphur differs from the sum of ingoing sulphur and the conclusion is that tall oil will contain sulphur.

4.4 Water cleaning

Ingoing material streams	Na [kg/Adt]	S [kg/Adt]		
Fresh water	0.88	0.31		
Sodium hydroxide	-	-		
Aluminium sulphate	-	0.26		
Total	0.88	0.57		
Outgoing material streams				
Mechanically cleaned water	0.55	0.19		
Chemically cleaned water	0.16	0.12		
Total	0.71	0.31		

Table 7. Mass balances of water cleaning plant.

The balance on water cleaning is good with respect to sodium and it differs a lot on sulphur. The explanation will be the measurement on sulphur on mechanically cleaned water is less accurate. It will be expected that the concentration of mechanically cleaned water will be in same regime as fresh water. The measurements of the concentration of sulphur is less accurate. One stream is expected to be missed and this is a sludge stream. If sludge is not removed from water cleaning there will be some problem with incruster in evaporation plant. The measurement on sulphur and the sludge stream explain the difference on sulphur. This sludge is aluminium silicate. There is no online measurement device for sodium hydroxide therefore N/A.

4.5 Waste water treatment

In this part of the process 3 mass balances have to be done, 1 total treating all ingoing mass streams and all outgoing mass streams. 2 smaller treating V1, BSB, V12 and V16 as ingoing together with V7 as outgoing, and 1 balance treating V2, V3, V4, V7, V11 and a rest stream as ingoing and V6, fibre sludge and bio sludge as outgoing material streams.

A mass balance over the second part of waste water treatment can be set up in the following way: In: V2, V3, V4 and V7 Out: V6 The following streams that are not measured is a rest stream: In: V10, V11 and V16 Out: Fibre sludge V14 is neglected because it is small.

Ingoing material streams	Na [kg/Adt]	S [kg/Adt]	
Effluent from bleaching plant. (V1)	11.3	4.44	
Wash water from bleaching. (BSB)	-	-	
Leach water from landfill. (V12)	0.78	0.19	
Effluent from debarking plant. (V16)	5*10^-3	1.8*10^-3	
Total	12.1	4.63	
Outgoing material stream			
Recirculated water from waste water treatment. (V7)	11.1	4.26	
Bio sludge	-	1.1*10^-3	
Total	11.1	4.26	

Table	8.	Mass	balances	of the	first	part of	waste	water	treatment
100000	∽•	1.1.0000	0	· · · · · ·		P **** 0 *			

Ingoing material streams	Na [kg/Adt]	S [kg/Adt]
Effluent from bleaching (V2)	1.39	0.94
Effluent from recovery boiler, digesting, evaporation and causticizing. (V3)	1.83	0.93
Effluent from recovery boiler, oxygen delignification and ash purging. (V4)	3.38	1.4
Effluent from waste water treatment. (V7)	11.1	4.26
V10, V11 and V16	-	-
Total	17.7	7.53
Outgoing material stream		
Fibre sludge.	1*10^-2	2*10^-2
Bio sludge.	-	1.1*10^-3
Total effluent. (V6)	15.6	12.6
Total	15.6	12.6

Table 9. Mass balances of the second part of waste water treatment.

Ingoing material streams	Conc. Na [mg/l]	Conc. S [mg/l]	Flow rate [m³/h]	Na [kg/Adt]	S [kg/Adt]
Effluent from bleaching. (V1)	728	285	743	11.3	4.44
Effluent from bleaching. (V2)	140	94.5	474	1.39	0.94
Effluent from recovery boiler, digesting, evaporation and causticizing. (V3)	66.0	33.5	1320	1.83	0.93
Effluent oxygen delignificati on, recovery boiler and ash purging. (V4)	1650	685	97.4	3.38	1.4
Effluent from chemical and causticizing. (V11)	377	239	1.73	0.03	8.7*10^-3
Leach water from landfill. (V12)	4700	1130	7.91	0.78	0.19

Table 10. Mass balances of waste water treatment.

Ingoing material streams	Conc. Na [mg/l]	Conc. S [mg/l]	Flow rate [m ³ /h]	Na [kg/Adt]	S [kg/Adt]
Effluent from debarking plant. (V16)	22.8	8.86	9.55	5*10^-3	1.8*10^-3
Total			2650	18.7	7.9
Outgoing material streams					
Fibre sludge				1*10^-2	2*10^-2
Total effluent (V6)	209	548.3	4140	15.6	12.6
Bio sludge				-	1.1*10^-3
Total			4140	15.6	12.6

Table 10. Mass balances of waste water treatment.

This balance is good with respect to sodium and less accurate to sulphur. From table 8 and 9 it can be concluded that the mass balances are good with respect to both sodium and sulphur.
4.6 Digesting and oxygen delignification plant

Ingoing material streams	Na [kg/Adt]	S [kg/Adt]
Wood chips	0.01	-
White liquor	266	73
Sodium hydroxide	0.23	-
Magnesium sulphate	-	0.82
Total	266	73.8
Outgoing material streams		
Pulp	7.26	2.8
Black liquor	229	57.0
Total	236	59.8

Table 11. Mass balances of digesting and oxygen delignification plant.

These balances are good with respect to both sodium and sulphur. Black liquor is also recirculated to the digester.

4.7 NaOH, MgSO₄ and H₂SO₄

The reported and calculated amounts of purchased sodium hydroxide, magnesium sulphate and sulphuric acid can be seen in table 12. The reported data by the mill are inventoried data [46].

Table 12. The amount of pure	chased and calculated	data of sodium	hydroxide,
magnesium sulphate and sulp	phuric acid.		

	Calculations [ton]	Reported data by the mill [ton]	Difference [%]
Sodium hydroxide	12 600	10 300	18
Magnesium sulphate	1880	1590	15
Sulphuric acid	5730	8580	50

The difference between online measurements and data reported by the mill are: 2300 ton (18%), 290 ton (15%), 2850 ton (50%) for sodium hydroxide, magnesium sulphate and sulphuric acid respectively. From these calculations it can be concluded that the

calculations by online measurements have limited accuracy, particularly for sulphuric acid. Sulphuric acid was the only one that gave a smaller amount with online measurement than data reported by the mill. To use the purchased amount of chemicals is better than online measurements.

4.8 Complementing laboratory analysis of sodium/sulphur

Table 13. Laboratory results of complementing analysis measurements of sulphur. These sample were taking out from the mill and analysed on the laboratory.

Substance	Sample location	Concentration S	Average	Width of variation (max-min)
Calcium oxide	Calcium oxide storage tank [mg/g]	[0.04 0.08 0.17]	97*10^-3	0.13
Fresh water	Before water cleaning [mg/l]	[3.9 3.3 3.7 3.2 3.3]	3.48	0.70
BB2 to AWP	Before AWP [mg/l]	[161.3 154.8 146.5 489 98.8]	210	390
Effluent	V1 [mg/l]	[261 299.5 305 324 235.9]	285	88.1
	V2 [mg/l]	[86.5 93.6 91.4 122.7 78.4]	94.5	44.3
	V3 [mg/l]	[5.5 10.4 24.7 94.3 32.7]	33.5	88.8
	V4 [mg/l]	[55.4 73.2 59.3 3141 94.6]	685	3090
	V6 [mg/l]	[85.3 98.7 103.8 143.6 116.9]	110	58.3
	V7 [mg/l]	[250.9 278.7 331.7 303 272.5]	287	80.8
	V11 [mg/l]	[85.4 310.4 226 303 272.5]	239	225
	V12f [mg/l]	[1.6 1.2 0.93 0.96 0.94]	1.13	0.67
	V16 [mg/l]	[9.7 9 9.7 3.9 12]	8.86	8.10
Fibre sludge	Waste water treatment [mg/g DS]	[1.2 2.8 3.7 3.97 2.1]	2.75	2.77

Substance	Sample location	Concentration S	Average	Width of variation (max-min)
Green liquor sludge	After centrifuge [mg/g DS]	[16.2 26.6 29.9 26.9 18.4]	23.6	13.7
Pulp	TM [mg/g DS]	[4.4 3.2 0.34 2.2 2.1]	2.45	4.06
	After AWP [mg/g DS]	[0.87 5.6 5.2 1 1.35]	2.8	4.73
Water	Before leaching tank [mg/l]	[5.1 3.3 3.6]	4	1.8
Effluent	V4 after leaching tank [g/l]	[66.2 55.8 56.4]	59.5	10.4
Lime mud	Green liquor sludge filter [mg/g DS]	[0.8 0.52 0.31 0.26 0.32]	0.44	0.54
VKK	After water cleaning plant [mg/l]	10.7	10.7	0
Soap	After evaporation plant [mg/kg]	7576	7580	0
Acid from tall oil digesting plant	After tall oil digesting plant [mg/l]	16300	16300	0

Table 13. Laboratory results of complementing analysis measurements of sulphur

The variation of the measurements are low in all cases except for V4. The explanation for this is when ash leaching stops the tank is cleared to V4 and this contains much sulphur. Some of the measurements were only measured 1 time and this not be representative, this can affect the result.

Table 14. Laboratory results of complementing analysis measurements of sodium. These sample were taking out from the mill and analysed on the laboratory.

Substance	Sample location	Concentration Na	Average	Width of variation (max-min)
Calcium oxide	Calcium oxide storage tank [mg/g]	[0.04 0.08 0.17]	97*10^-3	0.13
BB2 to AWP	Before AWP [mg/l]	[1500 1400 1300 1200 1100]	1300	400
Effluent	V11 [mg/l]	[180 452 349 455 450]	377	275
	V12f [g/l]	[6.5 7.5 2.7 3.2 3.6]	4.7	4.3
	V16 [mg/l]	[25 21 25 18 25]	22.8	7
Sludge	Waste water treatment [mg/g DS]	[1.25 1.85 2.5 1.9 1.9]	1.88	1.25
Green liquor sludge	After centrifuge [mg/g DS]	[70 89.3 69.3 58 48.6]	67.0	40.7
Pulp	After AWP [mg/g DS]	[6.1 8 8.3 7.1 6.8]	7.26	2.20
Water	Before leaching tank [mg/l]	[13 9.1 8.6]	10.2	4.40
Effluent	V4 after leaching tank [g/l]	[144 116 134]	131	28
Lime mud	Green liquor sludge filter [mg/g DS]	[7.2 10.2 9.1 8.2 10.4]	9.02	3.20
Soap	After evaporation plant [mg/kg]	87000	87000	0
Acid from tall oil digesting plant	After tall oil digesting plant [mg/l]	34000	34000	0

4.9 Losses of sodium/sulphur

The losses of sodium/sulphur are the amounts leaving the mill. From table 4 it can be seen the amounts of sodium/sulphur that leave the mill.

The sodium-to-sulphur ratio of the losses:

$$\frac{L_{Na}}{L_S} = \frac{852}{302} \approx 2.82$$

Typically values of this ratio are 3 or more on molar basis [30]. The calculations of the losses can be seen in appendix 8.

4.9.1 Losses in bleaching plant

From the calculations of effluents it can be concluded that a lot of sodium and sulphur are lost to V1. 11.3 kg/Adt for sodium and 4.44 kg/Adt for sulphur are lost to V1. The effluent V1 contains mainly the filtrates from the chelating stages from the bleaching plant.

A mass balance over the bleaching plant gives the losses:

Sodium:

Ingoing material streams are pulp and sodium hydroxide to the second and the fourth stage.

Outgoing material streams are pulp, filtrate from the second stage and effluents to V1.

Sulphur:

Sulphur enters the bleaching plant in the form of sulphuric acid, pulp and magnesium sulphate.

Outgoing material streams are pulp, filtrate from the second stage and effluents to V1.



Figure 9. Flowsheet of the water flows of bleaching plant at the Värö mill. Reference Jenny Svensson 2012.

Ingoing material streams	Na [kg/Adt]	S [kg/Adt]
Pulp	7.26	2.8
Sodium hydroxide	10.9	-
Sulphuric acid	-	1.28
Magnesium sulphate	-	0.27
Total	18.2	4.35
Outgoing material streams		
Pulp	0.64	2.2×10^-3
Filtrate (BB2)	6.79	1.1
Effluent (V1)	11.3	4.44
Total	18.7	5.54

Table 15. Mass balances of sodium and sulphur of the bleaching plant.

From table 15 it can be seen that the amounts of sodium and sulphur that enter the bleaching is approximate equal to the amounts that leave the bleaching plant. The bleaching plant can therefore be assumed to work as steady state. Also condensates

from the evaporation plant and chemical cleaned water are added as wash water. The condensate from the evaporation plant can contains sodium/sulphur but the chemical cleaned water contains no sodium/sulphur. To the stage 4 sodium hydroxide is added and the filtrate is expected to contain sodium, this filtrate is then recirculated to stage 1. Stage 1 is a chelating stage and this filtrate goes then to effluent (V1) to remove harmful metals. This could be one explanation to the big amount of sodium in V1.

Stage 4 can be compared to stage 2 and a mass balance of sodium over stage 2 shows the amounts that enter and leaves this stage:

Sodium enters stage 2 in the form of sodium hydroxide and leaves by wash water from stage 2 of bleaching plant.

The amount of sodium that enters stage 2 is calculated in appendix 1 to 3.85 kg/Adt. Calculations of the amount of sodium that leaves by wash water from stage 2 of bleaching can be seen in appendix 5 to be 6.79 kg/Adt. The difference between outgoing sodium and ingoing is 2.94 kg/Adt and this amount should come from the wash water and pulp. The sodium and sulphur content in wash water from stage 2 of bleaching can be seen in figure 10. Wash water from stage 2 of bleaching contains a lot of sodium therefore it is expected that BB4 also contains a lot of sodium which is lost in stage 1.



Figure 10. The sulphur and sodium content in wash water from stage 2 of bleaching.

5. Discussion

According to literature guideline values for sulphur emissions by flue gases from recovery boiler and lime kiln is 0.5 kg/Adt [29] and the result of this master's thesis is 0.040 kg/Adt, so this value is low. From table 4 it can be seen that the sum of ingoing mass differs a lot to the sum of outgoing mass for sulphur. The only outgoing stream that is low according to literature value is flue gases but this would have small impacts on the total because it differs a lot from the total. The calculations using flow rates from online measurements are rather inaccurate, the difference between inventoried data and calculated amount is big with respect to sulphuric acid.

Magnesium sulphate is added to the oxygen delignification and bleaching plant to protect the cellulose and typically value of added amount of magnesium sulphate is 2500 - 5000g/Adt [20]. The calculation of added magnesium sulphate is 3040g/Adt so this is in correct region.

When magnesium hydroxide is formed from magnesium sulphate it consumes hydroxide ions. It would be expected that the consumption of hydroxide ions is reduced if magnesium sulphate is replaced by magnesium hydroxide. This means that a smaller amount of sodium hydroxide needs to be added, giving less sodium in the effluent [19]. If magnesium sulphate is replaced by magnesium hydroxide it has been shown that a lower kappa number gained but also lower viscosity [19]. The consumption of bleaching chemicals is lowered if magnesium hydroxide is used but weaker pulp gained. When magnesium sulphate is used stronger pulp is obtained but the consumption of bleaching chemicals is higher. This means it is a balance between gain strong pulp or consume smaller amounts of bleaching chemicals.

The delignification reactions in bleaching plant require hydroxide ions, therefore sodium hydroxide is added. This sodium hydroxide is added to stage 2 and to stage 4. From stage 2 the filtrate is recirculated to the wash press in oxygen delignification plant, thus this amount of sodium is recovered. The filtrate from stage 4 should also contains sodium but this filtrate is recirculated to the wash press in stage 1 in bleaching plant which is a chelating stage. The filtrate from this stage goes then to effluent (V1) because it contains harmful metals. The conclusion from this thesis is therefore the high amount of sodium in V1 comes from recirculated filtrate from stage 4. The biggest losses of sodium is by effluent (18.1 kg/Adt) all the other streams that leaves the mill are comparatively low. The major part of sodium leaves by V1. The ratio between the losses of sodium and sulphur is 2.82 and typically values are 3 or more on molar basis [30]. From this it can be concluded that the losses of sodium and sulphur are in correct region.

6. Conclusions

It can be concluded that the mass balance over tall oil digesting plant and bleaching plant are good with respect to sulphur. The mass balance over the whole mill, recovery system, water cleaning plant, digesting and oxygen delignification plant and waste water treatment are less accurate. The mill loses much sulphur from waste water treatment. The differences between outgoing material streams and ingoing material streams from the waste water treatment are more than 20 %.

The difference between outgoing and ingoing material streams with respect to sodium over digesting and oxygen delignification plant and recovery system are big. The mass balance over bleaching plant, water cleaning plant, tall oil digesting plant and waste water treatment is good. It can be concluded that sodium is lost a lot from recovery system and digesting and oxygen delignification plant. The mass balance over the whole mill is good with respect to sodium. It can also be concluded that the mill loses much sodium from waste water treatment.

7. Proposals to improving sodium/sulphur-balances

To improve the sodium/sulphur-balances more studies have to be done. The result from this thesis shows that much sodium and sulphur are lost by the V1 and V4. Next step is to do more investigations about how sodium/sulphur enter the effluent. One important part of the process in this respect is the bleaching plant and particularly the filtrate from the first and the third stages. It might be possible to recirculate the filtrate as wash water from stage 4, which contains sodium, to stage 2 instead of to stage 1. This would decrease the amount of sodium in V1 because the filtrate from stage 2 is then recirculated to the wash press in oxygen delignification plant.

It would also be advantageous to replace magnesium sulphate by magnesium hydroxide because magnesium sulphate consumes hydroxide ions, so more hydroxide ions needs to be added in the form of sodium hydroxide. If it is possible to replace magnesium sulphate by magnesium hydroxide, the amount of added sodium hydroxide can be reduced and less sodium would go to the effluent.

Another department where sodium and sulphur are lost is the ash purging. Sometimes during the autumn of 2013 the ash purging was performed without sulphuric acid, the concentration of Cl and K were reduced. Perhaps it is possible to reduce the usage of sulphuric acid which would have an impact on the sulphidity, because less sulphur would go to the liquor cycle. More studies about this have to be done, for example regarding the effect of changing pH and temperature.

A third proposal is to install a chlorine dioxide plant. By using this, some of the makeup chemicals can be produced which reduce the cost of these chemicals.

References

[1] Saturnino DM. Modelling of Kraft Mill Chemical Balance [dissertation]. Toronto: University of Toronto; 2012. p.5-6.

[2] Earl PF, Hopmans J. Improving the Soda-Sulfur Chemical Make-up Balance: Modifications to the Chlorine Dioxide Plant to Make Neutral Saltcake. 2010. p.1.

[3] Warnqvist B. Handling alkali and sulphur balances in closed-cycle bleached mills - options, technology and costs. Minimum Effluent Mills Symposium. 1996: 33-37.

[4] Andersson P. A dynamic Na/S balance of a kraft pulp mill [Master's thesis]. 2014.

[5] Något om vedens sammansättning och morfologi. In: Theliander H, Paulsson M, and Brelid H, editors. Introduktion till massa- och pappersframställning. Gothenburg; 2002. p. 17.

[6] Kausticering. Sulfatmassateknik del 2; Kemikalieåtervinning, ånga, vatten, avloppsvatten; Södra Cell Värö; Utbildning av operatörer 2011. p.1.

[7] Brännvall E. Wood handling. The Ljungberg Textbook: Wood Chemistry and cellulose Technology II. 2004. p.2.

[8] Brännvall E. Pulping Technology. The Ljungberg Textbook: Wood Chemistry and cellulose Technology II. 2004. p.15.

[9] Något om vedens sammansättning och morfologi. In: Theliander H, Paulsson M, and Brelid H, editors. Introduktion till massa- och pappersframställning. Gothenburg; 2002. p.13.

[10] Massakokning enligt sulfatprincipen. In: Theliander H, Paulsson M, and Brelid H, editors. Introduktion till massa- och pappersframställning. Gothenburg; 2002. p.134.

[11] Massakokning enligt sulfatprincipen. In: Theliander H, Paulsson M, and Brelid H, editors. Introduktion till massa- och pappersframställning. Gothenburg; 2002. p.141.

[12] Massakokning enligt sulfatprincipen. In: Theliander H, Paulsson M, and Brelid H, editors. Introduktion till massa- och pappersframställning. Gothenburg; 2002. p.211.

[13] skogssverige.se [Internet]. Skogssverige, Inc.; [updated 2014-01-17; cited 2014-01-06]. Available from: <u>http://skogssverige.se/node/38653</u>.

[14] Indunstning. Sulfatmassateknik del 2; Kemikalieåtervinning, ånga, vatten, avloppsvatten; Södra Cell Värö; Utbildning av operatörer 2011. p.3.

[15] Theliander H. The recovery and burning of black liquor. The Ljungberg Textbook: Wood Chemistry and Cellulose Technology II. 2004. p.20-21.

[16] Kemikalieåtervinning. Sulfatmassateknik del 2; Kemikalieåtervinning, ånga, vatten, avloppsvatten; Södra Cell Värö; Utbildning av operatörer 2011. p.8.

[17] GonCalves C; Tran H; Braz S; Puig F, and Shenassa R. Chloride and potassium removal efficiency of an ash leaching system. Pulp & Paper Canada. 2008 Mar; 109(3): 33.

[18] Theliander H. The recovery of cooking chemicals: the white liquor preparation plant. The Ljungberg Textbook: Wood Chemistry and Cellulose Technology II. 2004. p. 3.

[19] Germgård U. Bleaching of pulp. The Ljungberg Textbook: Wood Chemistry and Cellulose Technology II. 2004. p.11.

[20] Bouchard J, Wang J, and Berry R. MgSO4 vs Mg(OH)2 as a cellulose protector in oxygen delignification. Holzforschung. 2011; 65(3):296.

[21] Germgård U, Na- and S-balances in the pulp mill, Nov 2013, p.85.

[22] Germgård U. Bleaching of pulp. The Ljungberg Textbook: Wood Chemistry and Cellulose Technology II. 2004. p.4.

[23] Blekning. Syrgasdelignifiering och blekning; Södra Cell Värö; Utbildning av operatörer 2011. p.1.

[24] Steg 1. Syrgasdelignifiering och blekning; Södra Cell Värö; Utbildning av operatörer 2011. p.1-4.

[25] Steg 2. Syrgasdelignifiering och blekning; Södra Cell Värö; Utbildning av operatörer 2011. p.1.

[26] Steg 3. Syrgasdelignifiering och blekning; Södra Cell Värö; Utbildning av operatörer 2011. p.1.

[27] Steg 4. Syrgasdelignifiering och blekning; Södra Cell Värö; Utbildning av operatörer 2011 p.1-2.

[28] Råvatten. Sulfatmassateknik del 2; Kemikalieåtervinning, ånga, vatten, avloppsvatten; Södra Cell Värö; Utbildning av operatörer 2011. p. 1-5.

[29] Matarvatten; Södra Cell Värö; Utbildning av operatörer 2011. p. 1-2.

[30] Earl PF, Hopmans J. Improving the Soda-Sulfur Chemical Make-up Balance: Modifications to the Chlorine Dioxide Plant to Make Neutral Saltcake. 2010. p.1-4.

[31] Kemikalieåtervinning. In: Theliander H, Paulsson M, and Brelid H, editors. Introduktion till massa- och pappersframställning. Gothenburg; 2002. p.218.

[32] Saturnino DM. Modelling of Kraft Mill Chemical Balance [dissertation]. Toronto: University of Toronto; 2012. p.9.

[33] EDU.fi[Internet].[Updated 2010 February 25; cited 2014 Oct 7]. Available from: http://www.edu.fi/flamfotometri

[34] Nasef M, Ujang Z. Introduction to Ion Exchange Processes. In: Inamuddin, Luqman M, editors. Ion Exchange technology I. New York: Springer; 2012. p. 24.

[35] SkogsSverige [Internet]. [publisher unknown] [updated 2014 January 17; cited 2014 Mar 24]. Available from: <u>http://skogssverige.se/node/38287</u>.

[36] Södra Cell Värö. Vedrapport.xls. 2012.

[37] Södra Cell Värö. Smst2012.xls. 2012

[38] Online measurement 67F050_1

[39] Runeson M. Svenskt vatten [Internet]. Växjö: Mark & Vatten Ingenjörerna; 2000 Nov 30 [cited 2014 April 7]. Available from: <u>http://www.svensktvatten.se/Documents/</u> Kategorier/Dricksvatten/Vattenverk%20och%20processer/Lutspädning.xls

- [40] Online measurement 48F259
- [41] Online measurement 45F231
- [42] Online measurement 45F075
- [43] Online measurement 765F174_MV
- [44] Online measurement 722F481.MV
- [45] Online measurement 822F122
- [46] Södra Cell Värö. Råvaror201201-12.xls. 2012

- [47] Bengtsson K. Certificate of analysis of sodium formate. 2009 sep 15.
- [48] Södra Cell Värö. Laboratory analysis of alvamix. 2010 jun 29.
- [49] Laboratory analysis 48LAB502
- [50] Online measurement 45F255
- [51] Online measurement 45F254
- [52] Online measurement 45F258
- [53] Online measurement 43F291

[54] Mettler Toledo [Internet]. [publisher unknown] [cited 2014 Mar 24]. Available from: <u>http://us.mt.com/us/en/home/supportive_content/application_editorials/</u> <u>Sulfuric_Acid_de_e.html</u>

- [55] Online measurement 822F123
- [56] Online measurement 45FF191.BER1
- [57] Online measurement 45F244
- [58] Online measurement 55F086
- [59] Online measurement 46F089.GIV
- [60] Online measurement 765F173_MV
- [61] Online measurement 722F936.MV
- [62] Online measurement 765F122_MV
- [63] Martinsson, Andreas. 2014. E-mail 24 Mars. andreas.martinsson@sodra.com>
- [64] Laboratory analysis 72LAB563
- [65] Laboratory analysis 78LAB501
- [66] Laboratory analysis 72LAB563
- [67] Laboratory analysis 78LAB501

- [68] Online measurement 722X874.BER1
- [69] Laboratory analysis 72LAB544
- [70] Laboratory analysis 72LAB547
- [71] Online measurement 722F883.MV
- [72] Online measurements 45F613, 45F614, 45F615, 45F616
- [73] Laboratory analysis 82LAB500
- [74] Online measurement 822F102.MV1
- [75] Laboratory analysis 82LAB504
- [76] Online measurement 11F002.BER1
- [77] Laboratory analysis 82LAB508
- [78] Online measurement 11F003.BER1
- [79] Laboratory analysis 82LAB512
- [80] Online measurement 11F004.BER1
- [81] Laboratory analysis 82LAB727
- [82] Online measurement 822F149.BER1
- [83] Online measurement 77F330_MV
- [84] Online measurement 822F135.MV
- [85] Online measurement 822F134.MV
- [86] Martinsson, Andreas. 2014. E-mail 5 Februari. andreas.martinsson@sodra.com>
- [87] Online measurement 67F039.MV
- [88] Online measurement 67LAB511
- [89] Online measurement 67F037.MV

[90] 82LAB517

[91] 82F041.BER2

Appendix 1

Ingoing material streams of sodium

Sodium enters the mill by chemicals, wood, fresh water and calcium oxide. The mass of these compounds are:

Wood

$$\rho_{\text{wood}} = 400 \frac{\text{kg}}{\text{m}^3} [35]$$

$$V = 2040000 \text{ m}^3 \text{fub} [36]$$

$$c_{Na} = 6 \text{ mg/kg}; [5]$$
Production = 418 866 ton [37]

$$m_{Na} = \frac{c_{Na} \rho_{wood} V}{\text{Production}} = \frac{6*10^{-6}*400*2040000}{418\,866} \approx 0.01 \text{ kg/Adt}$$

Fresh water

The fresh water is the water before water cleaning and contains the amount of sodium that enters the mill. The volume flow rate is $1.18 \text{ m}^3/\text{s}$.

$$c_{Na} = 9.83 \text{ mg/l Table 14}$$

$$\dot{V} = 1.18 \text{ m}^3/\text{s} [38]$$

Production = 418 866 ton [37]
t = Number of days of 2012 = 366 days

$$m_{Na} = \frac{\dot{c_{Na}Vt}}{\text{Production}} = \frac{9.83 \times 10^{-6} \times 1.18 \times 10^3 \times 366 \times 3600 \times 24}{418 866} \approx 0.88 \text{ kg/Adt}$$

Sodium hydroxide

Sodium hydroxide is added to oxygen delignification, bleaching, recovery system, tall oil digesting and external cleaning. The concentration of the purchased sodium hydroxide is 40% and is then diluted to 10% before used in the mill. In the oxygen and bleaching plant sodium hydroxide is important in the delignification reactions, scrub weak gases in tall oil digesting and adjust pH in the evaporation plant and external cleaning.

The purchased amount of sodium hydroxide of 2012 was 10 300 ton.

Production = 418866ton

$$m_{Na}^{NaOH} = \frac{X_{Na}^{NaOH}}{\text{Production}} = \frac{23}{23 + 16 + 1} * \frac{10300}{418866} \approx 14.1 \text{ kg/Adt}$$

The concentration of Na in NaOH:

Density of 10% sodium hydroxide: $\rho = 1.11 \text{ kg/l} [38]$ The total mass of 11 solution: $m_{tot} = \rho V = 1.11 * 1 = 1.11 \text{ kg}$

 $c_{NaOH} = 1.11 \text{ kg/l}$

10% of the total mass is pure sodium hydroxide: $m_{NaOH} = 0.10 * 1.11 = 0.111 \text{ kg}$

 $c_{NaOH} = 0.111 \,\text{g/l}$

The concentration sodium in sodium hydroxide:

 $c_{Na} = \frac{Na}{Na + O + H} c_{NaOH} = \frac{23}{23 + 16 + 1} * 0.111 \approx 0.0638 \ g/l$

Oxygen delignification

 $V = 2.82 \, \text{l/min} \, [40]$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days

$$m_{Na} = \frac{c_{Na}Vt}{\text{Production}} = \frac{0.0638 * 2.82 * 366 * 60 * 24}{418\ 866} \approx 0.226 \text{ kg/Adt}$$

Bleaching plant, stage 2

 $V = 48 \, \text{l/min} \, [41]$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days $m_{Na} = \frac{c_{Na}Vt}{\text{Production}} = \frac{0.0638 * 48 * 366 * 24 * 60}{418\ 866} \approx 3.85\ \text{kg/Adt}$

Bleaching plant, stage 4

 $\dot{V} = 80.09 \, \text{l/min} \, [41]$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days $m_{Na} = \frac{c_{Na}Vt}{\text{Production}} = \frac{0.0638 * 80,09 * 366 * 60 * 24}{418\,866} \approx 6.43 \,\text{kg/Adt}$

Tall oil digesting

$$\dot{V} = 0.16 \text{ l/min [41]}$$

Production = 418 866 ton [37]
t = Number of days of 2012 = 366 days
 $m_{Na} = \frac{\dot{c}_{Na}\dot{V}t}{\text{Production}} = \frac{0.0638 * 0.16 * 366 * 60 * 24}{418 866} \approx 0.01 \text{ kg/Adt}$

Imcondensor

V = 0.01 l/s [44]Production = 418 866 ton [37] t = Number of days of 2012 = 366 days

 $m_{Na} = \frac{c_{Na}Vt}{\text{Production}} = \frac{0.0638 * 0.01 * 366 * 3600 * 24}{418\ 866} \approx 0.048\ \text{kg/Adt}$

Waste water treatment

 $\dot{V} = 84.07 \text{ l/min } [45]$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days $m_{Na} = \frac{\dot{c}_{Na}\dot{V}t}{\text{Production}} = \frac{0.0638 * 84.07 * 366 * 60 * 24}{418 866} \approx 6.75 \text{ kg/Adt}$

Makeup chemicals

The makeup chemicals are sodium formate, alvamix and calcium oxide. Sodium formate and alvamix are added to the mix tank to replace the losses of sodium. The losses of sulphur is mainly replaced by sulphuric acid. Calcium oxide is added to the causticizing plant to replace the losses of lime mud. Sodium formate contains mainly sodium but also a small fraction of sulphur, alvamix is a source for both sodium and sulphur. The added amounts of sodium formate, alvamix and calcium oxide are 4240 ton, 8740 and 16 000 ton respectively [43].

Sodium formate

The concentration of sodium is 68 g/kg [47] Production = 418 866 ton [37] $m_{Na} = \frac{c_{Na}m_{\text{sodium formate}}}{\text{Production}} = \frac{68 \times 10^{-3} \times 4240 \times 10^{3}}{418 866} \approx 0.69 \text{ kg/Adt}$

Alvamix

DF = 55% [48] Mass fraction of sodium, $X_{Na} = 20\%$ of DS [47] Production = 418 866 ton [37] $m_{Na} = \frac{m_{Alvamix} DFX_{Na}}{Production} = \frac{8740 \times 10^3 \times 0.55 \times 0.20}{418 866} \approx 2.30 \text{ kg/Adt}$

Calcium oxide

Calcium oxide is added to the causticizing plant to replace the removed lime mud. The concentration of sodium is 0.097 mg/g [Table 14]. Production = 418 866 ton [37]

$$m_{Na} = \frac{c_{Na}m_{CaO}}{\text{Production}} = \frac{0.097 \times 10^{-3} \times 16\ 000 \times 10^{3}}{418\ 866} = 0.0037\ \text{kg/Adt}$$

The total amounts of sodium that enters the mill:

 $m_{Na}^{Total} = m_{Na}^{Wood} + m_{Na}^{Fresh water} + m_{Na}^{Calcium oxide} + m_{Na}^{NaOH} + m_{Na}^{Sodium formate} + m_{Na}^{Alvamix} = 0.01 + 0.88 + 0.0037 + 14.1 + 0.69 + 2.30 \approx 18.0 \text{ kg/Adt}$

Appendix 2

Ingoing material streams of sulphur

Sulphur is added to the mill in form of fresh water, bark, oils, chemicals and calcium oxide.

Fresh water

 $c_{S} = 3.48 \text{ mg/l Table 13}$

$$\dot{V} = 1.18 \text{ m}^3/\text{s}[38]$$

Production = 418 866 ton [37] t = Number of days of 2012 = 366 days

 $m_S = \frac{c_S V t}{\text{Production}} = \frac{3.48 \times 10^{-6} \times 1.18 \times 10^3 \times 366 \times 3600 \times 24}{418\,866} \approx 0.31 \,\text{kg/Adt}$

Makeup chemicals

The added amounts of sodium formate, alvamix and calcium oxide are 4240 ton, 8740 ton and 16 000 ton respectively [46].

Sodium formate

 $c_{S} = 0.004\% [47]$ Production = 418 866 ton [37] $m_{S} = \frac{c_{S}m_{Sodium \ formate}}{Production} = \frac{0.00004 * 4240 * 10^{3}}{418 866} \approx 4.05 * 10^{-4} \text{ kg/Adt}$

Alvamix

DF = 55% [48] 5% of DS is sulphur [48] Production = 418 866 ton [37] $m_S = \frac{m_{Alvamix}DF * 0.05}{Production} = \frac{0.05 * 0.55 * 8740 * 10^3}{418 866} = 0.57 \text{ kg/Adt}$

Calcium oxide

 $c_S = 0.06 \text{ g/kg Table 13}$ Production = 418 866 ton [37] $m_S = \frac{c_S m_{CaO}}{\text{Production}} = \frac{0.06 \times 10^{-3} \times 16\ 000 \times 10^3}{418\ 866} = 0.0023 \text{ kg/Adt}$

Oils

The oils are used in the recovery boiler and lime kiln when the mill starts up. These oils are EO1, EO5 and tall oil pitch.

EO5

 $\rho = 0.96 \text{ ton/m}^3 [37]$ $c_s = 0.40\% [37]$ **Recovery boiler:**Consumed: V = 811 m³ [37]
Production = 418 866 ton [37] $m_S = \frac{c_S \rho V}{\text{Production}} = \frac{811*0.96*1000*0.0040}{418 866} = 0.0074 \text{ kg/Adt}$

Lime kiln:

Consumed: V = 699 m³ [37] Production = 418 866 ton [37] $m_S = \frac{c_S \rho V}{\text{Production}} = \frac{699 * 0.96 * 1000 * 0.0040}{418 866} \approx 0.0064 \text{ kg/Adt}$

Tall oil pitch

 $\rho = 0.96 \text{ ton/m}^3 [37]$ $c_s = 0.30\% [37]$

Recovery boiler:

Consumed: V = 5863 m³ [37] Production = 418 866 ton [37] $m_S = \frac{c_S \rho V}{\text{Production}} = \frac{0.0030 * 0.96 * 10^3 * 5863}{418 866} \approx 0.040 \text{ kg/Adt}$

Lime kiln:

Consumed: V = 7020 m³ [37] Production = 418 866 ton [37] $m_S = \frac{c_S \rho V}{\text{Production}} = \frac{0.0030 * 0.96 * 10^3 * 7020}{418 866} = 0.048 \text{ kg/Adt}$

EO1

 $\rho = 0.92 \text{ ton/m}^3 [37]$ $c_s = 0.05\% [37]$

Recovery boiler: Consumed: $V = 183 \text{ m}^3[37]$ Production = 418 866 ton [37]

$$m_S = \frac{c_S \rho V}{\text{Production}} = \frac{0.0005 * 0.92 * 10^3 * 183}{418\,866} \approx 2.01 * 10^{-4} \text{ kg/Adt}$$

Lime kiln:

Consumed: V = 183 m³ [37] Production = 418 866 ton [37] $m_S = \frac{c_S \rho V}{\text{Production}} = \frac{0.0005 * 0.92 * 10^3 * 307}{418 866} \approx 3.37 * 10^{-4} \text{ kg/Adt}$

Synthetic gas

Another fuel that is used in the lime kiln is synthetic gas. The synthetic gas is formed from bark. Sulphur leaves the system by ash. The added amount of bark is 25 879 ton and its sulphur content is 0.04% [86].

Added sulphur by bark = $0.0004*25\ 879 \approx 10.4$ ton $m_S = \frac{10.4*10^3}{418\ 866} \approx 0.025$ kg/Adt

MgSO₄

Magnesium sulphate is added to the pulp tower in the oxygen delignification and to the pulp after the three first wash stages in the bleaching plant. Magnesium sulphate is added to protect the cellulose molecule. The value of concentration of magnesium sulphate that was used analysed 51 times at Södra Cell Värö. The volume flow rates to stage 1, stage 2, stage 3 and oxygen delignification plant are 3.22 l/min, 2.65 l/min, 3.45 l/min and 20.2 l/min respectively.

The purchased amount of magnesium sulphate of 2012 = 1590 ton Production = 418866 ton

 $m_{S}^{MgSO_{4}} = \frac{X_{S}^{MgSO_{4}}m_{MgSO_{4}}}{\text{Production}} = \frac{0.267 \times 1590 \times 10^{3}}{418866} \approx 1.01 \text{kg/Adt}$ The concentration of sulphur in MgSO₄ $c_{MgSO_{4}} = 121 \text{ g/l}[49]$ $c_{S} = \frac{S}{Mg + S + 4Q} c_{MgSO_{4}} = \frac{32}{24 + 32 + 4 \times 16} 121 \approx 32.3 \text{ g/l}$

Bleaching plant, stage 1

$$\dot{V} = 3.22 \text{ l/min [50]}$$
Production = 418 866 ton [37]
t = Number of days of 2012 = 366 days

$$m_S = \frac{\dot{c_S V t}}{\text{Production}} = \frac{32.3 \times 10^{-3} \times 3.22 \times 366 \times 60 \times 24}{418 866} \approx 0.13 \text{ kg/Adt}$$

Bleaching plant, stage 2

V = 2,65 l/min [51] Production = 418 866 ton [37] t = Number of days of 2012 = 366 days

$$m_S = \frac{c_S V t}{\text{Production}} = \frac{32.3 \times 10^{-3} \times 2.65 \times 366 \times 60 \times 24}{418\,866} \approx 0.11 \,\text{kg/Adt}$$

Bleaching plant, stage 3

V = 3.45 l/min [52] Production = 418 866 ton [37] t = Number of days of 2012 = 366 days

$$m_S = \frac{c_S V t}{\text{Production}} = \frac{32.3 \times 10^{-3} \times 3.45 \times 366 \times 60 \times 24}{418\,866} \approx 0.14 \text{ kg/Adt}$$

Oxygen delignification

V = 20.2 l/min [51]Production = 418 866 ton [37] t = Number of days of 2012 = 366 days $m_S = \frac{c_S V t}{Production} = \frac{32.3 \times 10^{-3} \times 20.2 \times 366 \times 60 \times 24}{418 866} \approx 0.82 \text{ kg/Adt}$

AlSO₄

Aluminium sulphate is added to the water cleaning plant to catch the colloidal particles. Consumed: 421 ton [43]

$$m_{S} = \frac{S}{Al + S + 4O} \frac{m_{AlSO_{4}}}{\text{Production}} = \frac{32}{26 + 32 + 4*16} * \frac{421*10^{3}}{418\,866} = 0.26 \text{ kg/Adt}$$

Sulphuric acid

Sulphuric acid is used in ash purging, tall oil digesting and to adjust pH of the water and the pulp. The concentration used at the mill is 40%. Sulphuric acid is added to waste water treatment, bleaching, final screening, tall oil digesting and ash purging. The mill has reported purchased amount of sulphuric acid 8580 ton. Production = 418866 ton

 $m_{S}^{H_{2}SO_{4}} = \frac{X_{S} * m_{H_{2}SO_{4}}}{\text{Production}} = \frac{0.327 * 8580 * 10^{3}}{418866} \approx 6.70 \text{ kg/Adt}$ The concentration of sulphur in H₂SO₄: Density $\rho = 1.30 \text{ g/ml}$ at the concentration c = 40% [54] Calculate on 1000 ml solution: $m_{tot} = \rho V = 1.30 * 1000 = 1300 \text{ g}$ 40% of the total mass is pure H₂SO₄: m = 0.40 * 1300 = 520 g c = 520 g/l $m_S = \frac{S}{2H + S + 40} m_{H_2SO_4} = \frac{32}{2*1 + 32 + 4*16} * 520 \approx 170$ g $c_S = 170$ g/l

Waste water treatment

 $\dot{V} = 1.71$ l/min [53] Production = 418 866 ton [37] t = Number of days of 2012 = 366 days

$$m_S = \frac{c_S V t}{\text{Production}} = \frac{170 \times 10^{-3} \times 1.71 \times 366 \times 24}{418\,866} = 6.1 \times 10^{-3} \text{ kg/Adt}$$

Bleaching plant, stage 1

$$\dot{m}_{H_2SO_4} = 6.53 \text{ kg/h} [56]$$

$$\dot{m}_S = \frac{S}{2H + S + 40} \dot{m}_{H_2SO_4} = \frac{32}{2*1 + 32 + 4*16} * 6.53 \approx 2.13 \text{ kg/h}$$

Production = 418 866 ton [37]
$$t = \text{Number of down of 2012} = 266 \text{ down}$$

t = Number of days of 2012 = 366 days

$$m_S = \frac{m_S t}{\text{Production}} = \frac{2.13 * 366 * 24}{418 866} \approx 0.045 \text{ kg/Adt}$$

Bleaching plant, stage 3

$$V = 5.76 \text{ l/min [57]}$$

Production = 418 866 ton [37]
t = Number of days of 2012 = 366 days

$$m_S = \frac{c_S V t}{\text{Production}} = \frac{170 * 10^{-3} * 5.76 * 366 * 60 * 24}{418\,866} \approx 1.23 \,\text{kg/Adt}$$

Final screening, pulp tank 3

$$\dot{V} = 0.43 \text{ l/min [58]}$$
Production = 418 866 ton [37]
t = Number of days of 2012 = 366 days

$$m_S = \frac{\dot{c_S V t}}{\text{Production}} = \frac{170 \times 10^{-3} \times 0.43 \times 366 \times 60 \times 24}{418 866} \approx 0.09 \text{ kg/Adt}$$

Final screening, mixing point

V = 5.68 l/min [59] Production = 418 866 ton [37] t = Number of days of 2012 = 366 days

 $m_S = \frac{c_S V t}{\text{Production}} = \frac{170 * 10^{-3} * 5.68 * 366 * 60 * 24}{418\,866} \approx 1.22 \text{ kg/Adt}$

Tall oil digesting

 $\dot{V} = 0.14 \text{ l/s [60]}$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days $m_S = \frac{c_S V t}{\text{Production}} = \frac{170 \times 10^{-3} \times 0.14 \times 366 \times 3600 \times 24}{418 866} \approx 1.80 \text{ kg/Adt}$

Ash purging

 $\dot{V} = 0.0076 \text{ l/s [60]}$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days $m_S = \frac{\dot{c_S V t}}{\text{Production}} = \frac{170 \times 10^{-3} \times 0.0076 \times 366 \times 3600 \times 24}{418 866} \approx 0.10 \text{ kg/Adt}$

The total amount of sulphur that enters the mill:

 $m_{S}^{Total} = m_{S}^{Fresh water} + m_{S}^{Alvamix} + m_{S}^{Sodium formiate} + m_{S}^{Calcium oxide} + m_{S}^{Oil} + m_{S}^{Synthetic gas} + m_{S}^{MgSO_{4}} + m_{S}^{H2O_{4}} + m_{S}^{H2O_{4}} = 0.31 + 0.57 + 4.05 \times 10^{-4} + 2.3 \times 10^{-3} + 0.10 + 0.025 + 1.01 + 0.26 + 6.70 = 8.98 \text{ kg/Adt}$

Appendix 3

Outgoing material streams of sodium

Sodium is lost a lot by effluent but also by tall oil, green liquor sludge, lime mud, fibre sludge and pulp.

Tall oil

The resins in the wood reacts with sodium to form sodium soap that is separated from the thin black liquor in the evaporation plant. The sodium soap is then reacted with sulphuric acid to form tall oil.

 $m_{tot} = 0,29 \text{ kg/s} [62]$ $c_{Na} = 800 \text{ ppm} = 0,080 \%$; Laboratory analysis

Production = 418 866 ton [37]

t = Number of days of 2012 = 366 days

 $m_{\rm Na} = \frac{m_{tot}c_{Na}t}{\rm Production} = \frac{8*10^{-4}*0.29*366*3600*24}{418\,866} \approx 0.018 \text{ kg/Adt}$

Pulp

The final product. $c_{Na} = 710 \text{ mg/kg DS Table 14}$ DF = 90% Production = 418 866 days [37] $m_{Na} = \frac{c_{Na}DF * \text{Production}}{\text{Production}} = \frac{710 * 10^{-6} * 0.90 * 418 866 * 10^{3}}{418 866} \approx 0.64 \text{ kg/Adt}$

Green liquor sludge

Green liquor sludge is undissolved particles of green liquor, this is removed in the causticizing plant.

 $c_{\text{Na}} = 67,0 \text{ mg/g DS Table 14}$ $m_{GLS} = 8660 \text{ ton [63]}$ DF = 27,76% [63]
Production = 418 866 [37] $m_{Na} = \frac{m_{GLS} DF c_{Na}}{Production} = \frac{8660 \times 10^6 \times 0.278 \times 67.0 \times 10^{-6}}{418 866} \approx 0.39 \text{ kg/Adt}$

Lime mud

Lime mud is removed from the mill to reduce non process elements, this means also a loss of calcium oxide and this has to be replaced.

The mass of removed lime mud is obtained from the added mass of calcium oxide. The reaction in the lime kiln: $CaCO_3(s) + Heat \Leftrightarrow CaO(s) + CO_2(g)$

From this reaction the fraction of formed calcium oxide is:

$$\frac{CaO}{CaO + CO_2} = \frac{40 + 16}{40 + 16 + 12 + 2*16} = 56\%$$

The added amount of calcium oxide corresponds to 56% of the removed lime mud. The mill has reported the amount of added calcium oxide is 16 000 ton [44].

$$m_{Lime\ mud} = \frac{16\ 000}{0.56} \approx 28\ 500\ \text{ton}$$

$$c_{\text{Na}} = 9.02\ \text{g/kg}\ \text{DS}\ \text{Table}\ 14$$

$$m_{Lime\ mud} = 28\ 500\ \text{ton}$$

$$\text{DF} = 81,8\%\ [65]$$

$$\text{Production} = 418\ 866\ \text{ton}\ [37]$$

$$m_{Na} = \frac{m_{Lime\ mud}DFc_{Na}}{\text{Production}} = \frac{28\ 500\ \text{*10}^3\ \text{*0.818}\ \text{*9.02}\ \text{*10}^{-3}}{418\ 866} \approx 0.50\ \text{kg/Adt}$$

Fibre sludge

Some of the fibres goes to the effluent and leaves the mill at the waste water treatment. The values of the dry fraction and the mass are taken from 2010.

 $c_{Na} = 1.88 \text{ mg/g DS Table 14}$ $m_{Sludge} = 4800 \text{ ton [63]}$ DF = 45% [63]
Production = 418 866 ton [37] $m_{Na} = \frac{m_{Sludge} DF c_{Na}}{Production} = \frac{4800 \times 10^6 \times 0.45 \times 1.88 \times 10^{-6}}{418 866} \approx 0.01 \text{ kg/Adt}$

Effluent

The outgoing material stream that leaving the mill is by V6 V6 $m_{Na} = 7340 \text{ ton } [37]$ Production = 418866 ton [37] $\dot{m}_{Na} = \frac{7340*10^3}{418866} \approx 17.5 \text{ kg/Adt}$

The total amount of sodium that leaves the mill:

 $m_{Na}^{Total} = m_{Na}^{Tall\ oil} + m_{Na}^{Pulp} + m_{Na}^{GLS} + m_{Na}^{Lime\ mud} + m_{Na}^{Sludge} + m_{Na}^{Effluent} = 0.017 + 0.64 + 0.12 + 39 * 10^{-3} + 5.7 * 10^{-3} + 15.5 \approx 16.3 \text{ kg/Adt}$

Appendix 4

Outgoing material streams of sulphur

Sulphur leaves the mill in the form of pulp, gases, lime mud, green liquor sludge and fibre sludge.

Pulp

 $c_S = 2.45 \text{ mg/kg DS Table 13}$ DF = 90 % Production = 418 866 ton [37] $m_S = \frac{c_S \text{DF} * \text{Production}}{\text{Production}} = \frac{2.45 * 10^{-6} 0.90 * 418 866 * 10^3}{418 866} \approx 0.0022 \text{ kg/Adt}$

Green liquor sludge

 $c_{\rm S} = 23.6 \text{ mg/g DS Table 13}$ $m_{GLS} = 8660 \text{ ton [63]}$ DF = 27,76% [67] Production = 418 866 ton [37] $m_{S} = \frac{c_{S}DFm_{GLS}}{\text{Production}} = \frac{23.6 \times 10^{-6} \times 0.278 \times 8660 \times 10^{6}}{418 866} \approx 0.14 \text{ kg/Adt}$

Lime mud

 $c_{\rm S} = 0.44$ g/kg DS Table 13 $m_{Lime\ mud} = 28\ 600$ ton DF = 81.8% [67] Production = 418\ 866 ton [37] $m_{\rm S} = \frac{c_{\rm S} DF m_{Lime\ mud}}{\text{Production}} = \frac{0.44 \times 10^{-3} \times 0.818 \times 28\ 600 \times 10^{3}}{418\ 866} \approx 24.6 \times 10^{-3} \text{ kg/Adt}$

Fibre sludge

 $c_{S} = 2,92 \text{ mg/g DS Table 13}$ $m_{Sludge} = 4800 \text{ ton [63]}$ DF = 45% [63]
Production = 418 866 ton [37] $m_{S} = \frac{c_{S} \text{DF} m_{Sludge}}{\text{Production}} = \frac{2.92 \times 10^{-6} \times 0.45 \times 4800 \times 10^{6}}{418 866} \approx 15.1 \times 10^{-3} \text{ kg/Adt}$

Effluent

The outgoing material streams that leaving the mill is by V6. V6

 $m_S = 5280 \text{ ton } [37]$

Production = 418 866 ton [37]

$$\dot{m}_S = \frac{5280 * 10^3}{418866} \approx 12.6 \, \text{kg/Adt}$$

Flue gases

The flue gases leaves the mill and contain sulphur in the form of sulphur dioxide and hydrogen sulphide. Flue gases leaves the mill from recovery boiler and lime kiln. Recovery boiler:

Emission of sulphur (SO₂): $m_S = 10500 \text{ kg} [35]$

Production = 418 866 ton [37] $m_S = \frac{m_S}{\text{Production}} = \frac{10\ 500}{418\ 866} \approx 0.025\ \text{kg/Adt}$

Lime kiln:

Emission of sulphur (SO₂): $m_S = 938 \text{ kg} [36]$

$$m_S = \frac{m_S}{\text{Production}} = \frac{938}{418\ 866} \approx 0.002\ \text{kg/Adt}$$

Emission of sulphur (H₂S): $m_S = 3590 \text{ kg} [36]$

$$m_S = \frac{m_S}{\text{Production}} = \frac{3590}{418\ 866} \approx 0.009\ \text{kg/Adt}$$

Weak gases

Weak gases are referred to as TRS and they are formed in those places where liquors are evaporated. Weak gases come from chip bin, tall oil digesting and different liquor tanks in the mill. These gases are measured three times each year. The major part are methanol and methyl mercaptan, methanol is separated in the stripper and is used as fuel in the lime kiln, the other gases goes to the atmosphere.

The emission of sulphur to the atmosphere: $m_s = 21400 \text{ kg}$

Production = 418 866 ton [37]

$$m_S = \frac{m_S}{\text{Production}} = \frac{21\,400}{418\,866} \approx 0.05 \text{ kg/Adt}$$

Strong gases

Strong gases are formed in blow tanks in digesting plant and in the evaporation plant and these are burned in recovery boiler or lime kiln. If the load in the recovery boiler is low they are incinerated by a torch.

Emission of sulphur by strong gases: $m_s = 37300 \text{ kg}[37]$

Production = 418 866 ton [37]

 $m_S = \frac{37300}{418\ 866} \approx 0.089\ \text{kg/Adt}$

Ash

Ash is a rest product when synthetic gas is formed. Produced ash: 475 ton [86] DF = 88% [86] Sulphur in ash: 184 mg/kg DS [86] Removed sulphur by ash: $0.88 * 475 * 10^3 * 184 * 10^{-6} \approx 77$ kg

$$m_S = \frac{77}{418\ 866} \approx 1.84 \times 10^{-4} \ \text{kg/Adt}$$

The total amount of sulphur that leaves the mill:

$$m_{S}^{Total} = m_{S}^{Pulp} + m_{S}^{GLS} + m_{S}^{Lime\ mud} + m_{S}^{Sludge} + m_{S}^{Effluent} + m_{S}^{Gases} + m_{S}^{Ash} =$$

= 2,2 * 10⁻³ + 0.14 + 24.6 * 10⁻³ + 15.1 * 10⁻³ + 12,6 + 0.18 + 1.84 * 10⁻⁴ ≈ 13.0 kg/Adt

Appendix 5

Sodium/sulphur material streams within the system

AWP means Andritz wash press and it is a wash press after the oxygen delignification plant. Laboratory analysis of the pulp can be seen below.

$$c_{Na} = 7,26 \text{ mg/g DS Table 14}$$

 $c_S = 2,80 \text{ mg/g DS Table 13}$
 $m_{Na} = \frac{c_{Na}}{10^{-6}} = \frac{7.26 \times 10^{-6}}{10^{-6}} = 7.26 \text{ kg/Adt}$
 $m_S = \frac{c_S}{10^{-6}} = \frac{2.80 \times 10^{-6}}{10^{-6}} = 2.80 \text{ kg/Adt}$

Ash purging

Chlorine and potassium are present in the system and these are harmful for the recovery boiler and have to be removed. This is performed by ash purging. Sulphuric acid is used as dissolving agent. Ash, water and sulphuric acid enter the leaching tank to form a slurry, this slurry is then dewatered in a centrifuge. The liquid phase goes then to effluent (V4) and the solid phase to the mix tank. The ash is represented as sodium sulphate and comes from recovery boiler and electrostatic precipitator.



Figure 8. Ash purging at the Värö mill. Reference Jenny Svensson 2012.

$$m_{Ash} = 939 \text{ kg/h} [68]$$

t = Number of days of 2012 = 366
The concentration of sodium and sulphur
 $c_{Na} = 294 \text{ g/kg} [69]$
 $c_{SO_4} = 580 \text{ g/kg} [70]$
 $c_S = \frac{S}{S+40} c_{SO_4} = \frac{32}{32+4*16} \times 580 = 193 \text{ g/kg}$
 $m_{Na} = \frac{c_{Na}m_{Ash}t}{Production} = \frac{294 \times 10^{-3} \times 939 \times 366 \times 24}{418 \times 866} \approx 5.79 \text{ kg/Adt}$
 $m_S = \frac{c_S m_{Ash}t}{Production} = \frac{193 \times 10^{-3} \times 939 \times 366 \times 24}{418 \times 866} \approx 3.80 \text{ kg/Adt}$

Water to ash purging

 $c_{Na} = 10.2 \text{ mg/l Table 14}$ $c_S = 4 \text{ mg/l Table 13}$ $. m_{H_2O} = 0.03 \text{ kg/h [71]}$ t = Number of days of 2012 = 366 daysProduction = 418 866 ton [37]

$$\rho_{H_2O} = 1000 \text{ kg/m}^3 \Rightarrow \dot{V}_{H_2O} = \frac{\dot{m}_{H_2O}}{\rho_{H_2O}} = \frac{0.03}{1000} = 3*10^{-5} \text{ m}^3/\text{h}$$

$$m_{Na} = \frac{\dot{c}_{Na}\dot{V}_{H_2O}t}{\text{Production}} = \frac{10.2*10^{-6}*3*10^{-5}*366*24}{418\,866} = 6.42*10^{-12} \text{ kg/Adt}$$

$$m_S = \frac{\dot{c}_S\dot{V}_{H_2O}t}{\text{Production}} = \frac{4*10^{-6}*3*10^{-5}*366*24}{418\,866} \approx 2.52*10^{-12} \text{ kg/Adt}$$

Dust to effluent

The liquid phase that goes to effluent contains mainly chlorine and potassium but also dust that is represented as sodium sulphate.

Total amount of dust is given from amount of sodium:

$$m_{tot}^{Dust} = \frac{m_{Na}}{X_{Na}}; \text{Where } X_{Na} \text{ is mass fraction of sodium}$$

$$X_{Na} = \frac{m_{Na}}{m_{Na} + m_S + m_O} = \frac{2*23}{2*23 + 32 + 4*16} \approx 0.324$$

$$X_S = \frac{m_S}{m_{Na} + m_S + 4m_O} = \frac{32}{2*23 + 32 + 4*16} \approx 0.225$$

$$m_{Na}^{Dust} = 1080 \text{ ton } [31]$$

$$m_S^{Dust} = X_S m_{tot}^{Dust} = X_S \frac{m_{Na}}{X_{Na}} = 0.225 * \frac{1080}{0.324} \approx 750 \text{ ton}$$

$$m_{Na} = \frac{1080 * 10^3}{418 866} \approx 2.58 \text{ kg/Adt}$$

$$m_S = \frac{750 * 10^3}{418 866} \approx 1.79 \text{ kg/Adt}$$

BB2

BB2 is the filtrate from the second bleaching stage and this is recirculated to the wash press after the reactors in oxygen delignification plant. $c_{Nz} = 1300 \text{ mg/l Table 14}$

$$c_{Na} = 1500$$
 mg/l Table 14
 $c_{S} = 210$ mg/l Table 13
 $...$
 $V = 4150$ l/min [72]
Production = 418 866 ton [37]
t = Number of days of 2012 = 366
$$m_{Na} = \frac{c_{Na}Vt}{\text{Production}} = \frac{1300 \times 10^{-6} \times 4150 \times 366 \times 24 \times 60}{418\,866} = 6.79 \text{ kg/Adt}$$
$$m_{S} = \frac{c_{S}Vt}{\text{Production}} = \frac{210 \times 10^{-6} \times 4150 \times 366 \times 24 \times 60}{418\,866} \approx 1.10 \text{ kg/Adt}$$

Black liquor

 $\dot{V} = 447 \text{ m}^{3}/\text{h}$ $\rho_{BL} = 1040 \text{ kg/m}^{3}; \text{ Density of black liquor}$ DF = 15% $X_{Na} = 16,1\%$ $X_{S} = 4,0\%$ t = Operating time of 2012 = 357 days $m_{Na} = \frac{\dot{V}\rho_{BL}X_{Na}DFt}{\text{Production}} = \frac{447*1040*0.161*0.15*357*24}{418\,866} \approx 230 \text{ kg/Adt}$ $m_{S} = \frac{\dot{V}\rho_{BL}X_{S}DFt}{\text{Production}} = \frac{447*1040*0.04*0.15*357*24}{418\,866} \approx 57.1 \text{ kg/Adt}$

White liquor

$$c_{Na} = 90.9 \text{ g/l}$$

$$c_{S} = 0.78 \text{ mol/l} = 0,78 * 32 = 25.0 \text{g/l}$$

$$\dot{V}_{1} = 72.1 \text{ m}^{3}/\text{h}$$

$$\dot{V}_{2} = 71 \text{ m}^{3}/\text{h}$$

$$\dot{V}_{tot} = \dot{V}_{1} + \dot{V}_{2} = 143 \text{ m}^{3}/\text{h}$$

$$m_{Na} = \frac{c_{Na}\dot{V}}{\text{Production}} = \frac{90.9 * 10^{-3} * 143 * 10^{3} * 357 * 24}{418 866} \approx 266 \text{ kg/Adt}$$

$$m_{S} = \frac{c_{S}\dot{V}}{\text{Production}} = \frac{25.0 * 10^{-3} * 143 * 10^{3} * 357 * 24}{418 866} \approx 73 \text{kg/Adt}$$

Mechanically cleaned water

 $c_{Na} = 9.83 \text{ mg/l Table 14}$ $c_S = 3.48 \text{ mg/l Table 13}$ · $V = 45.5 \text{ m}^3 / \min[87]$ t = Operating time of 2012 = 357 daysProduction = 418 866 ton [37]

 $m_{Na} = \frac{V^{C}_{Na}t}{\text{Production}} = \frac{45.5 \times 10^{3} \times 9,83 \times 10^{-6} \times 357 \times 24 \times 60}{418\,866} \approx 0,55 \text{ kg/Adt}$ $m_{S} = \frac{V^{C}_{S}t}{\text{Production}} = \frac{45.5 \times 10^{3} \times 3,48 \times 10^{-6} \times 357 \times 24 \times 60}{418\,866} \approx 0,19 \text{ kg/Adt}$

Chemically cleaned water

 $c_{Na} = 13.3 \text{ mg/l [89]}$ $c_{S} = 10.7 \text{ mg/l}; \text{ Table 13}$ \cdot $V = 9.48 \text{ m}^{3} / \text{min [89]}$ t = Operating time of 2012 = 357 daysProduction = 418 866 ton [37]

 $m_{Na} = \frac{V^{C}_{Na}t}{\text{Production}} = \frac{9.48 \times 10^{3} \times 13.3 \times 10^{-6} \times 357 \times 24 \times 60}{418\,866} \approx 0.15 \text{ kg/Adt}$ $m_{S} = \frac{V^{C}_{S}t}{\text{Production}} = \frac{9.48 \times 10^{3} \times 10.7 \times 10^{-6} \times 357 \times 24 \times 60}{418\,866} \approx 0.12 \text{ kg/Adt}$

Bio sludge

 $c_{S} = 15\ 000\ \text{mg/kg DS}$ DS = 2.6% . $V = 2.43\ \text{l/s}$ $\rho = 15500\ \text{mg/l}$ $t = \text{Operating time of } 2012 = 357\ \text{days}$ Production = 418 866 ton [37]

$$m_{S} = \frac{V^{C_{S}}DS\rho t}{\text{Production}} = \frac{2.43*15500*10^{-6}*0.026*15000*10^{-6}*357*24*60*60}{418\,866} \approx 0,0011\,\text{kg/Adt}$$

Soap $c_{S} = 7580 \text{ mg/kg}; \text{ Table 13}$ $c_{Na} = 87\ 000 \text{ mg/kg}; \text{ Table 14}$. $m_{Soap} = 0.99 \text{ kg/s}$ t = Operating time of 2012 = 357 daysProduction = 418 866 ton [37] $m_{S} = \frac{m_{Soap}c_{S}t}{\text{Production}} = \frac{0.99 * 7580 * 10^{-6} * 357 * 24 * 60 * 60}{418\ 866} \approx 0.55 \text{ kg/Adt}$ $m_{Na} = \frac{m_{Soap}c_{Na}t}{\text{Production}} = \frac{0.99 * 87000 * 10^{-6} * 357 * 24 * 60 * 60}{418\ 866} \approx 6.34 \text{ kg/Adt}$

Acid from tall oil digesting plant

 $c_{S} = 16\ 300\ \text{mg/l};$ Table 13 $c_{Na} = 34\ 000\ \text{mg/l};$ Table 14 $\dot{V} = 95.6\ \text{l/min}$ t = Operating time of 2012 = 357daysProduction = 418 866 ton [37] $m_{S} = \frac{c_{S}\dot{V}t}{\text{Production}} = \frac{16\ 300\ \text{*10}^{-6}\ \text{*95.6}\ \text{*}\ 357\ \text{*24}\ \text{*60}}{418\ 866} \approx 1.91\ \text{kg/Adt}$

 $m_{Na} = \frac{c_{Na}Vt}{\text{Production}} = \frac{34\ 000*10^{-6}*95.6*357*24*60}{418\ 866} \approx 3.99\ \text{kg/Adt}$

Appendix 6

Effluents

It can be concluded from table 8 that sodium/sulphur are lost a lot by effluent, the calculations can be seen below.

Sodium

V1

 $c_{Na} = 728 \text{ mg/l}[73]$ $\dot{V} = 743 \text{ m}^3/\text{h}[74]$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days

$$m_{Na} = \frac{c_{Na}Vt}{\text{Production}} = \frac{728 \times 10^{-6} \times 743 \times 10^{3} \times 366 \times 24}{418\ 866} \approx 11.3\ \text{kg/Adt}$$

V2

 $c_{Na} = 140 \text{ mg/l}[75]$ $\dot{V} = 474 \text{ m}^3/\text{h}[76]$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days $m_{Na} = \frac{c_{Na}\dot{Vt}}{\text{Production}} = \frac{140 \times 10^{-6} \times 474 \times 10^3 \times 366 \times 24}{418 866} \approx 1.39 \text{ kg/Adt}$ **V3** $c_{Na} = 66.0 \text{ mg/l}[77]$

$$c_{Na} = 66.0 \text{ mg/l}[77]$$

$$\dot{V} = 1320 \text{ m}^3/\text{h}[78]$$

Production = 418 866 ton [37]
t = Number of days of 2012 = 366 days

$$m_{Na} = \frac{c_{Na}Vt}{\text{Production}} = \frac{66.0 \times 10^{-6} \times 1320 \times 10^3 \times 366 \times 24}{418 866} \approx 1.83 \text{ kg/Adt}$$

 $c_{Na} = 1650 \text{ mg/l}[79]$ $\dot{V} = 97.4 \text{ m}^3/\text{h}[80]$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days

$$m_{Na} = \frac{c_{Na}Vt}{\text{Production}} = \frac{1650*10^{-6}*97.4*10^{-8}*366*24}{418\,866} \approx 3.37 \text{ kg/Adt}$$

V6

 $m_{Na} = 6543 \text{ ton } [37]$ Production = 418 866 ton [37] $m_{Na} = \frac{6540 \times 10^3}{418866} \approx 15.6 \text{ kg/Adt}$

V7

 $c_{Na} = 657 \text{ mg/l}[81]$ $\dot{V} = 876 \text{ m}^3/\text{h}[82]$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days $m_{Na} = \frac{c_{Na}Vt}{Production} = \frac{657 * 10^{-6} * 876 * 10^3 * 366 * 24}{418 866} \approx 12.1 \text{ kg/Adt}$

V11

 $c_{Na} = 377 \text{ mg/l Table 14}$ $\dot{V} = 0.48 \text{ l/s [83]}$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 $m_{Na} = \frac{c_{Na}Vt}{\text{Production}} = \frac{377 * 10^{-6} * 0.48 * 366 * 3600 * 24}{418 866} \approx 0.014 \text{ kg/Adt}$

V12f

 $c_{Na} = 4.7 \text{ g/l Table 14}$ $\dot{V} = 7.91 \text{ m}^3/\text{h} [84]$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days $m_{Na} = \frac{c_{Na}\dot{Vt}}{\text{Production}} = \frac{4.7 \times 10^{-3} \times 7.91 \times 10^3 \times 366 \times 24}{418 866} \approx 0.78 \text{ kg/Adt}$

 $c_{Na} = 22.8 \text{ mg/l Table 14}$ $\dot{V} = 9.55 \text{ m}^3/\text{h} [85]$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days

$$m_{Na} = \frac{c_{Na}Vt}{\text{Production}} = \frac{22.8 \times 10^{-5} \times 9.55 \times 10^{-5} \times 366 \times 24}{418\,866} \approx 0.005 \text{ kg/Adt}$$

Sulphur

V1 $c_{S} = 285 \text{ mg/l Table 13}$ $\dot{V} = 743 \text{ m}^{3}/\text{h} [74]$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days $m_{S} = \frac{\dot{c_{S}Vt}}{\text{Production}} = \frac{285 \times 10^{-6} \times 743 \times 10^{3} \times 366 \times 24}{418 866} \approx 4.44 \text{ kg/Adt}$ V2

v_{S}^{2} $c_{S} = 94.5 \text{ mg/l Table 13}$ $\dot{v} = 474 \text{ m}^{3}/\text{h} [76]$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days $m_{S} = \frac{c_{S} \dot{v}t}{\text{Production}} = \frac{94.5 \times 10^{-6} \times 474 \times 10^{3} \times 366 \times 24}{418 866} \approx 0.94 \text{ kg/Adt}$ V3 $c_{S} = 33.5 \text{ mg/l Table 13}$ $\dot{v} = 1320 \text{ m}^{3}/\text{h} [78]$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days

$$m_S = \frac{c_S V t}{\text{Production}} = \frac{33.5 \times 10^{-6} \times 1320 \times 10^3 \times 366 \times 24}{418\,866} \approx 0.93 \,\text{kg/Adt}$$

 $c_{S} = 685 \text{ mg/l Table 13}$ $\dot{V} = 97.4 \text{ m}^{3}/\text{h} [80]$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days $m_{S} = \frac{685 * 10^{-6} * 97.4 * 10^{3} * 366 * 24}{418 866} \approx 1.40 \text{ kg/Adt}$

V6

 $m_S = 5280 \text{ ton } [37]$ Production = 418 866 ton [37] $m_S = \frac{5280 \times 10^3}{418866} \approx 12.6 \text{ kg/Adt}$

V7

 $c_S = 287 \text{ mg/l Table 13}$ $\dot{V} = 876 \text{ m}^3/\text{h} [82]$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days $m_S = \frac{c_S V t}{\text{Production}} = \frac{287 \times 10^{-6} \times 876 \times 10^3 \times 366 \times 24}{418 866} \approx 5.27 \text{ kg/Adt}$

V11

 $c_{S} = 239 \text{ mg/l Table 13}$ $\dot{V} = 0.48 \text{ l/s [83]}$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days $m_{S} = \frac{\dot{c_{S}Vt}}{\text{Production}} = \frac{239 * 10^{-6} * 0.48 * 366 * 3600 * 24}{418 866} \approx 8.7 * 10^{-3} \text{ kg/Adt}$ V12f

 $c_S = 1.13 \text{ g/l Table 13}$ $V = 7.91 \text{ m}^3/\text{h} [84]$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days

$$m_S = \frac{c_S V t}{\text{Production}} = \frac{1.13 \times 10^{-3} \times 7.91 \times 10^3 \times 366 \times 24}{418\,866} \approx 0.19 \text{ kg/Adt}$$

 $c_S = 8.86 \text{ mg/l}$ Table 13 $\dot{V} = 9.55 \text{ m}^3/\text{h}[85]$ Production = 418 866 ton [37] t = Number of days of 2012 = 366 days $m_{S} = \frac{\dot{c_{S}Vt}}{\text{Production}} = \frac{8.86 \times 10^{-6} \times 9.55 \times 10^{3} \times 366 \times 24}{418\ 866} \approx 1.8 \times 10^{-3} \text{ kg/Adt}$

Appendix 7

The calculations by online measurements on sodium hydroxide, magnesium sulphate and sulphuric acid:

$$X_{Na}^{NaOH} = \frac{Na}{Na+O+H} = \frac{23}{23+16+1} = 0.575$$

$$m_{Na}^{NaOH} = 17.3 \text{ kg/Adt} \Rightarrow m_{NaOH} = \frac{17.3 \times 10^{-3}}{0.575} \times 418\ 866 \approx 12\ 600\ \text{ton}$$

$$X_{S}^{MgSO_{4}} = \frac{S}{Mg+S+4O} = \frac{32}{24+32+4\times 16} \approx 0.267$$

$$m_{S}^{MgSO_{4}} = 1.20 \text{ kg/Adt} \Rightarrow m_{MgSO_{4}} = \frac{1.20 \times 10^{-3}}{0.267} \times 418\ 866 \approx 1880\ \text{ton}$$

$$X_{S}^{H_{2}SO_{4}} = \frac{S}{2H+S+4O} = \frac{32}{2\times 1+32+4\times 16} \approx 0.327$$

$$m_{S}^{H_{2}SO_{4}} = 4.47 \text{ kg/Adt} \Rightarrow m_{H_{2}SO_{4}} = \frac{4.47 \times 10^{-3}}{0.327} \times 418\ 866 \approx 5730\ \text{ton}$$

Appendix 8

The calculations of the losses of sodium and sulphur: $L_S = 9.65 \text{ kg/Adt}$ $L_{Na} = 19.6 \text{ kg/Adt}$ $M_{Na} = 23 \text{ g/mole} \Rightarrow L_{Na} = \frac{19.6}{23 \times 10^{-3}} \approx 852 \text{ mole/Adt}$ $M_S = 32 \text{ g/mole} \Rightarrow L_S = \frac{9.65}{32 \times 10^{-3}} = 302 \text{ mole/Adt}$ $\frac{L_{Na}}{L_S} = \frac{852}{302} \approx 2.82$