A dynamic Na/S balance of a kraft pulp mill

Modeling and simulation of a kraft pulp mill using WinGEMS

En dynamisk Na/S balans av ett sulfatbruk
Modellering och simulering av ett sulfatbruk i WinGEMS

Per Andersson
Abstract

The main scope of this thesis was to create a simulation model of a kraft pulp mill and produce a dynamic Na/S balance. The model was made in WinGEMS 5.3 and the method consisted of implementing a static Na/S balance from the mill and created a model that described this chemical balance. Input data from the mill was collected and implemented in the model. A number of different cases were simulated to predict the effects of different process changes over time, dynamic balances. The result from the static balance showed that the model can describes the mill case. The result from the dynamic simulation showed that the model can be used to predict the effect of process changes over shorter periods of time.
Executive Summary

In the kraft mill the chemical balance is of interest to minimize the production cost. Normally there is an excess of sulfur and low levels of sodium, compared to what the process requires. In the future, the pulp mill will most likely produce other products than just pulp. These new production processes will also most likely affect the sodium and sulfur balance and there is a need to be able to predict this change. One way to predict these effects and thereby the costs, is to create a balance of the interesting process chemicals. These balances can be made with average production values or as a function of process changes over time, a dynamic simulation.

The main scope of this thesis was to create a model of Skoghall mill and produce a dynamic Na/S balance. The result should be a model that can be used for a number of different cases and generate both static and dynamic Na/S balances.

The model was made in the program WinGEMS 5.3 and the input value was production average data from the year 2013. The model was built with one fiber line and controlled the sulfidity in the white liquor by purging the electrostatic precipitator ash from the recovery boiler.

In the static Na/S balance the input values to the model were approximately the same as the mill values. There was a small difference in the output values, due to the tuning of the model, but the total balance was consistent with the mill. The result from a simulation of a theoretical case with only bleached production showed that there was a high amount of sodium and sulfur entering and leaving the system. The reason for this was the chemicals used in oxygen delignification and the bleach plant filtrate, which was circulated and used as wash liquor in brown stock. This lead to a high sulfidity and effective alkali in the white liquor. The theoretical static unbleached balance showed a significant lower intake and output of sodium and sulfur, since no beaching chemicals were used. This resulted in a lower sulfidity and effective alkali in the white liquor.

In the dynamic simulation model, the production of both unbleached and bleached pulp was simulated on one fiber line, with an interval of two days. The simulation generated a sulfidity variation over time and can be used to study the effects of process changes.

One way to control the sulfidity is to purge electrostatic precipitator ash from the recovery boiler. Simulations were made to evaluate what effect the purge had on the sulfidity and how fast a change would occur. One case was when the maximum ash amount was purged to see how fast the sulfidity dropped and one case where no ash was purged to see how the sulfidity increased.
The case where maximum ash was purged reduced the sulfidity from 42% to 37% in four days, the case where all the ash was recycled to the black liquor raised the sulfidity from 42% to 43.6% in four days.

Due to the large liquor volume, it will take time before any changes in composition of the liquor system is noticed. The result from the dynamic simulation showed, not surprisingly that if the tanks were drained, the system become more unstable.

An increased intake of CTMP effluent to the black liquor evaporation will have an effect on the static Na/S balance. To deal with the increased amount of sodium and sulfur, an increase purge of electrostatic precipitator ash was simulated. An increased flow of bisulfite to the CTMP plant could level out the effect of an increased intake of effluent.

A dynamic simulation where the fiber line was divided into one bleached and one unbleached line was performed. The results showed that this would generate a more stable mill operation because of the even flow of chemicals.

An increased production rate would generate a lower tank volume per produced ton of pulp (shorter residence time). A case with a 10% production increase and with the same ratio between bleached and unbleached pulp production as today was compared to current operation. The result showed that an increased production would generate a more unstable sulfidity at the higher production rate.
Acknowledgements

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Chapter 1. Introduction

1.1 Background
In the kraft mill the chemical balance is of interest to minimize the production cost. Normally in softwood mills there is an excess of sulfur and low levels of sodium, compared to what the process requires. The unbalance is adjusted in different ways depending on the mill.

In the future, the pulp mill will most likely produce other products than just pulp, which in turn might induce the introduction of new processes. These new production processes will also most likely affect the sodium and sulfur balance and there is a need to be able to predict this change.

One way to predict these effects and there by the costs, is to create a balance of the interesting process chemicals. These balances can be made with average production values or as a function of process changes over time, a dynamic balance.

1.2 Problem formulation
The main scope of this thesis was to create a simulation model of a kraft pulp mill and produce a dynamic Na/S balance. The model was made in Metso WinGEMS 5.3, which is used for simulating different process changes. The result should be a model that can be used for a number of different cases and generate both static and dynamic Na/S balances. The created model will be used as base in future concept studies.

The thesis was done at Stora Enso Research Center, Pulp Competence Center in Karlstad.

1.3 Delimitations
The study was made for Skoghall mill using a static Na/S balance for the pulp mill as base input. An existing WinGEMS model was rebuilt to fit today’s layout and production.
Chapter 2. Pulping background

2.1 Pulping background
The technology behind the chemical pulping process has been developed during the end of the nineteenth century. One of the first processes used straw and hardwood cooked in strong alkali solution under high temperatures, to produce pulp for papermaking (Biermann, C.J. 1996).

Today the most common chemical pulp technology is kraft pulping (sulfate process), where wood chips are cooked in white liquor. The white liquor is a mixture of different chemicals, where the active cooking chemicals are sodium hydroxide (NaOH) and sodium sulfide (Na₂S). The process releases the cellulose fibers from the wood chips which produces a brown pulp. The pulp is then washed and used as unbleached kraft pulp or bleached to produce white pulp. The pulp can then be used for different paper products in the range between fine paper to board (Gullichsen, J. Fogelholm, C.J. 1999a).

Other processes to produce pulp exist, and some of them are mentioned under the common term mechanical pulp. The mechanical pulp is obtained by grinding wood to release the fibers and there are some developments of the process. Thermo-mechanical pulp (TMP) is using heated steam to soften the wood and chemo-thermo mechanical pulp (CTMP) uses sodium bisulfite and heat to soften the wood chips before grinding. The mechanical pulp is used for example magazines and the middle layer inside some qualities of board. The pulp has a higher bulk but is a weaker pulp than chemical pulp (Höglund, H. 2010).

2.2 Development
One of the first chemical pulping processes was the soda process, where sodium hydroxide (NaOH) was used as the active cooking chemical and the raw material was straw or hardwood. The process was invented in England in 1851 by Burgess and Watts and the first mill started in 1866.

The sulfite process was first patented during 1867 in the U.S by Benjamin Tilghman. The sulfite mill uses sulfite (SO₃²⁻) or bisulfite (HSO₃⁻) as active cooking chemical depending on the pH-value. The counter ion can be sodium, calcium, potassium, magnesium or ammonium. The first sulfite mill in use was in Sweden and was started 1874 in Bergvik, using magnesium as base ion. The kraft process was invented 1879 by the German C.F Dahl and the process cooked the wood chips in an alkaline solution with hydrogen sulfide ions (HS⁻). The first kraft mill started 1890 in Munksjö, Sweden.

The sulfite process was previously dominating the market since the pulp was brighter and did not need as much bleaching as the kraft pulp. But when bleaching and oxygen delignification was further developed and improved, it made it easier to bleach the pulp and the stronger kraft pulp is today the dominating chemical pulp (Biermann, C.J. 1996, Gullichsen, J. Fogelholm, C.J. 1999a).
Chapter 3. Kraft process
3.1 Kraft process description
The kraft pulping process is a combination of many unit operations and it requires a lot of equipment in one mill. The main unit operations are the digester, evaporation plant, recovery boiler and lime cycle, see figure 1.

First the logs are barked and chipped. The wood chips are boiled in the digester with white liquor at a high temperature around 170°C in a strong alkali environment to release the fibers. The cellulose fibers are bound together by an organic compound called lignin which is a polymer and works as a binder in the wood. During the digester process the lignin dissolves in the liquor and the fiber are released. Lignin in pulp can cause smell, yellowish color and more chemicals are needed to dissolve the lignin in the following oxygen delignification and in the bleach plant. One method to determine the residual lignin content in pulp, the kappa number method may be utilized. The method is an ISO-standard titration method (ISO 302:2012). The wood chips contains about 27-28% lignin depending on the raw material. The unbleached kraft pulp contains only around 2-5% lignin and even though this is a small amount it still colors the pulp brown. In the oxygen delignification stage about 60-75% of the residual lignin is dissolved. The final rest are degraded and dissolved in the bleach plant to generate a white pulp (Gellerstedt, G. 2010a).

During the cook the active chemicals in the white liquor, hydroxide (OH⁻) and sulfide (HS⁻), splits the large lignin molecule into smaller fragments, that can be dissolved in the liquor. The cook can be divided in three phases; initial, bulk and residual delignification phase. The major part of the lignin will be dissolved in the initial and bulk phase and the more lignin that are dissolved, the more difficult it is to reduce the content further (Gellerstedt, G. 2010a, Gullichsen, J. Fogelholm, C.J. 1999a).
The main goal of the kraft pulping process is to dissolve lignin and release the fibers. The problem is to dissolve enough lignin without affecting the cellulose chains in the fiber. If the cook is too aggressive with high temperature, too long time and/or high chemical charge, the chains are affected. Either by peeling where the end groups of the chains are cut off, or by alkali hydrolysis, where the chain is cut of in pieces. This will create shorter cellulose chains and in the end a weaker pulp. One solution to the problem is to first cook to release the fibers and then apply oxygen delignification follow by bleaching to reduce the lignin content. If the lignin is reduced in the digester to a certain kappa number, the viscosity will be lower than if the pulp is cooked, oxygen delignified and bleached to the same kappa number. Viscosity is an ISO-standard measurement (ISO 5351:2010) that provides an indication of cellulose chains length, used to compare different pulp qualities and pulping strategies. A high viscosity means longer chains and normally a stronger pulp (Gellerstedt, G. 2010a).

The kraft pulp exiting the digester is dark brown and the spent cooking liquor needs to be washed away. The wash water from the oxygen delignification is transferred back to the digester. The spent cooking liquor and wash water from the digester is called weak black liquor.

The produced pulp can either be used as an unbleached kraft pulp which normally is a stronger pulp or the pulp can be bleached to higher brightness. The most commonly employed bleaching sequences in Sweden are elemental chlorine free (ECF) containing chlorine dioxide as bleaching agent. There are different bleaching sequences that can be used, some for example with hydrogen peroxide as agent (Gullichsen, J. Fogelholm, C.J. 1999a).

The weak black liquor is sent to the evaporation plant to increase the relative dry substance content from 15-20% up to 70-80%. The heavy black liquor is thereafter sent to the recovery boiler where it is injected and burned. The recovery boiler is often considered to be the heart of the mill where the used cooking chemicals are regenerated. The boiler also generates steam that is used on the mill. The black liquor is injected into the boiler and burned under a high temperature and both reducing and oxidizing environments.

The smelt that is created in the bottom of the boiler, consist mainly of carbon and inorganic salts, and the smelt are dissolved with water creating green liquor. The liquor is sent to the causticizing plant where the active cooking chemical hydroxide is formed by causticizing with reburned lime. (Gellerstedt, G. 2010c, Gullichsen, J. Fogelholm, C.J. 1999b).
3.2 Chemical recovery

Chemical recovery is an important part of the mill. Without it the chemical pulping would not be economic or environmental viable. The black liquor from the digester contains dissolved fibers, organic- and inorganic compounds. The liquor is sent to the recovery boiler where it is burned. The recovery boiler produces steam that is used in the mill. Possible excess steam can be used for production of green electricity or district heating to the nearby town or village.

In the burning process of the black liquor to char inside the boiler, the active cooking chemical sulfide is formed from sodium sulfate, see reaction 1. The smelt from the recovery boiler consists of carbon and the inorganic salts: sodium carbonate, sodium sulfide and a minor extent of sodium sulfate. The smelt is dissolved in wash water normally originating from the lime mud wash which thereafter is called green liquor. The green liquor contains mainly sodium, carbonate and hydrogen sulfide as ions. (Gullichsen, J. Fogelholm, C.J. 1999b).

**Reaction 1.** Reproduced sodium sulfide.

\[
4 \text{C (s)} + \text{Na}_2\text{SO}_4 (1s) \rightarrow \text{Na}_2\text{S (l,s)} + 4 \text{CO (g)}
\]

The liquor is causticized in the lime cycle, where the green liquor is mixed with burned lime (calcium oxide). First the burned lime reacts with water and becomes slaked lime, then the active hydroxide are reproduced by the formation of calcium carbonate, see reaction 2. To determine the efficiency of the slaker, the causticizing degree can be used. The degree is defined as the ratio of sodium carbonate that is transformed into sodium hydroxide. The reproduced white liquor is filtrated to remove the lime mud (Tikka, P. 2008a).

**Reaction 2.** Causticizing reaction in slaker.

\[
\text{CaO (s)} + \text{H}_2\text{O (l)} \rightarrow \text{Ca(OH)}_2 (s)
\]

\[
\text{Ca(OH)}_2 (s) + \text{CO}_3^{2-} (l) \leftrightarrow 2 \text{OH}^- (l) + \text{CaCO}_3 (s)
\]

The lime mud is then burned in a kiln to regenerate burned lime, see reaction 3. The lime kiln is a long tubular oven with a temperature of up to 1300 °C. The lime mud is entering the kiln from one side, and transferred towards the other side though rotation. The process releases carbon dioxide and burned lime is formed (Theliander, H. 2010b).

**Reaction 3.** Burning of lime mud.

\[
\text{CaCO}_3 (s) + \text{heat} \rightarrow \text{CaO (s)} + \text{CO}_2 (g)
\]

Up to 97% of the active cooking chemicals can normally be reused in a modern mill and the rest needs to be compensated with make-up chemicals (Axegard, P. Renberg, L. 1998).
3.3 Chemicals in a kraft pulp mill

The effective cooking chemicals in the white liquor are sodium hydroxide and sodium sulfide which are present in ionic forms as OH\(^{-}\) and HS\(^{-}\). The amount and ratio between them are important for the production and quality of the pulp. To determine the quality of the white liquor, sulfidity and alkali contents are measured, see equation 1-3. The sulfidity is the ratio between the amount of sodium sulfide divided by the sum of sodium sulfide and sodium hydroxide, normally expressed as percent. The alkali can be measured as effective or active alkali, both in grams per liter. The effective alkali describes the amount sodium hydroxide and sodium sulfide as OH\(^{-}\). The concentration of sodium sulfide is divided by two since it will create one HS\(^{-}\) and one OH\(^{-}\) ion. The active alkali describes the total alkali for both ions. The effective alkali is the most commonly used in Sweden and expressed as g NaOH (Gellerstedt, G. 2010b).

**Equation 1.** Sulfidity (\(\%\)) = \(\frac{2[HS^-]}{[HS^-]+[OH^-]}\) * 100

**Equation 2.** Effective alkali = NaOH + \(\frac{Na_2S}{2}\) (g/l)*

**Equation 3.** Active alkali = NaOH + \(Na_2S\) (g/l)*

* (as g NaOH, or as g Na\(_2\)O).

In the mill there are chemicals used for make-up of chemical losses and in different unit processes. Sodium hydroxide is used as a sulfur free make-up and for pH control. Magnesium sulfate (MgSO\(_4\)) is used in the oxygen delignification and peroxide stage in the bleach plant to protect the cellulose from being degraded and maintain the viscosity through the delignification. Sulfuric acid (H\(_2\)SO\(_4\)) is used for pH control and in the tall oil plant (Gellerstedt, G. 2010b).
3.4 Bleaching chemicals

There are a number of different bleaching chemicals used, but the most common are hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) and chlorine dioxide (ClO\textsubscript{2}). There can also be a stage were a chelation agent (EDTA or DTPA) is used, to remove metal ions before hydrogen peroxide bleaching (Gellerstedt, G. 2010b).

Elemental chlorine free bleaching uses chlorine dioxide as a bleaching chemical. Chlorine dioxide is an oxidizer in gaseous form that can be dissolved in water. The chemical is produced at the mill since it is a thermodynamically unstable chemical and also environmental hazardous, which makes it difficult to store and transport. There are different processes to produce the chlorine dioxide, which all results in different residual products, known as spent acid or salt cake. The spent acid comes from the production at atmospheric pressure, as the Mathieson process. The salt cake comes from the chlorine dioxide production at vacuum, and there are a few different processes. Different reducing agents can be used and the most common is methanol (MeOH) or hydrogen peroxide. The spent acid contains mainly of sodium sulfate (Na\textsubscript{2}SO\textsubscript{4}) and sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) in different amounts depending on the type of process and efficiency of the plant. The salt cake is a solid salt of sodium sulfate (Stockburger, P. 1993). The environmental regulation in Sweden regulates the amount effluent from the mill. Therefore it is important to take care of the residual product. The salt cake is often mixed into the black liquor thus entering the chemical cycle of the mill. The spent acid can be used as pH control or make-up in the chemical cycle (SFS 1998:808, The environmental code).

3.5 Non-process elements

There are a lot of elements entering the mill with the wood, impure make-up chemicals and other sources. Some of these elements are not beneficial for the pulping process and some can cause problems. These elements are called non-process elements (NPE) and some of them are more harmful than others. Chloride (Cl) can cause sticky dust in the recovery boiler, which can create process disturbances and decrease the efficiency of the boiler. Chloride can also cause corrosion. Potassium (K) can cause plugging, corrosion and will generate an increased load, which is costly to transport through the mill. A purging of ash from the recovery boiler will reduce the chloride and potassium levels in the system.

There are some heavy metals entering the mill that can accumulate, but usually they leave the mill with acidic effluents. These elements are toxic and it is important to reduce these. Other metals, like iron (Fe) and copper (Cu) can increase the need for chemicals in the bleach plant, and generate a cost increase (Gellerstedt, G. 2010b). Aluminum (Al) and magnesium (Mg) causes inert compounds in the lime cycle to form. Phosphor (P) and Nitrogen (N) emissions can lead to eutrophication, enrichment of chemical nutrients in nearby environment (Gullichsen, J. Fogelholm, C.J. 1999b). The closure of the modern pulp mill has increased the problems with accumulation of non-process elements. The alkaline wash water from the bleach plant can be used as wash water and the acidic wash water is sent to the effluent, since it contains more metal ions and heavy metals. Before the closure, elements were normally transported out with the wash filtrates, but today with the wash filtrate recycled back these outputs has been reduced (Tran, H. Vakkilanienn, E.K. 2008, Ulmgren, P. 1997).
3.6 Electrostatic precipitators
On top of the recovery boiler there are electrostatic precipitators (ESP) used to collect the ash from the flue gases that comes from the furnace. The ash contains mainly sodium sulfate, see table 1 (Ahlroth, M. et al. 2007). To minimize the sodium and sulfur loss in the mill the ash is reintroduced to the black liquor. The precipitator uses charged electrodes that charge the dust entering the precipitator and the particles are forced into an electric field where the ash is drawn to the charge plates (opposite charge of the particle), see figure 2. The dust will then stick onto the plates and about 0-10% of the ash is leaving with outlet gas, depending on the efficiency. The plates are cleaned continuously, the charge is the turned off and the plats are shaken so the dust falls off and are collected beneath (Parker, K.R 1996, Theliander, H. 2010a).

![Figure 2](image)

**Figure 2.** The principle behind the electric precipitator (Air clean Industrial-duty).

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass%</th>
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<tr>
<td>SO₄</td>
<td>62</td>
</tr>
<tr>
<td>Na</td>
<td>30</td>
</tr>
<tr>
<td>K</td>
<td>6</td>
</tr>
<tr>
<td>CO₃</td>
<td>2</td>
</tr>
<tr>
<td>Cl</td>
<td>1</td>
</tr>
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Table 1. Typical content in ash from the recovery boiler.

3.7 Non condensable gases
The evaporation plant and recovery boiler are emitting some sulfur containing gas under normal operation conditions. These gases are non-condensable, and are called non condensable gases (NCG). Some examples of compounds in NCG are hydrogen sulfide (H₂S), methyl mercaptane (CH₃SH) and dimethyl sulfide (CH₃SCH₃). Due to environmental and odor restrictions, these gases are not allowed to be released in to the atmosphere and therefore it needs to be oxidized to sulfur dioxide (SO₂). To be able to oxidize this sulfur gas a high temperature is needed which is found in a combustion unit as the recovery boiler, lime kiln or gas boiler. It is possible to build a separate furnace to deal with the NCG. After burning the oxidized gas it may be scrubbed with fresh sodium hydroxide and oxidized white liquor to create bisulfite which can be sold or used in other parts of the mill (Bordado, C.M. Gomes, F.P 1998).
3.8 Tall oil plant
In a kraft pulp mill that uses softwood as raw material the resins and fatty acid in the wood chips are converted to sodium salts. These salts are separated from the black liquor in the evaporation plant and float on the liquor, called soap. The soap are then separated and transported to the tall oil plant. The reason that the soap is recovered is because it otherwise will cause process problems if retained in the black liquor. The soap has a tendency to foam which will make it difficult to determine the amount of black liquor in tanks. If the foam sticks to the pulp, it will increase the drainage resistant of the pulp in the washers. In the evaporation plant the soap can causes scaling and foaming, decreasing the efficiency of the units (Tikka, P. 2008).

In the tall oil plant the soap is mixed with acid and heated. After the process the soap will split into two fractions, creating tall oil and an acid. The acid, normally denoted as spent or waste acid, is neutralized with sodium hydroxide and sent back to the evaporation plant. The product, tall oil is a valuable byproduct which is sold or used as a fuel (Foran, C.D. 1992).

3.9 Environmental regulations
There are environmental regulations in Sweden that determine the allowed production and emissions from the mill. The Environmental Code (Accepted by the Swedish Parliament 1999) is used as guide line when matters around the subject are tried in court. The mills need to apply for approval for production and emissions from the local county. There are regulations on emissions in effluents like for example total organic carbon (TOC), absorbable organic halogens (AOX), phosphor, nitrogen (NOX) and chlorate. There are also air emission regulations on sulfur containing compounds that can create odor and chloride in gas (SFS 1998:808, The environmental code).

During the last decade there have been a lot of improvements on the emission from the mills. Both air and water emissions have steadily declined even though the production has increased.
Sulfur emissions to the atmosphere have been a large problem previously, but with modern precipitators and scrubbers the emissions have decreased, see figure 3.

![Sulfur Emissions from Swedish pulp and paper mills](image)

**Figure 3.** Sulfur emissions from Swedish mills (Skogsindustrierna 2012).

There has also been a decrease in the carbon dioxide (CO₂) emissions from the mills. From 2001 to 2011 the mills have decreased the emission by 50% (based on the mills consumption on fossil fuels) per ton of sold pulp and paper (Skogsindustrierna 2012).

The new improved mills generate new issues for the sodium and sulfur balance, since fewer elements are leaving the mill through emissions which leads to an increased accumulation that can cause problems (Tran, H. Vakkilanienn, E.K 2008).
Chapter 4. Na/S balance

4.1 Na/S balance

In the kraft mill the chemical balance is of interest both to minimize the production costs and to control the process conditions. It is important to know the sodium and sulfur balance to be able to have a stable mill operation. The balance has an influence on the pulping yield and pulp quality (because of the sulfidity and effective alkali) and emissions of sulfurous gases. A general sodium and sulfur balance means that the intake is balanced with the outtake, i.e.,

\[ \text{In} = \text{Out}. \]

The problem is that in a mill it can be difficult to determine the amount of elements that are leaving the system with different streams. Another problem is accumulation in the system where concentrations of elements increase with time. A better estimated balance is then

\[ \text{In} + \text{Produced} = \text{Out} + \text{Accumulated} \]

where the accumulated elements are accounted for.

The balance can also be used to predict what will happen if a change is made in the system, for example closure of certain streams or a change to a different make-up chemical. The problem in the mill is that it takes a long time before any effect of the change is noticeable. It can take days before the change is noticed and then it will take time to correct the balance, and there by creating an oscillating process. This long time frame depends on the tank volumes and residence times in the different unit operations. In a mill there are a lot of tanks containing liquor, which is used as a buffer. This leads to that small changes are often not seen due to natural fluctuations in the system, but changes can also have a longtime effect. The full effect of a change in the system can take days and even weeks before it is noticed (Saturnio, D. M. 2012).

The usual problem in Scandinavian pulp mills is high concentrations of sulfur and low concentration of sodium. The balance has an impact on the pulping and a varying sulfidity and effective alkali can have effect on the pulp quality. A higher sulfidity in the kraft cook will give a higher delignification rate, lignin will dissolve faster and this gives a faster cook. The sulfidity has an effect on the viscosity. A higher sulfidity gives a higher viscosity at the same kappa number for the pulp. The down side is that a higher sulfidity gives more sulfur containing air emissions and odor. A higher effective alkali will give a faster delignification rate but it will also give a lower fiber yield. (Bränvall, E. 2010, Gullichsen, J. Fogelholm, C.J. 1999).

Due to environmental restrictions the mill need to control emissions, both to air and in the effluent. The odor can be a problem for a kraft pulp mill but there are many ways to deal with the problem. For instance a higher temperature in a new recovery boiler will decrease the emissions to the air and the electrostatic precipitators reduce the ash leaving with the flue gasses (Huppa, M 2008).
It is also important to know the balance because make-up chemicals are expensive, especially sulfur free sources of sodium, such as fresh sodium hydroxide. A material balance can be used to reduce the need of make-up chemicals and give a more stable mill operation.

4.2 System boundary
A sodium and sulfur balance can established for the entire mill or just for the fiber line with or without the bleach plant. It is important to specify the system boundary to be able to state the input and output streams. The system boundary can be described as a division of the system that is focused upon. All the sodium and sulfur containing input and output streams should be specified, even though this can be difficult due to diffuse sulfur emissions.

4.3 Sources of sodium and sulfur
Sodium enters the mill in form of chemicals as sodium hydroxide and sodium sulfate (NaSO₄). There is also some sodium in the spent acid from the chlorine dioxide plant. Depending on where the system boundary is drawn the bleach plant filtrate can be an input, if it is recirculated/used as wash water in the brown stock.

Sulfur enters the mill in form of chemicals such as sodium sulfate, magnesium sulfate used in the oxygen delignification- and hydrogen peroxide stage. Sulfuric acid is used for pH control and in the tall oil plant. Some sulfur is entering with the fuel to the lime kiln where the burnt lime absorbs some sulfur which is dissolved in the white liquor. A major source of sulfur comes from the spent acid from the chlorine dioxide plant which is used as pH control or as a make-up chemical (Saturnio, D. M. 2012).

There can also be inputs of external streams entering the system boundary, like a CTMP-effluent or chemicals imported from another industry.

4.4 Sodium and sulfur losses
Depending on the system boarder, sodium and sulfur are removed from the system with the pulp to the bleach plant, called wash losses. Both elements are also leaving the system boundary with the water effluent. An internal generation of chemicals inside the system boundary can be an output, for example sodium bisulfite created in the NCG burner that is used in the CTMP plant. Some sodium and sulfur are leaving with grids and dregs from the lime cycle. A major part of sodium and sulfur leaves the system boundary in form of ESP-ash which is purged from the recovery boiler. Sulfur can leave the mill in form of gaseous compounds and sodium and sulfur leaves with liquor streams or solids leaving the system boundary (Saturnio, D. M. 2012).
4.5 How to control the sodium and sulfur balance
In Scandinavian mills the sodium and sulfur balance is normally driven by the sulfidity of the mill. The sulfidity is different for different mills. In the Nordic countries the sulfidity is normally higher than for example in North American mills. To control the balance the ESP-ash from recovery boiler is usually purged. The ash contains mainly sodium (Na), sulfate (SO$_4^{2-}$), potassium (K), carbonate (CO$_3^{2-}$) and chloride (Cl) (Ahlroth, M. et al. 2007).

The purge of ESP-ash results in a loss of sulfur, sodium and some NPE, leading to a lower sulfidity. The amount of ash that is purged depends on the sulfidity and input of sodium and sulfur. To lower the sulfidity more ash is purged. If it is low, less or none ash is purged to increase the sulfidity. Purging ash will also generate a loss of NPE (mainly K and Cl) which is desired (because of corrosion and plugging). But a high purge will give a sodium (and sulfur) loss that might need to be compensated with make-up chemicals.

If there is a production of chemicals containing sodium and sulfur in the system boundary that is used outside, this stream can be increased to decrease the sodium and sulfur in the system.

4.6 Static Na/S balance
A static Na/S balance is used to show the total amount of sodium and sulfur that are entering and leaving the mill at a steady state. A steady state is a theoretical state where all input and output values are equal and stable. The balance is performed by taking the total amount sodium and sulfur per year, divided by the pulp production calculated in air dried ton or bone dried ton (ADt, 90% dry substance or BDt, 100% dry substance). A static balance is done by listing all sodium and sulfur containing streams in and out of the system boundary. Some streams need to be analyzed while the content in others are more easy to determine. The sulfur gases leaving the system are more difficult to determine then for example liquor effluents. The static balance can be done manually or in for example Microsoft Excel.

4.7 Dynamic Na/S balance
Na/S balances can be made from normal production or as a function of process changes over time, which is called dynamic-balances. A dynamic balance is done with a more complex computer program such as WinGEMS or ChemCAD (Metso WinGEMS 5.3, Chemstations ChemCAD 6.5).

A dynamic model can be used for short time periods (days up to month) tracking components in a flow or developing control strategies. To start a dynamic simulation, a static Na/S balance is needed to begin with and then program different cases and disturbances in the mill. The dynamic model can show the effects of a change on a short time frame and can be helpful to predict the time it takes for a change to affect the system (Metso WinGEMS 5.3, Saturnio, D. M. 2012).
Chapter 5. WinGEMS

5.1 Metso WinGEMS 5.3

WinGEMS is based on the GEMS software first developed at the University of Idaho Chemical Engineering department in the 1960s. In 1992 the first commercial product was released by Pacific Simulation, called WinGEMS (Windows General Energy and Material balance System). Today it is owned by Metso Automation and the Metso WinGEMS 5.3 is the latest release.

The program was developed for the pulp and paper industries for solving process and design problems in a mill. The program is built on a graphic interface using different blocks and streams to build process units, see figure 4.

![Figure 4. Graphic interface of a wash block and streams.](image)

The program uses modular sequential and an iterative method and calculates all input data until convergence is reached. The drawback with the program is that it does not contain any “chemistry”, it uses only mass balance calculations. The user needs to define all chemical reactions and reactions constants to be able to make a simulation with more complex simulations (Metso WinGEMS 5.3).

The modeling can be divided into three sections, building, specification and simulation. In the first section the user needs to build the mill using different controlled blocks and streams to connect them. In the specification, the user needs to specify all the input streams and the required block inputs. In the final simulation section the user can start doing simulations and validate the model (Saturnio, D. M. 2012).
There are different types of blocks in the program that are combined to create a process unit. The most commonly used are the reaction, mix and split blocks. The reaction block is a block where the user defines a reaction, for example a causticizing reaction. The mix block is where different steams and components are mixed together. There are split blocks which are used for splitting flow streams and/or components. There are also wash blocks for washing of example pulp or lime.

To create more detailed process units a compound block may be used. The compound block is a storage block for different blocks that are combined to create a unit inside the block. This is convenient when a larger simulation model is made. There are also pre-constructed compound blocks for more complex units in WinGEMS, such as digesters and lime slakers. The stream components are defined and the user can put in many different elements that can be interesting to observe. The model can be programmed to write all the data from the model to Excel for further calculations and treatment of data.

WinGEMS can be used to simulate a specific process, like the recovery boiler, or the user can create full mill models, depending on what type of problem that is processed. In a steady state simulation the model calculates all input and output data until it has converged and generate a static Na/S balance. This can be useful when performing economical and feasibility studies and is good for planning and de-bottlenecking at the mill.

In the dynamic simulation the model first calculates steady-state and then starts the dynamic simulation. A dynamic simulation is used for short time periods, tracking component flows or developing control strategies. The user defines the repetition by setting repeat with time and sets a time and which time steps that should be used. There are two important blocks for a dynamic simulation, tank and plug flow blocks. Nearly all the other blocks have the same function in steady-state and dynamic simulations (Metso WinGEMS 5.3).
5.2 Tank and plug flow
In the dynamic simulation, the tank and plug flow blocks are important. Both blocks have volume (capacity) and output flow that can be controlled. The output can either be controlled so the block has a perfect controlled volume or constant output flow from the block.

The tank block is a perfect mixed tank and variation in concentrations of the inlet streams will be diluted. The plug flow will generate a plug effect, where the first mass into the tank are the first out (the concentration difference in the tank will not mix). To adjust the plug flow from the block the user defines the number of plugs the flow will portrait. The output response from the block will more closely represent perfect plug flow behavior if more plugs are used.

In the mill there are tanks with high viscous liquors like strong black liquor. These flows might be better be described by a plug flow than a tank. The problem is that in a mill the tanks with high viscous liquor often have a stirrer inside them to prevent the plug flow effect.

In the mill and the model the volume of the tanks works as a buffer and like a “shock absorber”, to decrease the effect of a changes and making the system more stable (Dynamics Add-On For WinGEMS 5.3).
Chapter 6. Skoghall mill

6.1 Background

Skoghall mill is a modern integrated pulp mill that produces board. The mill started in 1919 at Skoghall and has undergone a lot of development and improvements over the years. The mill produces packaging board, for both liquid and dry food. The wood material is soft wood (spruce and pine) and the mill produces both kraft pulp and CTMP-pulp on the site. There are two board machines in the mill BM 7 and BM 8, which produces over 700,000 ton paperboard per year (Skoghall mill 2013a).

Historic events

1919 Start of the kraft mill.
1977 BM 7 in use, rebuilt in 1981 and 1994 to increase capacity.
1996 BM 8 is started.
1999 STORA and Enso form joint company Stora Enso.
2007 Investment to increase pulp production of both kraft and CTMP pulp.
2013-2014 Pulp mill improvements.

6.2 Process description

Skoghall mill produces bleached and unbleached kraft pulp in one fiber line, see figure 5. The mill is using ECF bleaching with chlorine dioxide and hydrogen peroxide to produce the bleached pulp. The kraft pulp is used in the outer layers of the board and depending on the quality, bleached and/or unbleached pulp is used. The mill also produces CTMP in a fiber line using sodium bisulfite as active chemical and the pulp is bleached with hydrogen peroxide. The CTMP is used in the middle layer of board to generate stiffness and bulk. The mill buys some short fiber pulp (birch or eucalyptus) that is mixed into the board outer layer to generate a better printability. Skoghall has one recovery boiler that was built in 2005 and the mill also has a separate furnace to burn the NCG, where the mill creates sodium bisulfite (NaHSO₃). The bisulfite can be used in the CTMP-plant. Skoghall produces tall oil in a separate tail oil plant (Skoghall mill 2013a).
Figure 5. Overview of Skoghall mill (Skoghall mill 2013b).

6.3 Production
Mills in Sweden needs to apply for production permission from the Environmental Court and receives a production limit. The limit is set due to environmental restrictions of emissions. Skoghall has been granted a production of board to 850 000 ton per year and a total of 665 000 ton pulp per year. The mill is allowed to produce 380 000 ton kraft pulp of which 250 000 ton is allowed to be bleached. The yearly production of CTMP should not exceed 285 000 ton and 200 000 ton is allowed to be bleached (Environmental Court 2013).
Chapter 7. Method

7.1 Input data
Prior to this work Skoghall mill has previously done a static Na/S balance in Excel which was used as a base for the model. The input data from the mill was extracted from WinMOPS (Eurocon MOPSsys), a program for data analysis. There are measuring points on the mill that is collecting data continuously and reports values to WinMOPS. The values that are used within this thesis are averages values from one year. Sulfidity and effective alkali are two important parameters for monitoring the quality of the white liquor and these values are measured online and imported into the WinMOPS system. The ESP-ash content is analyzed at lab regularly and the amount that is purged is measured online.

All input data was collected and divided by the production from the digester as air dried ton pulp per hour (ADt/h). Some data were obtained from the mill, like wash losses, which are not measured regularly.

7.2 WinGEMS model
The model was made in Metso WinGEMS 5.3. There was an existing model for Skoghall mill (from 2008) that was rebuilt to fit today’s layout and production. All process units in the new model were built with compound blocks and some larger units were done specific for Skoghall. The blocks were combined with streams to create a model of the mill and all input streams were specified. All the tanks in the mill within the system boundary were inserted and divided by the production of pulp per hour. All mill data was inserted, for example the evaporation plants efficiency and dry substance. All the wash efficiency for the wash blocks was defined as well as the wash water flows.

All input streams were defined to match the mill case (static Na/S balance from the mill). The outputs was controlled by the model and needed to be specified to get a good balance. The digester was made as a compound block with different reactions blocks. The digester was controlled by specifying its temperature, efficiency factor and yield. The evaporation plant was built in four different stages with the liquor tanks in between, see figure 6. The input values to the evaporation block were the dry substance out and condensate temperature.

The recovery boiler was the heart of the model and also the most difficult to control. The boiler block has many different tuning parameters to be able to get the right composition on the green liquor and flue gases leaving the boiler. The main parameters were enrichment- and tuning factors (efficiency factors for specific parameters). The flue gases leaving the recovery boiler were divided into two streams, one with flue gases and the other with ash. The ash enters the ESP-ash removal block and some of the ash was split (purged) and was controlled by the block to get a specified sulfidity in the white liquor. The ash that was not purged is recirculated back to the heavy black liquor, see figure 6.
The lime cycle was modelled with two slakers, see figure 7. The green liquor from the recovery boiler was divided to both slakers. The burnt lime was added as well as lime make-up in the slakers. The lime charge was defined as well as grits in the out stream. The grits and lime was split and the white liquor was sent to white liquor tanks and then to the digester. The slaked lime was transferred to the lime kiln and burned. The composition of the fuel and parameters of the kiln were specified, such as temperature and efficiency.

First the model ran a static simulation to determine the static balance. The static balance was for both bleached and unbleached pulp, to get the average static Na/S balance for a yearly total production.
After the static balance was established the dynamic simulation could be started. The dynamic simulations is a tool to be able to predict what will happen with different monitored parameters if a change occur during a simulation. The purpose of the calculations was to see what will happen with the Na/S balance when different production problems or changes in the mill occurred.

To perform the dynamic simulation, the so called scripts needed to be written. A script is an execution description for the program where the user can control different parameters. The dynamic simulation needs a script that specifies the repetition time and time steps the simulation should make. In the script the user can control parameters in a specified time, to be able to create a case.

The first dynamic simulation was to see how the sulfidity varies during the production of unbleached and then bleached pulp. Different cases where then made:

**Purge of electrostatic precipitator ash**
- The mill purges ESP-ash from the recovery boiler to control the sulfidity, but it can be difficult to know how much ash to purge and what effect it has. One case where as much ash as the mill can purge was simulated. Another case was with no ash purged was made to see the effect.

**Tank volume**
- There are much of tank capacity and volume in the mill that works as a buffer. Due to the large liquor volume, it will take time before any changes in the system is noticed. One case was where the tanks were drained was simulated to see the effect.

**Causticization disturbances**
- The lime cycle is important to generate the white liquor to the digester. Another case was the slakers were shot-down and fresh sodium hydroxide was added, to see what the effect it had on the sulfidity.

**Tall oil plant**
- Skogshall produces tall oil, which consumes both acid and alkali. The effect a stop of the tall oil plant has on the overall balance was a case simulated.

**Increased CTMP effluent**
- To be able to have less effluent and a more closed mill, an increased intake of CTMP effluent into the system boundary is desired. This will have an effect on the balance since the effluent contains both sodium and sulfur and a case made.

**New fiber line**
- The mill will rebuild the fiber line introducing a split after the digester with one line of unbleached and one with bleached. This will affect the dynamic balance and this case was performed in a simulation.
Chapter 8. Results

8.1 Tanks vs plug flow

It is the tank and plug flow blocks that are important in the dynamic simulation and will affect the system in different ways. The tank block is an ideal mixed tank where the components are mixed together. The plug flow block will not mix the components and maintain the concentration difference through the block.

The different behavior of the tank and plug flow blocks are illustrated in figure 8. The given volume was the same for both blocks. For both blocks the sodium concentration was set to zero to start with, and changed to 5 kg/ton of liquor when the simulation began. Sodium concentration in the outgoing stream from each block was different over time depending on the block type.

Figure 8. Comparison on how tank and plug flow blocks response to a concentration change in the inlet stream.

The tank block that mix the content inside the tank generates an output steam where the sodium concentration is converging towards the new given target value. The outgoing concentration from the plug flow block is seen as an instant but delayed change, where the delay is due to the residence time in the block. The slope on the change could be altered by using different defined plugs in the model.

In the model, both tank and plug flow blocks can be used in different ways to describe the situation at the mill as corrects as possible.
8.2 System boundary
The system boundary for the sodium and sulfur balance done for the kraft pulp mill at Skoghalls is shown in figure 9.

Figure 9. The system boundary for Skoghall mill

The CTMP plant was not included within the boundary, but the CTMP effluent that is taken to black liquor evaporation was considered as an input stream. The content of sodium and sulfur in the effluent was analyzed. The chlorine dioxide plant was also excluded and the spent acid used in the tall oil plant was considered as an input to the model. The bleach plant was not included in the balance and the system boundary was drawn before the chlorine dioxide bleaching stage. A part of the alkaline wash water from the bleach plant was used as wash water and considered as an input to the balance. Sodium and sulfur were measured on both bleached and unbleached pulp leaving the system (wash losses) as well as on the alkaline bleach plant filtrate used for brown stock washing. The board machines were excluded from the model.

Other output streams were lime mud, sludge and grits come from the lime cycle, containing both sodium and some sulfur. The air emission contains mainly sulfur, and emissions to water contain both sulfur and sodium.

The input chemicals were MgSO₄ to oxygen delignification, NaOH, used as pH control in the delignification and in the NCG-gas scrubber (to produce the sodium bisulfite) and H₂SO₄, which was used in the tall oil plant. Produced chemicals/liquors out from the model were both tall oil and acid from the NCG-burner, which was sent to the CTMP fiber line.
8.3 Skoghall mill model

The pulp mill at Skoghall has a single fiber line that produces both bleached and unbleached kraft pulp in campaigns. When creating the model, the line was divided after the oxygen delignification stage and the hydrogen peroxide stage, see figure 10. This means that when the mill produces unbleached pulp the chemicals to these stages were turned off. When the production of bleached pulp started, the chemicals were turned on and the pulp was sent to the bleach plant after the diffuser washer.

![Image of the fiber line at Skoghall mill made in WinGEMS.](image)

**Figure 10.** The fiber line at Skoghall mill made in WinGEMS.

The simulation started with a static Na/S balance base on average values of both bleached and unbleached pulp production. The model was built with one fiber line and produced one air dried ton pulp per hour (ADt/h). The model controlled the sulfidity of the white liquor by purging ESP-ash from the recovery boiler. There were no plug flow blocks in the model and only tank blocks were used.

The input values were average production values from the year 2013, but some values were older, like wash losses and bleach plant filtrate (from 2008) since these are not analyzed regularly.

During the dynamic simulation the model produced unbleached and bleached pulp in campaigns with an interval of two days. After the static simulation the unbleached production started by stopping all chemicals to the bleach plant and split the pulp to the storage tanks for unbleached pulp. The alkaline bleach plant filtrate used as wash water in the brown stock during bleached campaigns was stopped and fresh wash water was used for washing of unbleached pulp. After simulating two days of production, the model began to produce bleached pulp and all chemicals were turned on and the pulp was sent to the bleach plant. The sulfidity was controlled to 42.6%, which was the average value of 2013.

The dynamic simulation continued for as long as it was programmed to. The longest simulation in the presented results ran for 120 days. For every dynamic case that was tested, scripts were made to control the production.
A decrease in sulfidity was generated when the simulation started, see figure 11. This was because the balance used in the static simulation was an average of both bleached and unbleached pulp. When the simulation started with unbleached pulp production, the concentration of sodium and sulfur decreased more in the system than it would do if the simulation had started with bleached production. The effect disappeared when the simulation continued and the bleached production started. The sulfidity stabilized after 6 days.

**Figure 11.** The result of the sulfidity in the dynamic simulation.
8.4 Static Na/S balance

The simulation started with a static Na/S balance generated based on average values from the mill. The static balance from Skoghall mill and the one generated by the simulation in WinGEMS, are compared in figure 12 and table 2. The sodium and sulfur values were calculated as kilogram per air dried ton of pulp and presented in a graph, with sodium on the x-axis and sulfur on the y-axis. A stream containing only sodium will be a horizontal line and a stream that only contains sulfur will be a vertical line. Depending on the ratio between sodium and sulfur the slope will be different. This is considered as a convenient way to present a static Na/S balance and to be able to compare it with other cases.

![Static Na/S Balance for Skoghall mill](image_url)

**Figure 12.** Static Na/S Balance for Skoghall mill.

The input values were almost identical. Some inputs are not used in the model (bark press water) and some are not used in the balance from Skoghall mill (alum).

There were only slight differences between the output values, for example the wash losses and ESP-ash purge. But the difference of the total output values from the model and Skoghall was small. This was because the parameters in the model do not completely describe the reality of the mill. This difference was acceptable in the coming simulations since it will not affect the overall effect of a disturbance or changes made in the dynamic simulation.
The difference between input and output values for sodium for the WinGEMS model is due to calculation errors in the system, but the difference is small (0.3%) so it will not affect the results in the further simulations.
8.5 Bleached and unbleached Na/S balance
The model reflects the mill using one fiber line to produce the pulp. In the static Na/S balance both unbleached and bleached values was used (average). Static simulations have also been made with only bleached and only unbleached pulp production, see figure 13 and table 3.

The simulation of the static bleached Na/S case showed that the system has a lot of sodium and sulfur in circulation, see figure 13. There was a high amount of sodium and sulfur entering and leaving the system compared to the static balance based on average values. This generated a high effective alkali in the white liquor, due to the amount of fresh NaOH used in oxygen delignification stage and hydrogen peroxide stage. The ESP-ash purge was high to maintain the sulfidity on the target level.

The static simulation of the unbleached Na/S case showed that there was significantly lower sodium and sulfur circulation in the system, since no bleaching chemicals were added. The low intake of fresh NaOH results in a lower effective alkali concentration. The ESP-ash purge was larger in the unbleached balance than in the bleached. This was because the wash losses are lower for the unbleached pulp and to balance this, the model purged more ash.

![Bleached vs Unbleached Na&S Balance](image)

**Figure 13.** Theoretical bleached and unbleached production balance.
Table 3. Bleached and unbleached static Na/S balance from WinGEMS.

<table>
<thead>
<tr>
<th>WinGEMS</th>
<th>Sodium [kg/ADt]</th>
<th>Sulfur [kg/ADt]</th>
<th>Sodium [kg/ADt]</th>
<th>Sulfur [kg/ADt]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input</strong></td>
<td>Bleached</td>
<td>Unbleached</td>
<td>Bleached</td>
<td>Unbleached</td>
</tr>
<tr>
<td>Wood</td>
<td>0.01</td>
<td>0.11</td>
<td>0.01</td>
<td>0.11</td>
</tr>
<tr>
<td>NaOH to O2 and OP</td>
<td>6.36</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>NaOH to tall oil</td>
<td>1.65</td>
<td>0.00</td>
<td>1.65</td>
<td>0.00</td>
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<tr>
<td>NaOH to GD scrubber</td>
<td>5.40</td>
<td>0.00</td>
<td>5.40</td>
<td>0.00</td>
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<td>NaOH make-up</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Recycled filtrate - bleached</td>
<td>0.98</td>
<td>0.20</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>CTMP effluent</td>
<td>1.69</td>
<td>0.66</td>
<td>1.69</td>
<td>0.66</td>
</tr>
<tr>
<td>MgSO(_4)</td>
<td>0.00</td>
<td>0.56</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>H(_2)SO(_4) to soap acidulation</td>
<td>0.00</td>
<td>0.69</td>
<td>0.00</td>
<td>0.69</td>
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<tr>
<td>Spent acid to soap acidulation</td>
<td>1.75</td>
<td>3.28</td>
<td>1.75</td>
<td>3.28</td>
</tr>
<tr>
<td>Alum</td>
<td>0.00</td>
<td>0.05</td>
<td>0.00</td>
<td>0.05</td>
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<tr>
<td>Fuel to lime kiln</td>
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<td>0.52</td>
<td>0.00</td>
<td>0.08</td>
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<tr>
<td>Lime make-up</td>
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<td>0.07</td>
<td>0.24</td>
<td>0.07</td>
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<tr>
<td>Methanol</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>Sum in:</strong></td>
<td><strong>18.14</strong></td>
<td><strong>6.12</strong></td>
<td><strong>10.75</strong></td>
<td><strong>4.92</strong></td>
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</table>

<table>
<thead>
<tr>
<th><strong>Output</strong></th>
<th>Bleached</th>
<th>Unbleached</th>
<th>Bleached</th>
<th>Unbleached</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wash loss - bleached pulp</td>
<td>11.44</td>
<td>1.76</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Wash loss - unbleached pulp</td>
<td>0.00</td>
<td>0.00</td>
<td>5.06</td>
<td>0.61</td>
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<tr>
<td>Dregs, grits and lime mud</td>
<td>0.75</td>
<td>0.16</td>
<td>0.13</td>
<td>0.04</td>
</tr>
<tr>
<td>Diffuse S emissions</td>
<td>0.00</td>
<td>0.07</td>
<td>0.00</td>
<td>0.03</td>
</tr>
<tr>
<td>Dust and SO(_2) from RB, GD and LK</td>
<td>0.10</td>
<td>0.54</td>
<td>0.04</td>
<td>0.11</td>
</tr>
<tr>
<td>White liquor to pH-regulation + sold</td>
<td>0.83</td>
<td>0.19</td>
<td>0.26</td>
<td>0.07</td>
</tr>
<tr>
<td>Condensate</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>ESP ash purging</td>
<td>2.85</td>
<td>1.73</td>
<td>4.29</td>
<td>2.75</td>
</tr>
<tr>
<td>Tall oil</td>
<td>0.00</td>
<td>0.14</td>
<td>0.00</td>
<td>0.14</td>
</tr>
<tr>
<td>Bisulphite to CTMP</td>
<td>1.37</td>
<td>1.38</td>
<td>1.02</td>
<td>1.11</td>
</tr>
<tr>
<td>Effluents</td>
<td>0.70</td>
<td>0.16</td>
<td>0.21</td>
<td>0.06</td>
</tr>
<tr>
<td><strong>Sum out:</strong></td>
<td><strong>18.04</strong></td>
<td><strong>6.12</strong></td>
<td><strong>11.00</strong></td>
<td><strong>4.93</strong></td>
</tr>
</tbody>
</table>

The difference between input and output values for sodium for the WinGEMS model was due to calculation errors in the system, but the difference was small (0.2% for bleached and unbleached) so it will not affect the results.
Chapter 9. Results from the Dynamic simulations

9.1 Dynamic simulation in WinGEMS

The simulation started with a static Na/S balance based on average values for both bleached an unbleached pulp production. Then the dynamic simulation started and produced unbleached pulp and bleached pulp in campaigns with an interval of two days. The sulfidity and ESP-ash purge was monitored in an interval of 120 days, see figure 14.

**Figure 14.** Sulfidity and ESP-ash purge during dynamic simulation. Bleached and unbleached pulp are produced in campaigns with two days interval.

The sulfidity varied from 41-44% in the simulation because of the shifting production. This can be related to the theoretical static bleached and unbleached balance where the difference of sodium and sulfur entering the system was shown. The model tried to control the sulfidity to 42.6% by increasing and decreasing the ESP-ash purge. The average sulfidity in the simulation was 42.6% which was the target value. The average ESP-ash purge was 8 kg/ADt pulp. The mill average ESP-ash purge from 2013 was 10 kg/ADt pulp.
The sulfidity varies in the Skoghalls mill because of the pulp production. A case was to simulate the production from a specific time frame from the mill. The model purged the same amount of ESP-ash as the mill at any given time during the time period and the campaign production of unbleached and bleached pulp is the same. The result is show in figure 15.

![Sulfidity comparison](image)

**Figure 15.** The sulfidity and ESP-ash from the mill simulated in WinGEMS.

The result showed that the model produced a more stable sulfidity than the mill. This was because the model had an even flow of chemicals and production, for example tall oil production and bisulfite to the CTMP plant. This will generate a more stable process than for the mill case. The average sulfidity from the simulation was 43% and from the mill 43.3%.
9.2 Purge of electrostatic precipitator ash

One way to control the sulfidity is to purge ESP-ash from the recovery boiler. Today an average of 11 kg/ADt is purged to maintain the sulfidity value at the mill. The maximum amount of ash that can be purged is 23 kg/ADt, due to limitations in the equipment.

During the dynamic simulation the ash purge was controlled by the model to keep the sulfidity at 42.6%. Simulations were made to evaluate what effect the purge has on the sulfidity level and how fast a change would occur. One case was to purge the maximum amount of ash as possible to see how fast the sulfidity dropped and one case was to purge no ash to see how the sulfidity increased. The simulations were set up to run for 6 days before the ash purge was controlled.

The case where maximum ash was purged (23 kg/ADt) was found to reduce the sulfidity from 42% to 37% in four days, see figure 16. In the case where all the ash was recycled to the black liquor, the sulfidity raised from 42% to 43.6% in four days.

The result showed that it was a quicker response to lower the sulfidity then it was to increase it. This is because the mill reintroduces most part of the ash continuously and the amount that is purged is not that much of the total ash produced by the recovery boiler. The amount of ash that is produced in the mill is not measured. The amount of ash created in the model for the static Na/S balance with bleached and unbleached pulp, was 151 kg/ADt and only 10.4 kg/ADt was purged, which is a percentage of 6.9%.

![ESP-ash purge effect](image)

**Figure 16.** The effect of ESP-ash purging on sulfidity in the dynamic simulation cases. The maximum ash purge is 23 kg/ADt.
The case where no ash was purged gave an increase in the sulfidity from 42% to 43.6% in four days. After a maintenance shutdown the sulfidity might be low, because the mill actively tries to lower the total liquor volume in the tanks before the shut-down. Therefore the mill tries to increase the concentrations of sodium and sulfur in the system. A case where a low sulfidity of 35% and no ESP-ash purge was simulated to see how long time it would take for the sulfidity to increase to the target value, with normal tank volume. All available ash was recycled to heavy black liquor. The simulations show that it would take up to 10 days before the sulfidity reaches the desired level, see figure 17.

**Figure 17.** Sulfidity effect when all ESP-ash is reintroduced.

In the figure, the campaign production of bleached and unbleached pulp is show in the variation of the increasing sulfidity curve. This is because the bleached production will increase the sulfidity more compared to the unbleached production, due to the bleaching chemicals used.
### 9.3 Tank volume

There are a number of tanks with storage capacity used as a buffer in the mill. Due to the large liquor volume, it will take time before any changes in the system is noticed. Today an average of 65% of the total tank capacity is used to ensure a stable operation. If the tanks were drained, the system would become more unstable, see figure 18. The sulfidity was controlled by the model to the average of 42.6% in both cases.

![Sulfidity comparison with different tank volume](image)

**Figure 18.** Sulfidity comparison between normal liquor levels in tanks and empty tanks.

The sulfidity in the normal case varied between 41 to 44%. In the case where the tanks were empty, it varied between 30 to 50%. The effect of the production of bleached and unbleached pulp can be seen in the variation of the sulfidity. The bleached production will increase the sulfidity and the unbleached production generates a lower sulfidity. The system becomes more unstable and the effect of the shifting production is more apparent.

A similar case with a higher production rate and thereby shorter residence time in tanks would enhance the instability in the system.
9.4 Causticization disturbances

A worst case scenario is a shot-down, or a delayed start-up after a maintenance stop of the causticization plant. This will lead to an insufficient production of white liquor and in the end a mill stop. A simulation was made to illustrate the effect of replacing white liquor with fresh NaOH in order to prevent a total shut-down of the mill.

Fresh NaOH was added to the white liquor tank to get an efficient flow of liquor to the digester. There was a drastic drop in sulfidity due to the lack of sulfide ions (HS⁻), see figure 19.

![Sulfidity in the dynamic simulation](image)

**Figure 19.** Sulfidity when introducing fresh NaOH to the white liquor tank.

The sulfidity in the black liquor was calculated as Sulfidity (%) = \( \frac{[S]}{[Na] + 2} \times 100 \)

The sulfidity in the white liquor dropped drastically, due to the addition of the fresh alkali. The decrease in the black liquor sulfidity was delayed because there was liquor in the system that contains both sodium and sulfur that will help to maintain the sulfidity.
9.5 Tall oil plant
The tall oil plant uses fresh sodium hydroxide (NaOH), sulfuric acid (H₂SO₄) and spent acid from the chlorine dioxide plant. The tall oil production can sometimes stop and this will affect the Na/S balance. A case in which the tall oil plant shuts down was tested in which chemicals to the plant were turned off. The spent acid that normally goes to the tall oil plant was instead added directly to the evaporation plant. The tall oil plant was turned off after 12 days in the simulation.

The effect was that the model lowers the ESP-ash purge due to the lower intake of sodium and sulfur, see figure 20. The overall effect was small, and the system maintains sulfidity. The ESP-ash purge was lowered from 8.8 kg/ADt to 7.9 kg/ADt. The overall effect was small compared to the natural fluctuations from bleached and unbleached production.

![Tall oil plant disturbance](image.png)

**Figure 20.** The effect of shutdown of the tall oil plant (made at day 12).
If the spent acid was not taken to the evaporation plant/liquor cycle when the tall oil plant was out of operation, the sulfidity will drop, because the high intake of sulfur with the acid are lost. If the tall oil plant was stopped after 12 days, as in the simulation, this would generate a sulfidity decrease from 42.6 to 35% in 20 days, see figure 21. The ash purge from the recovery boiler was zero. The effect of the shifting production was seen in the sulfidity. The unbleached pulp production will decrease the sulfidity more than the bleached pulp production.

![Tall oil plant and spent acid off](image)

**Figure 21.** The loss of sulfidity when tall oil plant and spent acid is off.

The results indicated that a constant flow of spent acid should generate a steadier sulfidity since it has a large impact on the system due to the high content of sodium and sulfur.
9.6 Increased CTMP effluent

An increased intake of CTMP effluent to the black liquor evaporation will have an effect on the static Na/S balance of the mill. The CTMP effluent contains both sodium and sulfur. Three different cases with increased flow, from 11 to 42%, were simulated. To deal with the increased amount of sodium and sulfur, the model increased the ESP-ash purge, see table 4. An increased ash purges will generate an increase in sodium and sulfur loss. An increased intake of effluent with 11% would increase the ESP-ash purge with 4%.

Table 4. CTMP effluent increase effect on sodium and sulfur intake.

<table>
<thead>
<tr>
<th>CTMP effluent increase</th>
<th>Na (kg/ADt)</th>
<th>S (kg/ADt)</th>
<th>ESP ash purge (kg/ADt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal case</td>
<td>1.69</td>
<td>0.66</td>
<td>10.4</td>
</tr>
<tr>
<td>11%</td>
<td>1.88</td>
<td>0.73</td>
<td>10.8</td>
</tr>
<tr>
<td>21%</td>
<td>2.05</td>
<td>0.79</td>
<td>11.0</td>
</tr>
<tr>
<td>42%</td>
<td>2.41</td>
<td>0.93</td>
<td>11.7</td>
</tr>
</tbody>
</table>

The mill produces sodium bisulfite from the off-gases from the NCG burner inside the system boundary. Part of the sodium bisulfite is sent to the CTMP plant as a chemical in the pulp production, and is an output from the boundary. An increased flow of bisulfite to the CTMP plant can level out the effect of an increased intake of effluent, table 5.

Table 5. Increased sodium bisulfite flow as a function of increasing the input of CTMP-effluent.

<table>
<thead>
<tr>
<th>CTMP effluent increase</th>
<th>Acid flow (liters/ADt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal case</td>
<td>13.05</td>
</tr>
<tr>
<td>11%</td>
<td>13.73</td>
</tr>
<tr>
<td>21%</td>
<td>14.46</td>
</tr>
<tr>
<td>42%</td>
<td>15.43</td>
</tr>
</tbody>
</table>

The results showed that an increase of bisulfite to the CTMP plant can lower the sulfidity. The problem in the mill is to get a stable concentration of the bisulfite, in the model the production was stable with a constant flow and concentration.

The amount of bisulfite from the mill can be increased even more, and the ESP-ash purge would be decreased. This could be a way for the mill to decrease the amount of ESP-ash that is purged.

The static Na/S balance from the increased CTMP effluent can be found in Appendix A.
9.7 New fiber line

The current operation with campaign production of bleached and unbleached pulp in a single fiber line results in an unstable sulfidity. The mill will rebuild the fiber line introducing a split after the digester with one line of unbleached pulp and one with bleached pulp. Simulation of this case generated a more stable sulfidity, due to the steadier flow of bleaching chemicals entering the system, figure 22.

The target sulfidity was kept at 42.6% and the average ESP-ash purge was 8 kg/ADt in the simulation. The model tried to purge ash to keep the sulfidity stable and a longer simulation time would give a more stable value.

**Figure 22.** Comparison of the sulfidity and ESP-ash purge on the current and a new fiber line.

The sulfidity varied between 41-44% with the current fiber line outline and for the new outline between 42-43%. The steadier sulfidity would generate a more stable mill operation and in turn pulp quality. The simulation of the new fiber line was based on the current outline, with same chemical charge and operation.
An increase of the production rate will generate a lower tank volume per produced ton of pulp (shorter residence time). A case with a 10% production increase and with the same ratio between bleached and unbleached pulp as today was compared to current operation, see figure 23. The result showed that an increased production will generate a more unstable sulfidity with a higher production rate. The sulfidity is more stable than for current shifting production.

**Figure 23.** Comparison of sulfidity with a higher production rate.

The effects of having lower tank volume in the model made it easier for the system to purge ESP-ash to control the sulfidity. This generated in a steadier sulfidity much quicker than in current production rate.

The result can be compared with the case when the tank volume was lowered (figure 18), because it will affect the system in the similar way.
Chapter 10. Discussion

In a model a process unit can be described by several or a mixture of tank and plug flow blocks to describe the situation at the mill as correct as possible. This simulation model was made in WinGEMS using only tank blocks and no plug flow blocks. This was due to the difficulty to determine what part of the liquor cycle that will have a plug flow appearance. High viscous liquors, such as strong black liquors, might show a plug flow effect but agitation in the tanks increase mixing. It is therefore difficult to estimate how these liquors will respond to a step-change in the concentration. The tanks in the model are perfectly mixed tanks, which is not the case in the mill. One way to improve the model would be to introduce a step-change or add traceable chemicals added to the tank and sample the outgoing stream at the mill. A specific tank in the mill could thereafter be described by several smaller tank blocks or a mixture of tank and plug flow blocks.

A static Na/S balance is a state of equilibrium based on average values for a longer time period, which is rarely found in a mill. There are some differences in the output values from the static Na/S balance made in WinGEMS when comparing to mill data. This is due to difficulties to control the model, where several parameters (as efficiency factors on wash blocks) need to be tuned to get a “perfect” simulation. The differences are small (as most 3.4%) and concerns mainly wash losses, effluent and ESP-ash purges (table 2). This will not have a significant effect on the dynamic result from the dynamic simulation since the results show a step-effect. The effect will be similar even if there was a difference in some of the output values compared to the static balance based on mill data. The difference has a larger effect on the static Na/S balance that has been simulated.

The static Na/S balances for the bleached and unbleached pulp production are extreme cases, because the mill is never running bleached or unbleached campaigns long enough to reach equilibrium in the system (figure 13). However, the difference between bleached and unbleached campaigns explains the sulfidity variation that exists during normal operation.

The dynamic simulation produced bleached and unbleached pulp in campaigns with an interval of two days. The model had some difficulties to control the sulfidity with the ESP-ash purge due to the different amount of sodium and sulfur that enters the system during bleached and unbleached campaigns (figure 14). The mill purges the ash based on sulfidity level and to some extent based on the capacity of the pump that purges the ash.

It is difficult to perform a dynamic simulation of the mill describing a specific event that has occurred, for example a decrease in the sulfidity at a specific time. In reality pulp production as well as input and output streams vary during a day, which makes it difficult to know the total sodium and sulfur concentrations in the system. To perform a simulation that exactly describes a sulfidity change seen in the mill it would be necessary to know all concentrations in the tanks and the exact flows in the current time frame. This would require a lot of input data and analyzes.
One case that was simulated was the production from a specific timeframe from the mill. The result showed that the model produced a more stable sulfidity than the mill. This is because the model has an even flow of chemicals and a more stable production, for example of tall oil and the flow of bisulfite to the CTMP plant, because of the average input values. This will generate a more stable process within the model, see figure 15. The average sulfidity from the simulation was the same as the average sulfidity from the mill during the specified time frame.

One case simulated was when the maximum ash amount was purged to see how fast the sulfidity dropped and one case where no ash was purged to see how the sulfidity increased. The case where maximum ash was purged reduced the sulfidity from 42% to 37% in four days, the case where all the ash was recycled to the black liquor raised the sulfidity from 42% to 43.6% in four days (figure 16). It is difficult to compare this result with the mill, due to the fact that the mill has a more varying production. The mill has periods with no ash purge, one which gave an increase from 40 to 42% in 5 days, which is consistent with the result in the simulation.

Due to the large liquor volume, it will take time before any changes in the liquor system is noticed. The result from the dynamic simulation showed that if the tanks were drained, the system become more unstable, which is expected due to the absorbing effect the tank has (figure 18). A larger liquor volume in the tanks will generate a more stable system.

A dynamic simulation where the fiber line was divided into two lines was simulated. The results showed that this would generate a more stable mill operation because of the even flow of chemicals compared to the current layout (figure 22). This would generate a more stable process and pulping in the mill and could generate a more stable pulp quality.

An increased production rate would generate a lower tank volume per produced ton of pulp (shorter residence time). The result from the simulation showed that an increased production would generate a more unstable sulfidity, which can be compared to the effect the draining of tank volume has.

The model created in this thesis work can be used to predict what will happen when a disturbance or change occur. The model can be programmed/modified to simulate the effects of process modifications.
10.1 Conclusions
The main scope of this thesis work was to create a simulation model of the pulp mill at Stora Enso Skoghall and produce a dynamic Na/S balance.

The produced model made in WinGEMS is capable of simulating both static and dynamic balances. The result from the static Na/S balance shows that the results from the model are consistent with the mill values. The results from the dynamic simulations show that the model can be used to predict an effect of a change in the mill.

10.2 Future work
To acquire an even better simulation of the mill, the output values used in the model can be adjusted to achieve an even more adapted model. There were some old input values used during this work than can be updated to get an even better model.

A way to improve the model would be to introduce a step-change or add traceable chemical to the tank and sample the outgoing stream at the mill. A specific tank in the mill could thereafter be described by several smaller tank blocks or a mixture of tank and plug flow blocks.

The model can be used to simulate additional cases, for example introduction of a new production process and other disturbances that are interesting for the future.
Chapter 11. References


Enviromental Court (2013), Svea Court of Appeal. Application of production change, Skoghall mill. Case number: 11449-12, Stockholm


Metso WinGEMS 5.3


### Appendix A.

**Table 1. CTMP effluent increase with ESP ash increase.**

<table>
<thead>
<tr>
<th>CTMP increase</th>
<th>Sodium [kg/t90]</th>
<th>Sulfur [kg/t90]</th>
<th>Sodium [kg/t90]</th>
<th>Sulfur [kg/t90]</th>
<th>Sodium [kg/t90]</th>
<th>Sulfur [kg/t90]</th>
<th>Sodium [kg/t90]</th>
<th>Sulfur [kg/t90]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input</strong></td>
<td>Normal</td>
<td>11%</td>
<td>21%</td>
<td>42%</td>
<td>Normal</td>
<td>11%</td>
<td>21%</td>
<td>42%</td>
</tr>
<tr>
<td>Wood</td>
<td>0.01</td>
<td>0.11</td>
<td>0.01</td>
<td>0.11</td>
<td>0.01</td>
<td>0.11</td>
<td>0.01</td>
<td>0.11</td>
</tr>
<tr>
<td>NaOH to O2 and OP</td>
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<td>3.18</td>
<td>0.00</td>
<td>3.18</td>
<td>0.00</td>
<td>3.18</td>
<td>0.00</td>
</tr>
<tr>
<td>NaOH to tall oil</td>
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<td>1.65</td>
<td>0.00</td>
<td>1.65</td>
<td>0.00</td>
<td>1.65</td>
<td>0.00</td>
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<td>NaOH to GD scrubber</td>
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<td>5.40</td>
<td>0.00</td>
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<td>0.00</td>
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<td>0.00</td>
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<td>0.00</td>
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</tr>
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<td>Recycled filtrate - bleached</td>
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<td>0.71</td>
<td>0.11</td>
<td>0.71</td>
<td>0.11</td>
<td>0.71</td>
<td>0.11</td>
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<tr>
<td>Recycled filtrate - unbleached</td>
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<td>0.00</td>
<td>0.00</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>CTMP effluent</strong></td>
<td><strong>1.69</strong></td>
<td><strong>0.66</strong></td>
<td><strong>1.88</strong></td>
<td><strong>0.73</strong></td>
<td><strong>2.05</strong></td>
<td><strong>0.79</strong></td>
<td><strong>2.41</strong></td>
<td><strong>0.93</strong></td>
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<td>MgSO4</td>
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<td>0.00</td>
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<td>0.00</td>
<td>0.28</td>
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<td>0.00</td>
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<td>0.00</td>
<td>0.05</td>
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<td>0.00</td>
<td>0.28</td>
<td>0.00</td>
<td>0.29</td>
<td>0.00</td>
<td>0.30</td>
</tr>
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<td>0.27</td>
<td>0.07</td>
<td>0.27</td>
<td>0.07</td>
<td>0.27</td>
<td>0.07</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>0.00</td>
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<td>15.02</td>
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<td>15.38</td>
<td>5.81</td>
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<td>21%</td>
<td>42%</td>
<td>Normal</td>
<td>11%</td>
<td>21%</td>
<td>42%</td>
</tr>
<tr>
<td>Wash loss - bleached pulp</td>
<td>5.47</td>
<td>0.60</td>
<td>5.49</td>
<td>0.60</td>
<td>5.51</td>
<td>0.60</td>
<td>5.56</td>
<td>0.61</td>
</tr>
<tr>
<td>Wash loss - unbleached pulp</td>
<td>2.84</td>
<td>0.55</td>
<td>2.86</td>
<td>0.55</td>
<td>2.88</td>
<td>0.55</td>
<td>2.93</td>
<td>0.56</td>
</tr>
<tr>
<td>Dregs, grits and lime mud</td>
<td>0.52</td>
<td>0.13</td>
<td>0.53</td>
<td>0.13</td>
<td>0.54</td>
<td>0.14</td>
<td>0.57</td>
<td>0.14</td>
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<td>0.07</td>
<td>0.00</td>
<td>0.07</td>
</tr>
<tr>
<td>Dust and SO2 from RB, GD and LK</td>
<td>0.09</td>
<td>0.43</td>
<td>0.09</td>
<td>0.34</td>
<td>0.09</td>
<td>0.34</td>
<td>0.10</td>
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<tr>
<td>White liquor to pH-regulation + sold</td>
<td>0.67</td>
<td>0.18</td>
<td>0.68</td>
<td>0.18</td>
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<tr>
<td>ESP ash purging</td>
<td><strong>3.20</strong></td>
<td><strong>2.02</strong></td>
<td><strong>3.32</strong></td>
<td><strong>2.09</strong></td>
<td><strong>3.41</strong></td>
<td><strong>2.15</strong></td>
<td><strong>3.61</strong></td>
<td><strong>2.27</strong></td>
</tr>
<tr>
<td>Tall oil</td>
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<td>0.14</td>
<td>0.00</td>
<td>0.14</td>
<td>0.00</td>
<td>0.14</td>
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<td>0.14</td>
</tr>
<tr>
<td>Bisulphite to CTMP</td>
<td>1.28</td>
<td>1.36</td>
<td>1.28</td>
<td>1.35</td>
<td>1.29</td>
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<td>Effluents</td>
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<td>0.55</td>
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<tr>
<td>Sum out:</td>
<td>14.62</td>
<td>5.60</td>
<td>14.81</td>
<td>5.58</td>
<td>14.98</td>
<td>5.66</td>
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Table 2. CTMP effluent increase with sodium bisulfite increase.

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<tr>
<th>CTMP increase</th>
<th>Sodium</th>
<th>Sulfur</th>
<th>Sodium</th>
<th>Sulfur</th>
<th>Sodium</th>
<th>Sulfur</th>
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<tbody>
<tr>
<td></td>
<td>Normal</td>
<td>11%</td>
<td>Normal</td>
<td>11%</td>
<td>Normal</td>
<td>11%</td>
<td>Normal</td>
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<td>Wood</td>
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<tr>
<td>NaOH to O₂ and OP</td>
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<td>NaOH to tall oil</td>
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<td>NaOH to GD scrubber</td>
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<td>0.11</td>
<td>0.71</td>
<td>0.11</td>
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</tr>
<tr>
<td>Recycled filtrate - unbleached</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>H₂SO₄ to soap acidulation</td>
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<td>0.69</td>
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<tr>
<td>Spent acid to soap acidulation</td>
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<tr>
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<td>0.00</td>
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<td>Fuel to lime kiln</td>
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<td>Lime make-up</td>
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<td>0.27</td>
<td>0.07</td>
<td>0.27</td>
<td>0.07</td>
<td>0.27</td>
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<tr>
<td>Methanol</td>
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<tr>
<td><strong>Sum in:</strong></td>
<td><strong>14.66</strong></td>
<td><strong>5.51</strong></td>
<td><strong>14.85</strong></td>
<td><strong>5.60</strong></td>
<td><strong>15.02</strong></td>
<td><strong>5.67</strong></td>
<td><strong>15.38</strong></td>
<td><strong>5.83</strong></td>
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<tr>
<td><strong>Output</strong></td>
<td><strong>Normal</strong></td>
<td><strong>11%</strong></td>
<td><strong>21%</strong></td>
<td><strong>42%</strong></td>
<td><strong>Normal</strong></td>
<td><strong>11%</strong></td>
<td><strong>21%</strong></td>
<td><strong>42%</strong></td>
</tr>
<tr>
<td>Wash loss - bleached pulp</td>
<td>5.47</td>
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<td>5.51</td>
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<td>5.55</td>
<td>0.61</td>
<td>5.62</td>
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<tr>
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<td>2.91</td>
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<td>Dregs, grits and lime mud</td>
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</tr>
<tr>
<td>Dust and SO₂ from RB, GD and LK</td>
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<td>0.09</td>
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<td>0.10</td>
<td>0.35</td>
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<tr>
<td>White liquor to pH-regulation + sold</td>
<td>0.67</td>
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<tr>
<td>ESP ash purging</td>
<td><strong>3.20</strong></td>
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<td><strong>3.21</strong></td>
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<td>Tall oil</td>
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<td>0.14</td>
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<td>0.14</td>
</tr>
<tr>
<td>Bisulphite to CTMP</td>
<td><strong>1.28</strong></td>
<td><strong>1.36</strong></td>
<td><strong>1.35</strong></td>
<td><strong>1.41</strong></td>
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<td>0.56</td>
<td>0.14</td>
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<td>0.14</td>
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<tr>
<td><strong>Sum out:</strong></td>
<td><strong>14.62</strong></td>
<td><strong>5.60</strong></td>
<td><strong>14.81</strong></td>
<td><strong>5.59</strong></td>
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