

Sodahuskommittén

Sodahuskommitténs Rapport 2007-1
Examensarbete Jimmy Lundström KTH

Sodahuskommitténs pris till bästa examensarbete inom
sulfatmassafabrikens kemikalieåtervinning 2007

Chloride and potassium balances in the future energy efficient pulp mills

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Rapport 2007-1

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c/o Ångpanneföreningens Forskningsstiftelse
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Chloride and potassium balances in the future energy efficient pulp mills

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Master of Science Thesis

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Stockholm 2007

Acknowledgements

I would like to thank my supervisor Åsa Samuelsson for being exceptionally supportive, positive and encouraging during my diploma work at STFI-Packforsk. I also want to thank my examiner, Mikael E Lindström Associate Professor at The Royal Institute of Technology.

Anders Lundström, Karin Lindgren and Rickard Wadsborn are greatly acknowledged for helping me with the computer simulations and other helpful discussions. Further, I wish to thank Niklas Berglin for valuable guidance during the study and Anna von Schenck for reading and commenting on the final report. Lennart Delin (ÅF) is acknowledged for informative consultation.

Finally I would like to thank everyone at STFI-Packforsk who were most helpful and made my time at STFI-Packforsk enjoyable.

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1 Abstract

The pulp and paper industry in Sweden has entered a new era with higher energy prices. High prices for electricity and the fact that electricity produced from biomass in Sweden is classified as green electricity has updated further development of the recovery boiler technology in order to produce more electricity. In broad outlines the maximum power generation in a steam turbine is increased with steam pressure and temperature. The major problem that is limiting the temperature of the high pressure steam produced in the recovery boiler originates from the accumulation of non-process elements (NPE's). Especially chloride (Cl) and potassium (K) cause problems with corrosion and plugging, and the problems become more severe with increased steam temperature.

The most common way to regulate Cl and K levels in the kraft process today is to simply purge electrostatic precipitator (ESP) dust. A major economical drawback with purging ESP dust is that it mainly consists of the cooking chemicals sodium (Na) and sulphur (S), which have to be replaced with make-up chemicals. An environmental aspect of purging ESP dust is the fact that it possibly will be prohibited to purge ESP dust in the future, mainly due to its content of cadmium. Different techniques have throughout the years been developed to serve as kidneys where Cl and K are removed from the process and the cooking chemicals can be recovered and recirculated to the system.

In this study two different K/Cl kidneys, a leaching process and an evaporation/crystallization process, were by energy and material balances compared to the purging alternative. The comparison was performed through computer simulations in two theoretical full mill simulation models of a softwood and a hardwood kraft market pulp mill. The model mills are hypothetical pulp mills representing the best available, commercially proven Nordic technology in 2003. The softwood mill has a surplus of S while the hardwood mill has a deficit of S, which may affect the choice of kidney.

The initial and fundamental conclusion in this Thesis was that a significant increase in sold electricity can be expected when the recovery boiler is operated with high steam data. It is on the contrary most probably so that the mill levels of Cl and K somehow have to be balanced in order to maintain trouble-free operation of the recovery boiler, when operating with high steam data. The lowering of the Cl and K concentrations should naturally be performed in the economically and environmentally most beneficial way. In this study the results clearly indicate an economic advantage for the two evaluated K/Cl kidneys compared to purging of ESP dust, if a mill intends to lower the levels of K and Cl. However, the best choice of K/Cl separation process is somewhat more difficult to interpret. For the softwood mill, with a surplus of S, the two kidneys showed almost identical net total benefit, while the evaporation/crystallization process proved to be somewhat more beneficial for the hardwood mill, with the deficit of S.

2 Introduction

The pulp and paper industry in Sweden has entered a new era with higher energy prices. High energy prices can be considered as a problem but at the same time it offers a great opportunity for kraft pulp mills that are self sufficient in energy to further increase their production of electricity and by that means increase the income from sold electricity. For integrated mills, which can't be self sufficient in energy, it is on the other hand desirable to lower the share of purchased electricity and thus reduce the expenses for electricity. A major economical advantage for the pulp- and paper industry in Sweden is that the produced electricity is classified as green electricity and thus qualifies for green certificates.

High prices for electricity and the fact that electricity produced from biomass in Sweden is classified as green electricity has updated further development of the recovery boiler technology in order to produce more electricity. In broad outlines the maximum power generation in a steam turbine is increased with steam pressure and temperature. The major problem that is limiting the temperature of the high pressure steam produced in the recovery boiler originates from the accumulation of non-process elements (NPE's). Especially chloride (Cl) and potassium (K) cause problems with corrosion and plugging and the problems become more severe with increased steam temperature. Environmental restrictions has for decades forced the industry to continuously increase the extent of closure in the mills. One important outcome of increased closure is accelerated accumulation of different NPE's which generates problems in many parts of the mill.

The most common way to regulate Cl and K levels in the kraft process today is to simply purge electrostatic precipitator (ESP) dust. A major economical drawback with purging ESP dust is that it mainly consists of cooking chemicals sodium (Na) and sulphur (S) that have to be replaced with make-up chemicals. An environmental aspect of purging is the fact that it in the future possibly will be prohibited to purge precipitator dust, mainly due to its content of cadmium.

Different techniques have throughout the years been developed to serve as kidneys where Cl and K are removed from the process and the cooking chemicals can be recovered and recirculated to the system. The first aim of this study was to briefly present the problems that arise from enrichment of Cl and K in pulp mills and then give an overview of the available techniques for removal of Cl and K from the chemical recovery cycle. The two most promising processes should then be applied in two theoretical full mill simulation models of a softwood and hardwood a kraft market pulp mill. The model mills are hypothetical pulp mills representing the best available, commercially proven Nordic technology in 2003. They are described within the frame of the research programme FRAM. The softwood mill has a S surplus while the hardwood mill has a S deficit, which may affect the choice of kidney. Implementation in the full mill models offered an opportunity to thoroughly investigate the effects on entire process. A cost benefit analysis would finally give an economic outcome for the different cases.

3 Objective and limitations

The first main objective of this study was to carry out a literature survey concerning the problems that arise from enrichment of Cl and K in kraft pulp mills. Within the literature survey an investigation of available techniques for removal of Cl and K from pulp mills was also included. With the literature survey as a background the two most promising techniques were evaluated by implementation in the STFI-Packforsk softwood and hardwood reference mills, which are full mill models created in a simulation tool called WinGEMS. Implementation in the full mill models offered an opportunity to thoroughly investigate the effects on the material and energy balances for the entire mill. Finally a cost benefit analysis including investment and operating costs would give the economic outcome for the different cases.

The results presented in this Thesis are limited by the fact that they are based on computer simulations which make use of constant operating parameters and steady state calculations. The model mills used in this study are also highly effective and thus the results of the cases naturally will be affected in different ways. For example the implementation of the K/Cl kidneys and the resulting cost benefit analysis would for a less effective mill possibly show a somewhat different pattern than what is presented in this study.

4 Background

The energy situation in the world today is an important matter for all kinds of industries. Though, electricity intense base industries like steel and chemical are particularly affected because of the high electricity prices. The forestry industry, together with other base industries like steel and chemical, consumes two thirds of the total power consumption in Sweden. [1] The pulp and paper industry is highly energy consuming but has the advantage of simultaneous production of power in different types of boilers with back pressure steam turbines. Produced energy mainly originates from burning of biomass such as bark and the main by-product from kraft chemical pulp processing, called black liquor. Electricity produced from biomass is denoted green electricity and thus qualifies for the green certificates which make it even more economically competitive.

4.1 The kraft pulping process

When producing chemical pulp from wood the totally dominating technology today is the kraft process. In the kraft process wood chips are treated with process chemicals, sodium hydroxide and sodium sulphide, under high pressure and temperature in a digester. One of the most important advantages with the kraft process, compared to other processes, is the fact that the process chemicals can be regenerated. Roughly generalized the result from kraft cooking of wood is two main products: one pulp stream containing mainly cellulose and hemicellulose from which paper is produced and the other stream called black liquor containing foremost lignin and process chemicals. The manufacturing of paper can be performed in different ways depending on the type of paper produced but those processes will not be further described in this work. An exemplifying scheme of an integrated Fine paper mill is presented in Figure 1.

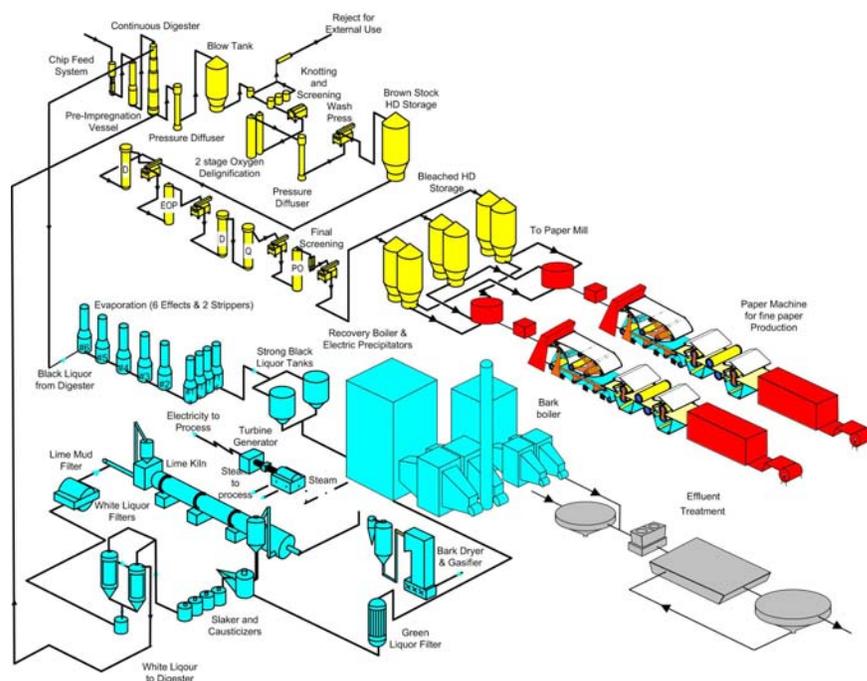


Figure 1. Exemplifying scheme of an integrated Fine paper mill. [2]

Depending on what type of paper the final paper product is the properties of the pulp, and hence the yield from wood to paper varies but approximately 50 % of the wood ends up as pulp and 50 % as black liquor. Thus the black liquor stream possesses a rather high energy value which makes it a good source for energy production. Since black liquor also contain valuable process chemicals it is desirable to regenerate them and recirculate them back to the pulping process. This is accomplished in the chemical recovery cycle.

4.2 Chemical recovery

The chemical recovery cycle has two main tasks: to regenerate the process chemicals and to produce energy from the organic content in the black liquor. A typical chemical recovery cycle is the part marked with blue in Figure 1. The chemical recovery cycle consists of four main sub-processes: evaporation plant, recovery boiler, white and green liquor preparation plant and a lime kiln. Because of its importance concerning this thesis the recovery boiler and particularly the heat transfer section will be described more thoroughly compared to the other sub-processes.

4.2.1 Evaporation

The evaporation plant consists of series of evaporators, called evaporator train, where mainly water is continuously evaporated from the black liquor. The purpose of the evaporation is simply to raise the dry solids content, and thus the heating value, of the black liquor before burning. Incoming black liquor, called weak black liquor, has a dry solids content of 15-20 % and with that amount of water the effective heating value is negative. When leaving the evaporation plant the strong black liquor, with a dry solids content of about 70-80 %, possesses a rather high effective heating value, 14.5 MJ/kg ds[3] , and is fed to the recovery boiler for burning. [4]

4.2.2 Recovery boiler

The purpose of combusting black liquor is twofold: to extract the latent heat in the organic material and to recover Na and S in the form of sodium carbonate (Na_2CO_3) and sodium sulphate (Na_2SO_4) in the smelt. Recovery boilers today are of the Tomlinson type and were first developed around 1930. Black liquor with a dry solids content of approximately 70-80 % is burned in the recovery boiler and heat is transferred from the hot flue gases to a steam generating system. The steam is then used to generate electricity in back pressure turbines and for numerous process applications. In the recovery boiler furnace the cooking chemicals, Na and S (both organic and inorganic), forms a smelt and thus takes a first step in the chemical regeneration cycle. In Figure 2 an example of a recovery boiler operating at what can be considered as modern steam pressure and temperature is presented.

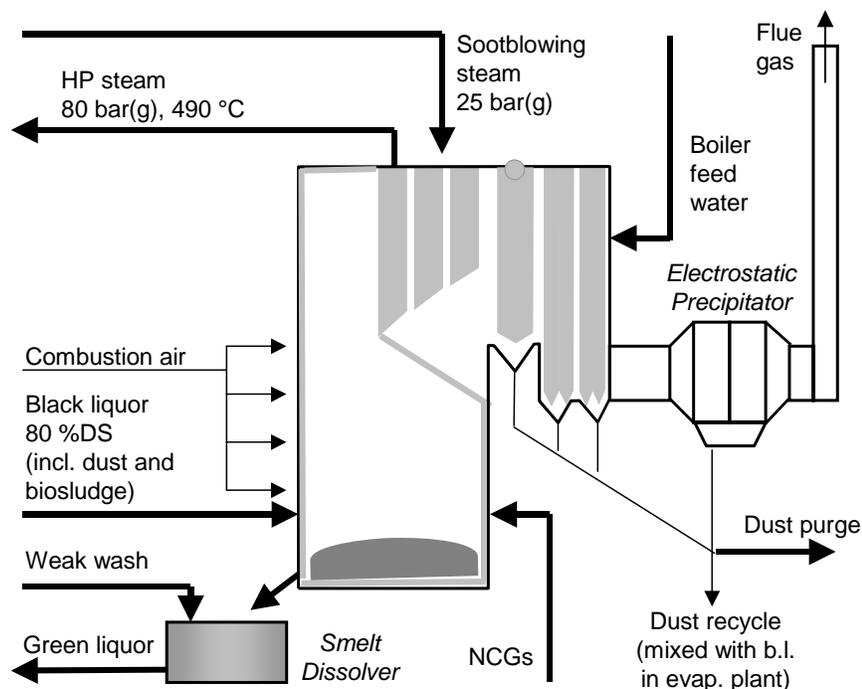


Figure 2. Schematic description of a recovery boiler operating at somewhat higher steam pressure and temperature than traditional levels.

A small, but significant, part of the incoming compounds are emitted to the flue gas and entrained upstream towards the heat transfer areas. This stream is called fly ash and has to be separated from the gas stream because of two main reasons: environmental regulations for dust discharge to air and that it mainly consists of useful process chemicals, where Na_2SO_4 is the dominating salt. [4] The separation is carried out in an electrostatic precipitator which generates a dust, ESP (Electrostatic Precipitator) dust that can be recirculated back to the black liquor right before the black liquor is fed to the recovery boiler. The recycling of ESP dust has been estimated to account for approximately 10 % of the inorganic content in the black liquor. [5]

4.2.2.1 Heat transfer area

The heat transfer section consists of a superheater, a boiler bank, and an economizer, and may sometimes also include a set of screen tubes. The different sections are shown in Figure 3 (right).

Heat transfer from the gas to the tube banks is largely by convection, but radiation may also contribute to a significant part. Tubes in the superheater and boiler bank sections are comparatively widely spread in order to accommodate the substantial amount of carryover particles reaching in from the furnace. The high content of particles in the flue gas combined with the high temperatures inevitably causes continuous deposition and fouling on the outside of the tubes. Automatic sootblowers are used to clean the tube surfaces but substantial fouling and complete plugging of the gas flow passages is still a quite common problem. The deposition of fly ash on the tubes lowers the heat transfer

capacity and this has to be accounted for when the needed heat transfer area is calculated. The total amount of heat transfer surface area required in a kraft recovery boiler would be sufficient to generate twice as much steam with a non-fouling fuel.

The flue gas temperature change in the recovery boiler range from about 1000 to 200°C according to Figure 3 (left). The huge temperature change and the rate of which the temperature of the flue gas is changing are important to keep in mind when plugging problems related to Cl and K are discussed later in the report.

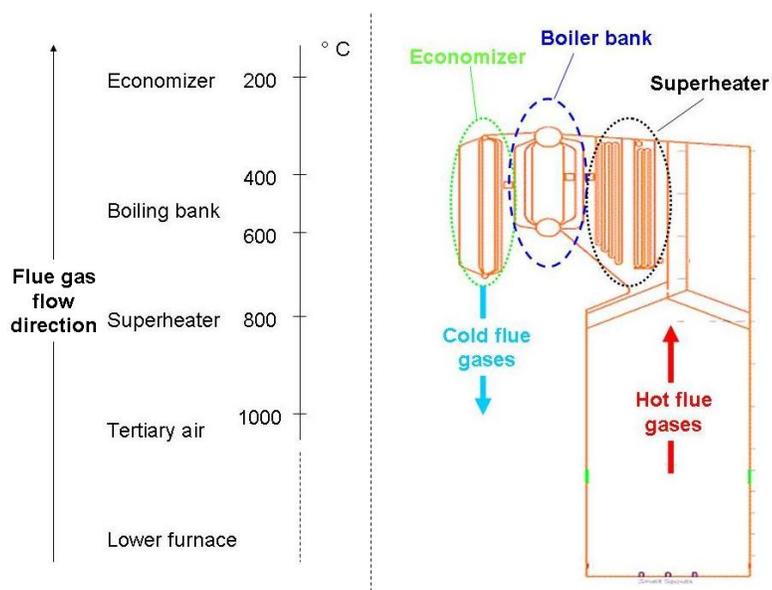
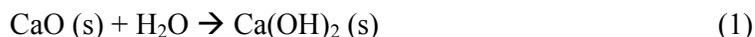


Figure 3. Flue gas temperature range in the recovery boiler (left) and a schematic picture of the location of the different heat exchanger regions (right).

4.2.3 Green and white liquor preparation

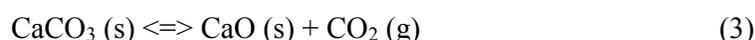
The green and white liquor preparation plant is the part of the recovery cycle where the smelt from the recovery boiler is converted to white liquor that can be used in the pulping process. Smelt from the recovery boiler is dissolved in weak white liquor, which is the filtrate from the washing of lime mud, to form green liquor. The main cations in green liquor are Na (~90 %) and K (~10 %) and the most frequent anions are carbonate (CO_3^{2-}), sulphide (S^{2-}) and hydroxide (OH^-). There are also small amounts of solid material present in the green liquor called “green liquor dregs”. The “dregs” are separated and purged before the green liquor is further fed to the causticizing plant. The separation is performed using a clarifier or a filter. In the causticizing plant burned lime mud, CaO, is added to the green liquor in order to convert CO_3^{2-} into OH^- . The converting process takes place according to reactions 1 and 2.



White liquor and solid lime mud, CaCO_3 (s), are then separated through clarification or filtration. The white liquor containing the regenerated process chemicals hydroxide and sulphide is transported to the digester while the lime mud is fed to the lime kiln.

4.2.4 Lime kiln

Causticizing, lime mud wash and lime mud reburning are often referred to as the “lime cycle”. The lime mud from causticizing is first washed, where the washing procedure generates so called weak white liquor and cleaned lime mud. The lime mud is further transported to the reburning system, called the lime kiln, and the weak white liquor is used in the green liquor preparation. In the reburning system the lime mud is dried and heated to above 850°C which makes CaCO_3 decompose into CaO and carbon dioxide (CO_2) according to reaction 3. [4]



4.2.5 Important definitions concerning chemical charges

The white liquor consists of sodium hydroxide (NaOH) and sodium sulphide (Na_2S) where the active cooking chemicals are OH^- and HS^- ions. The white liquor concentration of OH^- ions can however not be expressed as the amount of NaOH charged since Na_2S is hydrolysed to OH^- and HS^- . The OH^- ions in the white liquor thus derive from both NaOH and Na_2S which make it necessary to express the amount of OH^- as effective alkali (EA) according to equations 1 and 2. [4]

$$\text{EA (mole)} = n_{\text{NaOH}} + n_{\text{Na}_2\text{S}} \quad (1)$$

$$\text{EA (mole/L)} = [\text{OH}^-] \quad (2)$$

The sulphide charge can be given by the sulphidity of the white liquor. The amounts of Na_2S and NaOH are related to each other and changes in the alkali charge inevitably affects the sulphide charge and vice versa. This relation has led to the use of the term sulphidity which relates the alkali charge to the sulphide charge. The sulphidity can be expressed in a number of ways but one common definition is shown in equation 3. [4]

$$\text{Sulphidity (\%)} = 100 \times \frac{2 \cdot [\text{HS}^-]}{[\text{HS}^-] + [\text{OH}^-]} \quad (3)$$

4.3 Maximized power generation

In order to achieve a higher power output from the recovery boiler efforts have been made to improve and develop the existing technology. In broad outlines the maximum power generation is increased with increased steam pressure and temperature.

The limiting factor for steam temperature lies within the recovery boiler. Flue gases that enter the heat transfer areas contain high amounts of dust, approximately 20 g/m^3 . [6] When steam temperature increases the temperature of the heater tubes also increases. If the temperature gets too high the dust will also melt, to a larger extent stick on the tubes and cause corrosion and plugging of the heater areas. Corrosion of the tubes can to a

large extent be prevented by using expensive types of special corrosion resistant stainless steel. [7] The melting temperature of the dust is controlled by its composition and particularly the amount of the non-process elements, Cl and K. Limiting factor for the steam pressure is not, within reason, the recovery boiler but instead the turbine. [6] To achieve the desired temperature increase in the recovery boiler, in order to increase power production, research has shown that the levels of Cl and K most likely have to be lowered in a majority of all pulp mills compared to today's levels.

Another possibility to achieve an increased power output from the recovery boiler is to modify the steam cycle. Reheating of the steam after the first turbine passage is one example of steam cycle modification. The reheating procedure gives an energy efficient usage of any incoming fuel and increases the amount of electricity produced. [6, 8]

4.4 WinGEMS 5.0

The computer simulations in this thesis were performed using the simulation program WinGEMS. WinGEMS is a modular program, created by Pacific Simulation, which is adapted for calculations specifically important for the pulp and paper industry. GEMS in WinGEMS stand for General Energy and Material balance System which represents that the program is designed to perform mass- and energy balance calculations. The calculations are executed in modules, called blocks, where one module may represent a specific unit operation, such as a wash press for instance. The calculations are made iteratively to finally converge to a solution. [9]

4.5 STFI-Packforsk reference mill

The theoretical process simulation reference mill models were developed at STFI-Packforsk, in cooperation with ÅF-Process, from 2003 to 2005 within the Swedish national research programme: Future Resource-Adapted Pulp Mill (FRAM). Detailed full mill simulation models were developed for the following types of pulp and paper mills:

- Bleached market pulp mill, operating with campaigns of hardwood and softwood.
- Integrated fine paper mill, pulp mills as above.
- Integrated kraft liner mill.
- Magazine paper mill, producing bleached super calendered (SC) TMP.

The simulations performed in the frame of this Thesis however focused on the Softwood and Hardwood market pulp mills. A brief process description including some operating parameters for the softwood reference mill is presented in Table 1.

Table 1. Brief process description including some operating parameters for the softwood market pulp mill.

Production (ADt/a)	653 200 (2000 ADt/d)
Operating days (Days/a)	355
Availability (%)	92
HP steam temperature (°C)	490
HP steam pressure (bar)	81
Turbine	Back pressure + Condensing
Lime kiln fuel	Gasified bark
Bleach sequence	D(OP)DQ(PO)
Oxygen stage	Double
Evaporation	~6 effects
Black liquor as fired (DS)	80 %
Cl enrichment ratio	2.5
K enrichment ratio	1.6

The reference mill is a hypothetical model mill representing best available, existing and commercially proven Nordic technology. It has been constructed as a Green Field mill. The model includes balances for more than 70 different species (pulp, water, metals, anions, etc.) and rigorously deal with thermodynamic properties and chemical equilibriums. Detailed sub-process models have been developed for the digester, different bleaching stages, recovery boiler, wash equipment etc.

Due to new and efficient equipment resource utilisation is comparatively small for the reference mill. One important outcome of the efficient process is that the reference mill has a surplus of steam which is used to produce electricity in a condensing turbine. In total the reference mill thus can export electricity. Since bark is used as fuel in the lime kiln, where it is common to use oil, the reference mill can export biofuels and so called green electricity to society, which replaces fossil fuel and lower the total amount of CO₂ emission. It is also noteworthy that the reference mill uses no fossil fuel. [10]

5 Non-process elements

Elements which do not play a useful role in chemical pulping, bleaching or recovery are classified as non-process elements (NPE). Examples are Cl (in the form of Cl⁻), K, phosphorous (P), calcium (Ca), magnesium (Mg) and manganese (Mn). NPE's are present in all kraft pulping processes and enter the pulp mill with the wood (raw material), make-up chemicals, bleaching chemicals and mill process water. The NPE's that enter the kraft mill with the wood are to a large extent dissolved and extracted from the wood during cooking and bleaching stages. [11, 12] Where in the process NPE's end up depends on a multiple of factors but enrichment in the recovery cycle is common.

Problems that can be related to the accumulation of NPE's in the recovery cycle include scaling in black liquor evaporators, corrosion and plugging of heat transfer surfaces in the recovery boiler. [13] Enrichment of NPE's in the pulping process can also be related to increased consumption of bleaching chemicals. [11]

The continuously harder environmental regulations have forced the pulp and paper industry to continuously reduce the environmental impact of the mills. Increased closure of the mill is one common way to minimize the amount of incoming water and by that means lower the environmental impact. However, reducing effluent volumes from the mill inevitably results in an increased accumulation which give rise to higher concentrations of the NPE's in the process streams.

Generally speaking the NPE's can be divided in two main groups: those that are purged with the green liquor dregs and those that are accumulated in the liquor cycle. [12, 14, 15] A schematic description of the NPE flows in a kraft pulp mill is shown in Figure 4.

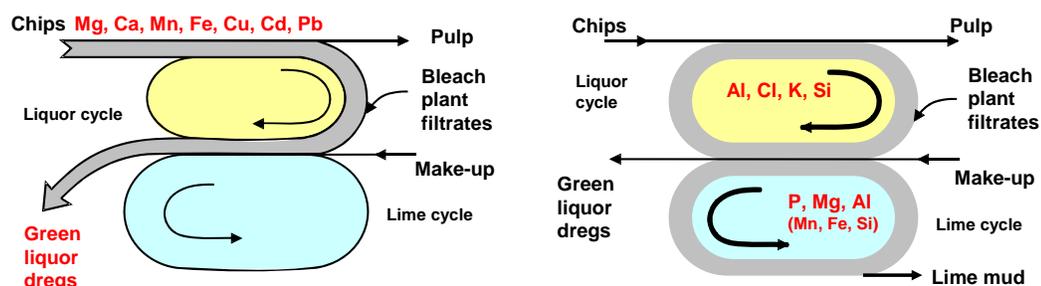


Figure 4. Left: NPE's that are purged with green liquor dregs but accumulate in the lime cycle. Right: Accumulation of NPE's in liquor and lime cycles. [12]

5.1 Chloride and potassium

When Cl and K have entered the liquor cycle they accumulate until they possibly reach a steady state concentration. The steady state concentration is determined by the input, the degree of closure and the liquor sulphidity. A high sulphidity results in an increased NaCl vaporization from the smelt and thus more Cl leaves the system with the flue gases [16] .

Under normal operating conditions Cl mainly enters the mill with wood, bleaching chemicals and to a smaller degree with the water and make-up chemicals. On the other hand K almost entirely enters the mill with the wood. [17] As a consequence of the sometimes huge differences in the input amounts of Cl and K and the degree of closure, levels of Cl and K vary considerably from mill to mill. There are also many different ways, e.g. units and sampling locations, of presenting the results which further complicates a direct comparison between different surveys. A compilation over a number of surveys is however presented below as an illustration over the very wide range in which levels of Cl and K can end up in a kraft pulp mill.

Tran and co-workers carried out an extensive survey [18] based on material balances of 45 kraft mills to determine the approximate concentration range for Cl and K in important parts of the mills. The survey showed that Cl input from wood ranges between 1.2-14 kg/ADt while K input lies between 0.7-4 kg/ADt. For inland mills the Cl content in the black liquor as fired varied from 0.2-0.6 wt % Cl on dry solids and proved to be higher, 1-2 wt % Cl, for mills that either use caustic make-up contaminated with NaCl or partially recover bleach plant effluents. For mills that are located near the coast and use seaborne logs the levels of Cl in black liquor as fired were as high as 3-5 wt % Cl on dry solids. The K content in the black liquor as fired typically varied between 0.8-0.9 wt % K on dry solids for softwood mills and 2-5 wt % K for hardwood mills. [18]

Another study performed by Tran and co-workers [19] showed that the Cl and K content in recovery boiler deposits for inland mills, where there are no other sources of Cl and K than wood, typically ranges between 1-4 % by mole Cl/(Na + K) and 4-7 % by mole K/(Na + K). With Cl and K input from other sources such as seaborne logs, make-up chemicals and hardwood Cl and K contents in recovery boiler deposits can be as high as 25 % by mole Cl/(Na + K) and 20 % by mole K/(Na + K). [19]

Examples of white liquor concentrations of Cl and K in a modern kraft mill have by Ulmgren et.al. been estimated to 0.03-0.1 mol/L and 0.2-0.3 mol/L, respectively. [12]

The levels of Cl intake with wood have in two other surveys been analyzed to be 40-200 g/ADt [3] and 300-800 g/ADt [20] . Corresponding levels for K intake was 800-1200 g/ADt [3] and 300-800 g/ADt [20] . Another review performed by Keitaaniemi et.al. presented average Cl input levels of 630 g/ADt and K levels of 1100 g/ADt. [21] It is also important to mention that generally speaking hardwood contains higher amounts of Cl and K compared to softwood.

Direct contact has also been taken with two Swedish kraft pulp mills by the author. The results are presented in Table 2 and Table 3.

Table 2. Average Cl and K concentration levels in white liquor for two Swedish kraft pulp mills. (*The value is based on sporadic sampling.)

Mill	Cl (mol/L)	K (mol/L)	Period
A	0.04	0.38	Jan 2005-Feb 2007
B	0.01	0.28*	Jan – Dec 2006

Table 3. Average Cl and K concentration levels in ESP dust for two Swedish kraft pulp mills. The values originate from sporadic sampling.

Mill	Cl% by mole (Cl/(Na + K))	K % by mole (K/(Na + K))	Period
A	4.1	11.8	Sporadic sampling
B	1.0	9.3	Sporadic sampling

Examples of levels of Cl and K in caustic make-up, saltcake make-up, lime make-up and fresh water are presented in Table 4.

Table 4. Examples of levels of Cl and K in make-up chemicals and make-up water. [17]

Source	Cl (ppm)	K (ppm)
Caustic make-up	1000	700
Saltcake make-up	5000	100
Lime make-up	100	100
Fresh water (Fiberline and recovery)	20	2

A brief summary of the Cl and K intake with wood and concentration range in different locations of the mill given in the surveys above is presented in Table 5. It is important to notice that the most extreme Cl levels originate from mills that use seaborne logs and thus not represent a common mill situation. The main purpose of presenting the concentration range is however to exemplify the big variations that can occur when comparing mills.

Table 5. Summary of the concentration range for Cl and K in wood and different parts of the mill given in the surveys presented above.

Wood (g/ADt)		Black liquor as fired (wt % on dry solids)		White liquor (mol/l)		ESP dust (by mole %)	
Cl	K	Cl	K	Cl	K	Cl/(Na+K)	K/(Na+K)
40- 14000	300- 4000	0.2-5	0.8-5	0.01- 0.1	0.2-0.38	1-25	4-20

5.2 Enrichment ratio

Due to the highly volatile nature of Cl and K at high temperatures they vaporize from the recovery boiler char bed and from in-flight burning black liquor particles. As the flue gas temperature decreases in the back side of the boiler these compounds condense and become enriched in the ESP dust.

The enrichment ratio (ER) is important when comparing levels of for example Cl in different parts of pulp mills. The ER is defined as the ratio of the Cl concentration in process liquor, deposited material or dust, to the Cl concentration in black liquor as fired. For example the ER of Cl in ESP dust is calculated from equation 4. [16]

$$ER_{ESP\ dust} = \frac{\left(\frac{[Cl]}{[Na] + [K]} \right)_{ESP\ dust}}{\left(\frac{[Cl]}{[Na] + [K]} \right)_{BL\ Solids}} \quad (4)$$

Figure 5 shows the ER for Cl in different pulp mill streams as an average of 17 mills. As can be seen in Figure 5 the ER is highest in the ESP dust. [18]

A similar enrichment pattern was also observed for potassium but the values of the ER are somewhat lower compared to chloride. [18]

Another review based on a mill study of five Finnish pulp mills showed levels of ER according to Figure 6. No direct explanation to the big variation in ER between the mills was presented by the authors, but it is noteworthy that the ER may vary considerably, especially for Cl, from mill to mill. [11]

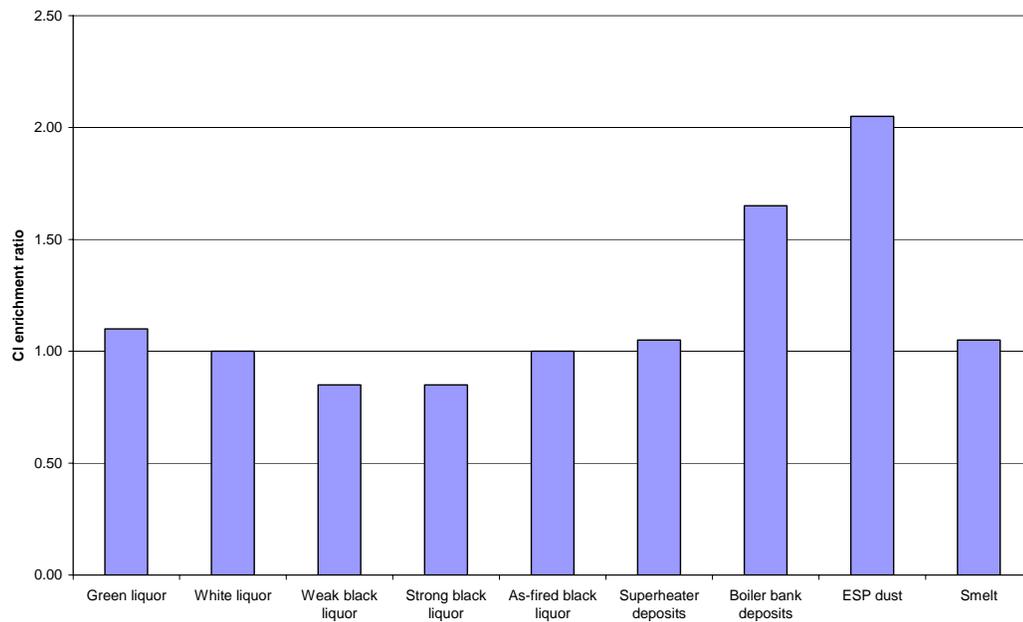


Figure 5. Typical Cl enrichment ratio in the kraft recovery cycle. [18]

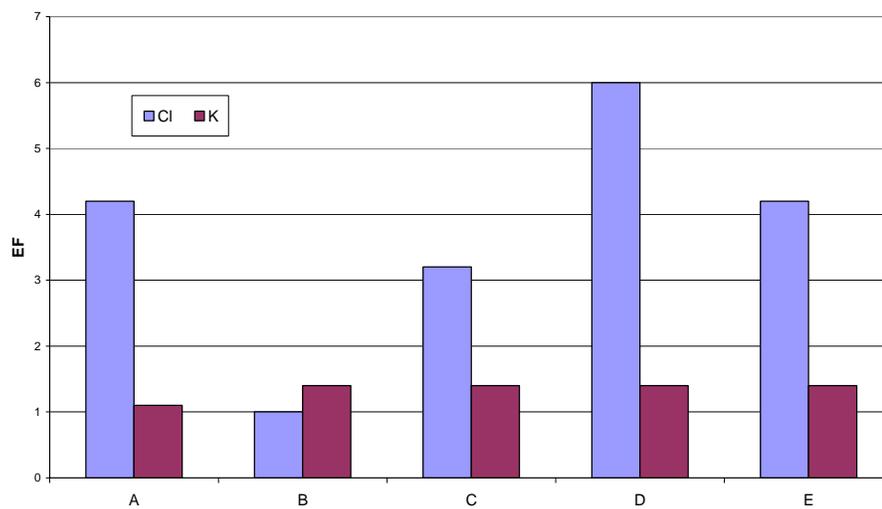


Figure 6. Levels of the enrichment ratio (ER) for five Finnish pulp mills. [11]

Data from fourteen operating recovery boilers showed an average ER for Cl in ESP dust of 2.6 with a standard deviation of less than 1.5. Corresponding ER for K in the same survey was 1.6 with a standard deviation of less than 0.3. [22] These two values of ER in ESP dust for Cl (2.6) and K (1.6) are in literature often considered to be default values.

6 Effect of Cl and K concentration

Massive build up of deposits causing plugging and corrosion in flue gas passages of the recovery boiler is a frequent problem in the pulp and paper industry. The occurrence of Cl and K in pulp mills has been proved to be very important since they strongly influence the thermal properties of deposits in kraft recovery boilers. Because of their volatile nature at high temperatures, Cl and K compounds (NaCl and KCl) vaporize from the recovery boiler char bed. The effect of the vaporization is an enrichment of Cl and K in the deposits. Despite the relatively low concentration of Cl and K they accelerate plugging of flue gas passages by lowering the sticky temperature of the carryover deposits. Cl and K also facilitate the rate of deposit sintering and have been linked to increase the corrosion rate of superheater tubes. [19]

6.1 Deposit formation

Deposits are built up from two distinctly different sources:

1. Carryover. Smelt and/or partially burned black liquor particles physically entrained in the flue gas.
2. Condensation. Fume or dust that originates from condensation of compounds volatilized from the low parts of the furnace. The condensation can occur directly on cool surfaces or indirectly in the flue gas stream forming particles that may be transferred to the cool surfaces.

The main part of the carryover and condensed material follows the dust stream to the electrostatic precipitators and can be recycled back to the black liquor while a small amount is lost with the stack gas. However portions of the carryover and condensed material sticks on the heater tubes as deposits. To what extent the carryover and condensed material sticks on the tubes, and thus cause plugging and corrosion, is determined by their thermal properties. [19]

6.2 Deposit properties

Deposits consist to more than 99.8 wt % of water soluble compounds. These are mainly sodium sulphate and sodium carbonate but there are also small amounts of NaCl, NaOH, potassium salts and reduced sulphur compounds. As can be seen in Figure 7 there is an obvious difference in composition between carryover and condensed material. The totally dominating compound in condensation deposits is Na₂SO₄ while the main part of the carryover material consist of almost equal amounts of Na₂SO₄ and Na₂CO₃.

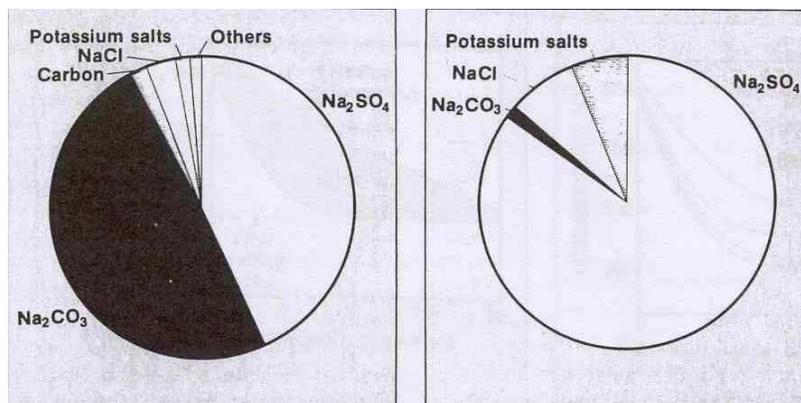


Figure 7. Chemical composition of carryover (left) and condensation deposits (right). [19]

The chemical composition of the actual deposits will end up somewhere between the composition of carryover and condensed material. Due to the complex chemical and thermal nature in the recovery boiler furnace and flue gas passages the proportions of the mentioned compounds also varies with location in the boiler.

As a consequence of the varying chemical composition of the deposits also its thermal properties will vary. Deposits, like many mixtures of chemical compounds, melt gradually during a temperature interval that can be several hundred degrees Celsius. There are two really distinct melting temperatures. The first melting temperature, T_0 , is the temperature at which liquid phase first appears. The second distinct melting temperature is the temperature at which the deposit is completely molten, T_{100} . Between these two temperatures there are at least two other temperatures that are important. The sticky temperature, T_{15} or T_{STK} , is the temperature above which the deposits contain enough liquid phase to become sticky. The radical deformation temperature, T_{70} or T_{RD} , is the temperature above which the amount of liquid is sufficient to make the deposit fluid. [11, 19]

The sticky temperature and the radical deformation temperature are very important for the rate of accumulation of deposits. Below T_{STK} the deposits are relatively “dry” and will not accumulate readily. Above T_{RD} accumulation decreases since the deposits simply run off. Figure 8 shows the effect of Cl on T_{STK} and T_{RD} for a typical carryover deposit containing 5 mole% $\text{K}/(\text{Na}+\text{K})$. T_{STK} decreases drastically from 700°C to 560°C as the Cl value increases from a typical value of 1.5 mole% to 9 mole% $\text{Cl}/(\text{Na}+\text{K})$, while T_{RD} decreases more slowly. An important consequence of the more drastic decrease in T_{STK} is that the temperature range in which deposits may build up increases with rising Cl content up to approximately 7 mole% $\text{Cl}/(\text{Na}+\text{K})$. [16]

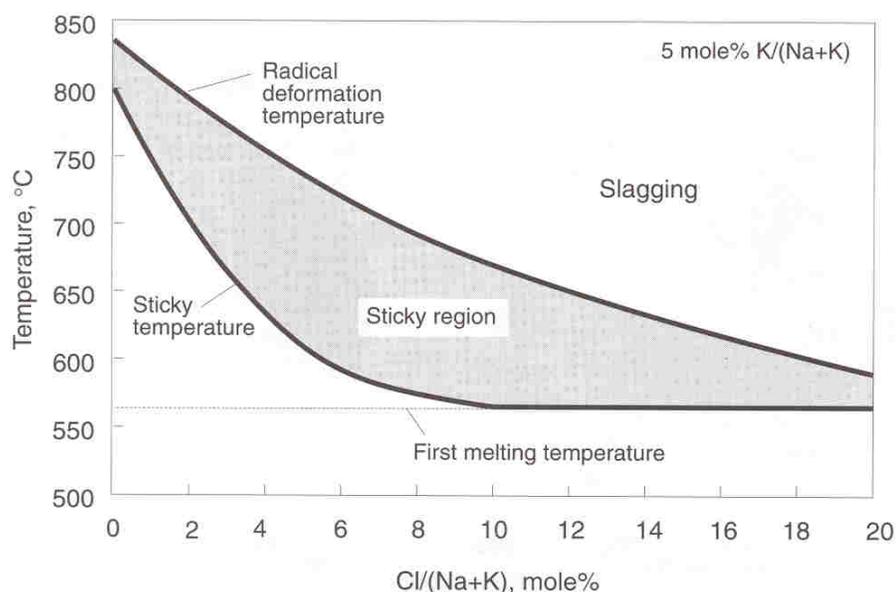


Figure 8. Effect of Cl on deposit sticky temperature zone. K concentration was kept at the constant value 5 mole% K/(Na + K) which represent a fairly normal K level in recovery boiler deposits. [16]

6.2.1 Sticky temperature

Stickiness of deposits is one of the most important factors that determine the rate of deposition in the heat exchanging region of the recovery boiler. Deposit stickiness is affected by many parameters of which temperature, composition, surface conditions, particle size and flue gas velocity are the most important. The particles are usually molten at the superheater entrance and later in the heat exchanger region passes the sticky region as they are gradually cooled down in the flue gas flow. [23] For a deposit to be sticky it must contain a certain amount of liquid phase. The amount of liquid phase increases with both temperature and Cl content at temperatures above the first melting temperature. The sticky temperature, T_{STK} , is classified as the temperature at which the share of liquid phase exceeds 15 %. Figure 9 shows the sticky temperature of carryover deposits as a function of both Cl and K content. [19]

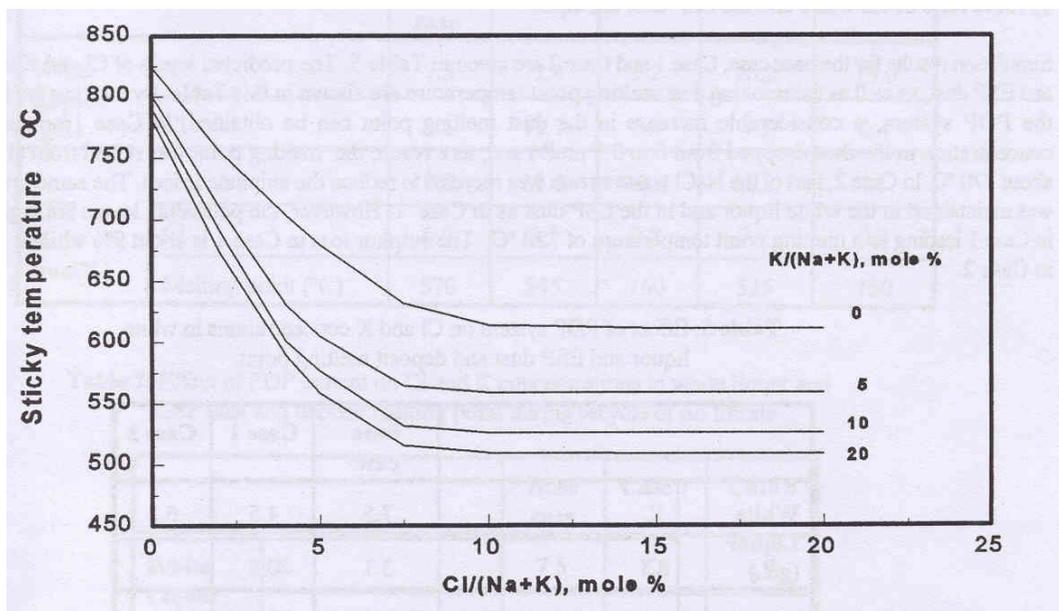


Figure 9. Effect of Cl and K on the sticky temperature of ESP dust. [19]

When the Cl content increases from 0 % to 5 % by mole Cl/(Na + K) the sticky temperature is substantially lowered. The effect of K content is much less remarkable, especially when the Cl content is very low. When the K concentration exceeds 6 % by mole K/(Na + K), K has only a minimal effect on the deposit sticky temperature.

High K concentration also has been proved to lower the first melting temperature of the deposits. Low first melting temperature generally increases the probability for superheater corrosion. [11]

6.2.2 ESP dust adhesive properties

The adhesive properties of ESP dust are another way of expressing the stickiness and thus the propensity of the ash to plug heat exchanging areas of the recovery boiler. One test method for laboratory analysis of the adhesive properties that has been developed shows the adhesive force as a function of temperature. As the heating temperature becomes high the adhesive force rises gradually and reaches its maximum at a certain temperature. After the maximum the adhesive force gradually drops. Figure 10 shows an example of adhesive force measurements where ashes with different compositions have been evaluated. [24]

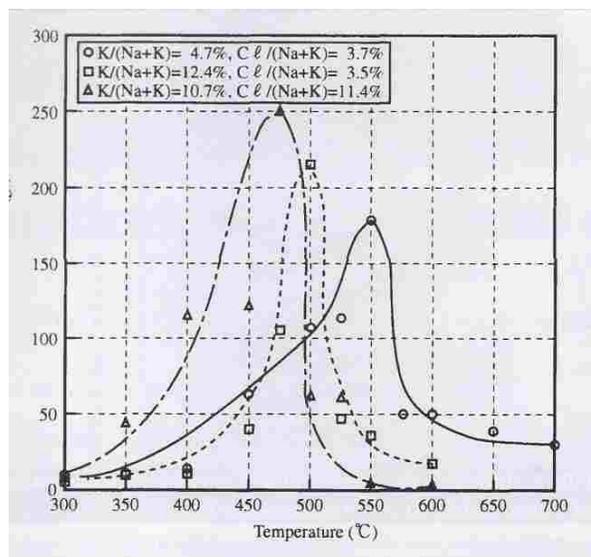


Figure 10. Example of ash adhesive force measurement result. (Adhesive force on the Y-axis). [24]

In Figure 11 the relationship between the temperature which showed the maximum adhesive force and $Cl/(Na + K)$ by mole% is presented. Figure 11 includes results from various kinds of synthetic ash and actual boiler ESP dust.

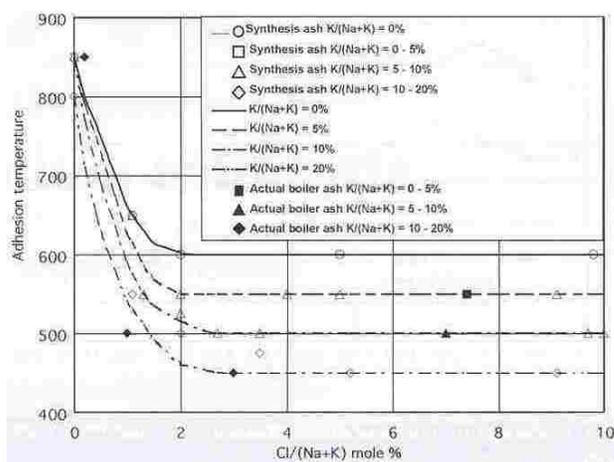


Figure 11. Relationship between $Cl/(Na + K)$ by mole% and adhesion temperature. [24]

The conclusions from Figure 10 and Figure 11 were by the authors [24] summarized as follows:

- With constant K concentration the maximum adhesion temperature is lowered by an increase in Cl concentration. It is however important to notice that almost constant maximum adhesion temperature occurs regardless of Cl concentration if $Cl/(Na + K)$ by mole% becomes higher than 2 %.

- With a constant K concentration it is necessary to reduce Cl/(Na + K) by mole% equal to or less than 2 % in order to improve the maximum adhesion temperature.
- Maximum ash adhesion temperature rises by eliminating Cl and K simultaneously and low Cl and K concentration in the ash may solve ash plugging problems.

6.3 Plugging

Due to the stickiness, and hence adhesive properties, of the fly ash deposits accumulate in the heat exchanger region of the recovery boiler causing fouling and plugging of the flue gas passages. The generating bank inlet is the most common location for plugging because of two main reasons: the boiler bank inlet has relatively narrow tube spacing and the fact that the flue gas temperature often is in the temperature range within, or in the proximity of, the sticky region. From this point of view it is fundamental to minimize the sticky region of the dust since it results in a more narrow temperature range where the dust may cause plugging. According to Figure 8 the sticky region can be minimized by lowering the dust content of Cl and K. Another important parameter is to lower the temperature of the flue gas as rapidly as possible since a slow temperature decrease will have the consequence that the dust is sticky during a longer period of time. A rapid reduction of the flue gas temperature is accomplished while the heat exchanger surfaces are clean, such as after a water wash, but it will gradually slow down because of the formed deposit layer. Figure 12 schematically shows how an increased sticky region may lead to plugging at the boiler bank inlet. The increased sticky region can be a result of both high Cl and K content or slow temperature reduction of the flue gas. [16]

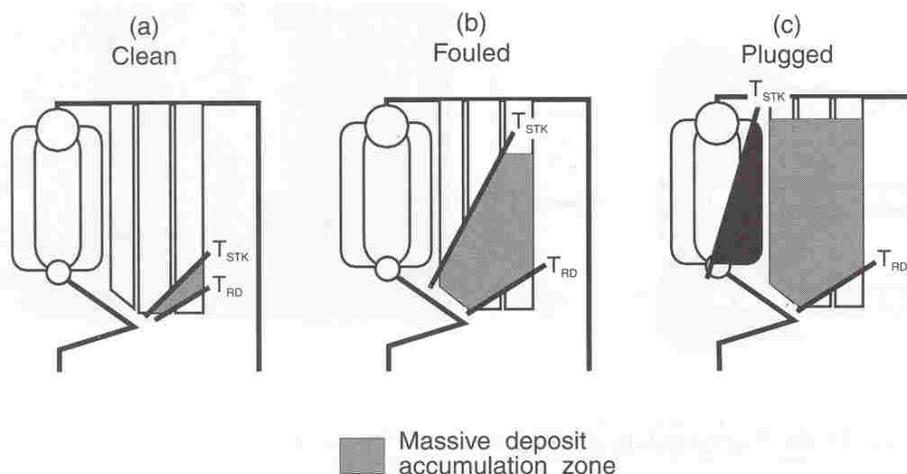


Figure 12. Schematic description of a possible plugging scenario at the boiler bank inlet due to an increased sticky region. [16]

Plugging is generally prevented through steam blowing in the recovery boiler tube banks using sootblowers. Steam consumption, for sootblowing, in mills that have severe plugging problems could exceed 10 % of the total steam production. For an 800 ton/d kraft pulp mill a 3 % unit reduction of the total steam consumption have by Uloth et.al. been calculated into fuel savings of \$600,000 per year. [25] Another important preventive method for avoiding plugging is to minimize the amount of carryover which may be accomplished through tuning of different process parameters of the recovery boiler. [16] Problems with plugging can in some cases also to some extent be avoided by lowering steam temperature though resulting in a reduced electricity generation by the mill turbines. Another possible consequence of extensive plugging is a total shutdown of the recovery boiler for water wash. A total shutdown of the recovery boiler is a highly undesirable measure that lowers the availability and inevitably affects the economy of the mill in a negative way. There are also possibilities to install so called thermal or loud shock equipment.

It should be mentioned that plugging also might come about due to so called sintered fume deposits in the generating bank and sticky fume deposits in the economizer region, which originate from the SO_2/SO_3 content of the flue gas. [16] These sources for plugging will however not be investigated further in this work.

6.4 Corrosion

Corrosion can occur in different parts of the recovery boiler. The most vulnerable areas are though the furnace and the superheater regions since the highest temperatures appear there. An important factor for the corrosion rate is the first melting temperature (T_0) which is strongly influenced by the K content of the ESP dust. [26] A clear relationship between metal loss, e.g. corrosion rate, and T_0 has been shown where metal loss increases with a decrease in T_0 . The effect of Cl on metal loss proved to be small when the T_0 was high, i.e. low K concentration, but the effect of Cl becomes greater in the case of a low T_0 , i.e. high K concentration. [27] Research for new corrosion resistant materials has given positive results which make it possible that to a certain extent prevent corrosion by choosing the most suitable material. The materials used in modern recovery boilers, with high pressure and temperature, generally have high chromium content in order to withstand corrosion. [28] It should though be stated that today there are no tube materials that in long-term can prevent corrosion if the fly ash melts on the tube surfaces. Therefore the Cl and K content in ESP dust has to be kept at relatively low levels if the temperature and pressure of the steam are supposed to be increased. [29]

7 Processes for Cl and K removal

The dominating way of controlling Cl and K levels in pulp mills today is by simply purging ESP dust periodically. Despite the fact that Cl and K are enriched in the ESP dust they only represent 4-20 wt %. [30] The remaining part of the purged material consists of the cooking chemicals Na, SO₄ and CO₃. Consequently more make-up chemicals must be added to the liquor cycle in order to compensate for the loss when purging ESP dust.

There is a possibility that it, in the future, will be prohibited to purge ESP dust, partly because of the cadmium (Cd) content. The installation of a K/Cl kidney could consequently also be the result of environmental regulations. Unfortunately nothing could be found in literature about how Cd is split in the K/Cl kidneys. However Metso Power claims that the major part of the Cd is recycled back to the process and by that means can be purged with the green liquor dregs when a leaching unit is installed. [31]

Future energy efficient pulp mills with high steam pressure and temperature in the recovery boiler will in most cases have to lower the levels of Cl and K compared to today in order to avoid problems with plugging and corrosion. This in combination with the cost for purging cooking chemicals makes a process for selective removal of Cl and K desirable.

Numerous methods have during the last five decades been proposed for removal of Cl and K from the chemical recovery cycle. There are two main, realistic, locations in the recovery cycle where Cl and K can be removed: media from the recovery boiler, mainly ESP dust, or from liquor in the liquor cycle.

Because of the enrichment of Cl and K in ESP dust all today commercially available techniques for removal of Cl and K treat ESP dust. Four main technologies are used for the treatment of ESP dust:

1. Leaching
2. Evaporation/crystallization
3. Freeze crystallization
4. Ion exchange

The first three processes take advantage of the same basic solubility difference principle and a simple process scheme is shown in Figure 13.

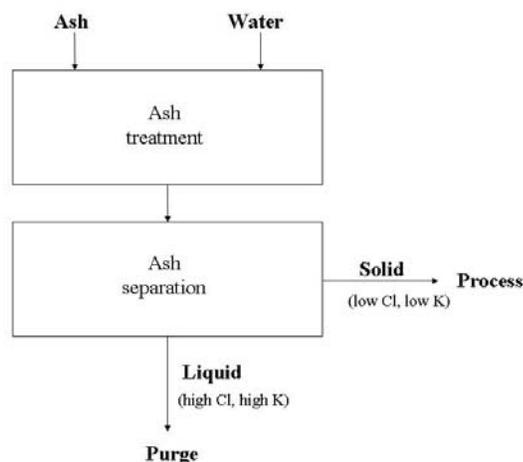


Figure 13. Basic process scheme for Cl and K separation from ESP dust using leaching, evaporation/crystallization or freeze crystallization.

Processes one to three make use of the differences in solubility between the ESP dust salt compounds. It is primarily the solubility difference between alkali sulphates (Na_2SO_4 and K_2SO_4) and alkali chlorides (NaCl and KCl) that enable the Cl and K separation. When performing ion exchange the process uses a proprietary resin which selectively absorbs NaCl and KCl . All four processes remove Cl and K in a purge stream and recycle the purified process chemicals back to the chemical recovery cycle.

Processes that make use of solubility differences of the salts have to handle the very complex aqueous solution. In solutions of mixed salts the presence of NaCl substantially decreases the solubility of Na_2SO_4 due to the common ion effect. This is positive during leaching and crystallization. However other salts are also present which complicate the solubility of the system. Both during leaching and crystallization the conditions that separate NaCl from Na_2SO_4 also tend to remove Na_2CO_3 and thus valuable Na is lost.

K removal is more complicated than Cl removal because of the variety of compounds K can form. K may be present as K_2SO_4 , or the double salt glaserite ($3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$) after dissolving and re-crystallization. Those K containing compounds tend to behave in a similar manner as Na_2SO_4 in the system resulting in a reduced K removal during leaching and crystallization processes. [32]

In practice it is impossible to achieve a complete separation why it is necessary to weigh the extent of Cl and K removal against Na, SO_4 and CO_3 recovery.

7.1 Leaching

Leaching processes for removal of Cl and K from ESP dust make use of the high solubility of NaCl and KCl compared to the relatively insoluble Na₂SO₄. The insoluble character of Na₂SO₄ is enforced in a saturated NaCl solution why it is desirable to aim for the saturation concentration of NaCl. Generally the leaching process consists of two main unit operations:

1. A leaching tank where ESP dust is mixed with water, and possibly recycled leachate, to form a slurry or paste. The salt concentration in the leaching tank has to be monitored in an accurate way in order to promote the dissolution of Cl and K salts without dissolving Na₂SO₄. Selectivity of the process is also improved by a high temperature since more Cl salts and less SO₄ salts are dissolved in the system.
2. The second stage is typically a filter or a centrifuge where the separation of solid and liquid phase is performed. The solid phase, that mainly contains Na₂SO₄, is recycled back to the liquor cycle while the leachate, that is rich in Cl and K, is recycled back to the first step. Removal of Cl and K is performed by purging a part of the leachate.

7.1.1 Metso AshLeach™

One ESP dust leaching system is available from Metso Power and named AshLeach™. The first unit was built at the Aracruz mill in Brazil 2002, because of their problems with corrosion in the recovery boilers which limited the steam temperature to 430°C. [33] The AshLeach™ system at Aracruz was designed to process about 60 ton/d of precipitator ash from one of three boilers at Aracruz. Metso has since 2002 delivered, or contracted, a number of AshLeach™ processes and the locations and capacities are shown Table 6.

Table 6. Summary of delivered or contracted Metso AshLeach™ processes. [31]

Delivery year	Customer	Country	Capacity (ton/day)
2008	UPM-Kymmene Oyj, Kymi	Finland	109
2007	Portucel S.A, Setubal	Portugal	160
2007	Södra Cell AB, Värö	Sweden	85
2007	Suzano Celulose e Papel S.A, Unidade Mucuri	Brazil	260
2005	Aracruz Celulose S.A	Brazil	202
2005	Stora Enso/Aracruz Celulose, Veracel	Brazil	168
2004	Suzano Celulose e Papel S.A, Unidade Mucuri	Brazil	180
2004	Asia Pulp & Paper, Jinhai (Hainan)	China	169
2002	Aracruz Celulose S.A	Brazil	56

The AshLeach™ process system in Figure 14 consists of three main components: a leaching tank, a centrifuge and a reject tank.

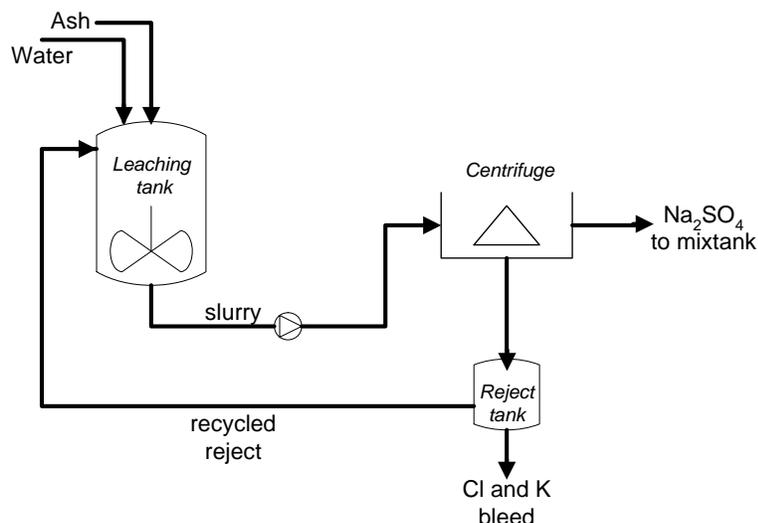


Figure 14. Schematic scheme of Metso AshLeach™. [29]

ESP dust is mixed with water to form slurry in the leaching tank. The temperature of the water is set to 90°C in order to facilitate dissolution of NaCl and KCl while Na₂SO₄ remains solid. No pH regulation is performed but depending on the composition of the ESP dust the slurry will be more or less basic. The ash-to-water ratio at Aracruz is set to 1.25:1 and well monitored in order to maximise the dissolution of Cl and K while minimizing the dissolution of Na₂SO₄. It is desirable to maximise the concentration of Na₂SO₄ but there is a limitation set by the concentration of K in the slurry. If the K concentration is too high formation and precipitation of glaserite will lower the K removal rate. The slurry is pumped to the centrifuge that separates the solids, rich in Na₂SO₄, from the liquid that is rich in Cl and K. The solids are fed to the black liquor mixing tank for Na and S recovery. The liquid phase is pumped to the reject tank from which purging of Cl and K from the system is controlled. There is a possibility to recycle a part of the liquid phase but any recycling depends on the concentration K in the incoming ash. If recycling of liquid phase should be performed the K concentration in the ash has to be lower than 4 wt %. [29, 34]

The performance of the ash leaching system is determined by its ability to remove Cl and K from the ash but also its ability to recover Na and S. These values can be obtained from the mass flow rates and the compositions of slurry and product. Table 7 summarizes the average material balances for Cl, K, Na, and S around the ash leaching system. It is important to note that an increase in removal efficiency of Cl and K inevitably results in a lowered recovery of Na and S.

Table 7. Average Cl and K removal efficiency and Na and S recovery efficiency for the AshLeach™ in Aracruz. [34]

	In (ton/d)	Out (ton/d)	Removal efficiency (%)
Cl	3.0	2.7	90
K	2.6	2.1	82

	In (ton/d)	Out (ton/d)	Recovery efficiency (%)
Na	12	7.5	63
S	7.3	5.0	68

Data in Table 7 shows that the ash leaching system at Aracruz removes about 90 % of the Cl input and 82 % of the K input while recovering an average of approximately 65 % of the Na and S. [34] Experiences has also shown that the dryness of the solids from the decanter centrifuge is approximately 85 % which means that the black liquor will not become diluted when the solids is added to the black liquor mixtank. [33]

Cl levels in the ESP dust, and mill liquor, have been significantly lowered since the ash leaching system was installed at Aracruz. Despite the high K removal efficiency, the K concentration in the ESP dust and mill liquor has however remained about the same as before the ash leaching system was installed. A proposed probable explanation to the difference in behaviour between Cl and K concentration is the fact that the mill started to operate with higher white liquor sulphidity about the same time as the ash leaching system was installed. High sulphidity results in more Cl emissions from the recovery boiler in the form of HCl emissions but at the same time more K_2SO_4 is produced which makes the K removal less effective. [34]

7.1.2 Andritz leaching

In Andritz leaching process ESP dust is first mixed with hot water, around 60°C, to form slurry with an ash-to-water ratio of about 1.2-1.6 by weight. No pH regulation is performed which results in a pH of approximately 11. The major difference between Andritz leaching process and Metso AshLeach™ is the solid/liquid separation process. Andritz uses a drum filter or a vacuum belt conveyor filter instead of a decanter centrifuge. Another difference between the Metso AshLeach™ and Andritz leaching process is that no recycling of the Cl and K liquid stream is performed.

The Cl removal efficiency is estimated to be 70-85 % and the Na recovery 60-80 %. Just like most of the Cl and K processes removal processes a high Na recovery results in a lowered Cl and K removal also for the Andritz leaching system. [29]

7.2 Evaporation/Crystallization

Evaporation/Crystallization processes also take advantage of the relatively low solubility of Na_2SO_4 . Though evaporation/crystallization processes use the solubility difference in the opposite manner to leaching. ESP dust is first completely dissolved in water, or recycled condensate, and then the solution is evaporated. Due to the lower solubility of Na_2SO_4 , it will during evaporation crystallize first. Purified Na_2SO_4 is filtered and recycled back to the liquor cycle. Most of the fluid phase, rich in Cl and K, is returned to the crystallizer but a small share is purged to remove Cl and K. It is important to point out that the evaporation/crystallization processes generate comparatively large crystals, compared to the leaching processes, which results in a solid phase that is easier to separate.

There are three commercially available evaporation/crystallization processes: HPD CRPTM (Chloride Removal Process), Andritz ARC (Ash Re-Crystallization process) and Eka Chemicals PDR (Precipitator Dust Recovery). In principle the processes are similar although they operate with different evaporator designs.

7.2.1 HPD systems CRPTM

Worldwide there are six Champion International CRPTM (Chloride Removal Process) operating. The system was initially a part of The BFRTM (Bleach Filtrate Recycle) concept manufactured by Champion International in Canton, USA. BFRTM aimed for increased closure of the mills bleach plants.

Figure 15 shows a schematic description of the HPD CRPTM. ESP dust is first completely dissolved in hot water, around 75°C, to produce a solution of ash/water at a target of about 26 % dissolved solids concentration, which represents approximately 85 % of saturation. [35] The solution is then evaporated in a forced evaporator/crystallizer to above the solubility limit for Na_2SO_4 , but below the solubility limit for K_2SO_4 and KCl. The evaporator operates under vacuum with an external reboiler. Both single- and multi-effect systems are now in use depending on the amount of ash treated and the integration of the CRPTM in the black liquor evaporation train. Low pressure steam is fed to the crystallizer reboiler. The solid liquid separation was initially performed by an internal wash column but nowadays external washing with centrifuge is used.

In order to increase the Na recovery rate sulphuric acid (H_2SO_4) can be provided to convert Na_2CO_3 into Na_2SO_4 . Addition of H_2SO_4 though contributes to an increased sulphidity which for a modern mill seldom is recommended since the sulphidity of a modern mill often is high. [29]

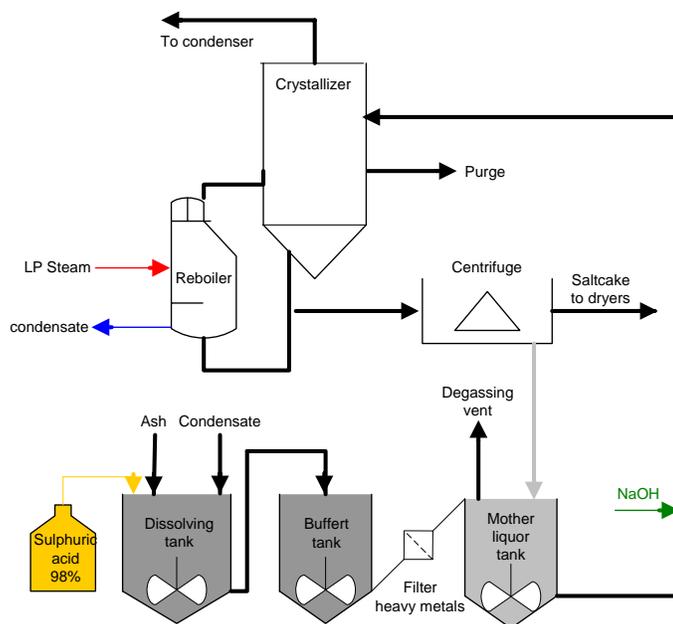


Figure 15. Schematic description of the CRP™ based on the process in Tumut, Australia. [29]

Published data from one installation of CRP™ shows a Cl removal efficiency of 95 % and 80 % S recovery. Removal of K can vary considerably, between 50-85 %, depending on the concentration of K in the ESP dust and the settled balance between K removal and Na and S recovery. [36]

7.2.2 Andritz ARC™

The Andritz ARC™, Ash Re-Crystallization, process was first tested in a pilot plant at UPM Kymmene in Pietarsaari and in January 2005 the first full scale unit was installed at the Soporcel mill in Figueira da Foz, Portugal. One unit will also be started in Spain during 2008.

In the ARC process ESP dust is initially completely dissolved in warm water. The ash-to-water ratio is approximately 0.4 kg dust/kg water. The slurry is then fed to a falling film lamella type evaporative crystallizer where about 2 kg water/kg ESP dust is evaporated. Formed crystals of Na_2SO_4 and Na_2CO_3 are separated using a vacuum drum filter or a centrifuge and recycled back to the chemical recovery cycle. The water content in the solid phase is approximately 10-15 % which means that the black liquor will not become diluted when the solids is added to the mixtank. The liquid phase, enriched in Cl and K is partly recirculated and partly sent to sewer. Although pH is about 11 in the liquid phase the solution is corrosive, due to the high concentration of Cl, which makes it necessary to use relatively expensive corrosive resistant stainless steel in the equipment. [29, 37]

The degree of Na recovery strongly affects the removal efficiency of Cl and K. Figure 16 shows a comparison of measured Cl removal efficiency for the ARC process compared to leaching, as a function of Na loss. The ARC figures are based on the full scale installation in Soporcel and the leaching figures on pilot-scale tests. From Figure 16 can be read that the ARC process shows a higher Cl removal at a set Na loss compared to the performed pilot leaching trials. According to Andritz a Cl and K removal efficiency of 85 % is achieved with a Na recovery of 75-80 %. [37] Simulations performed by Andritz also show that if the Na recovery is 77.5 % and the CO₃ content of ESP dust is 15 %, SO₄ recovery is 86 % and CO₃ recovery 56 %. [38]

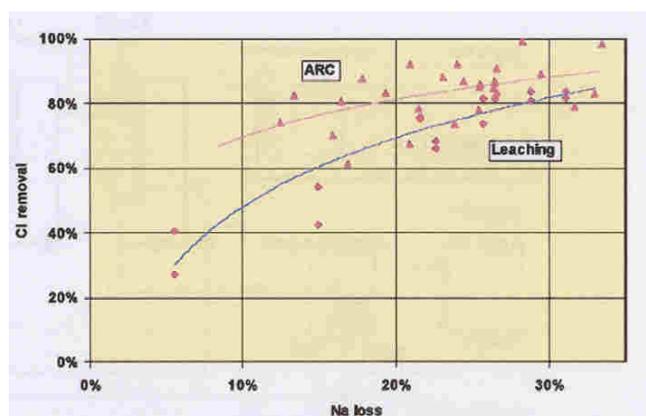


Figure 16. Cl removal efficiency of ARC and leaching processes as a function of Na loss. [37]

The ARC process is operated at low temperatures, 50-90°C, which opens an opportunity of using different low temperature secondary heat streams in addition to live steam. One option is to integrate the crystallizer to the black liquor evaporator train where steam is fed from effect 2 to the ARC and steam from the ARC is fed to effect 4. There is also a possibility to connect the ARC after the last evaporation effect. Another possibly economically beneficial energy source for many mills is the recovery boiler smelt dissolving tank. Green liquor from the dissolving tank is recirculated to a flash tank and flashed vapour is fed to the ARC. [37]

The full scale ARC unit at the Soporcel mill was designed to treat all the produced ESP dust (167 ton/d) of the new 2400 tDS/d recovery boiler. The principle flowsheet of the Soporcel ARC system is presented in Figure 17. The heat energy is taken from the recovery boiler dissolving tank making electricity the only energy cost for the system at Soporcel. The electricity consumption is approximately 29 kWh/ton treated ESP dust.

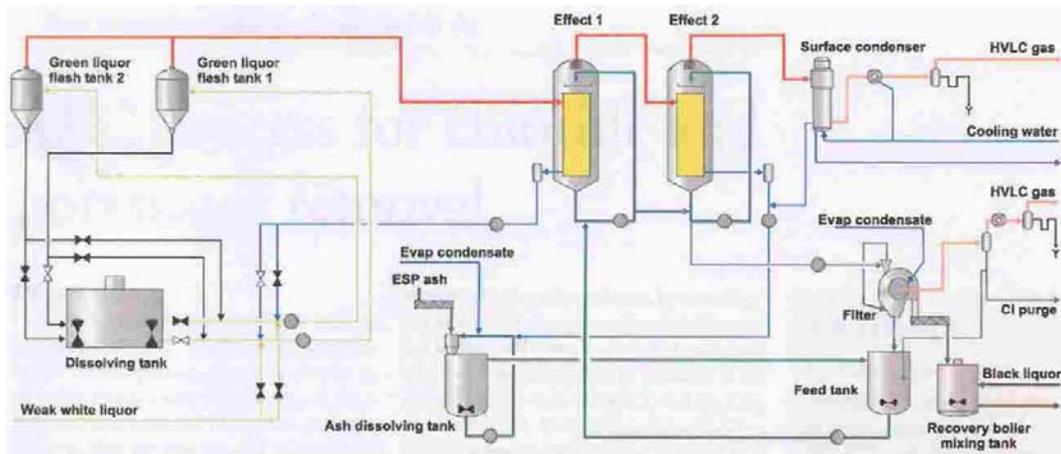


Figure 17. Principal flowsheet of the ARC at Soporcel mill. [37]

The trend of Cl and K concentration in virgin black liquor at Soporcel is shown in Figure 18. Before the start-up of the ARC, Cl and K concentration was about 0.8 and 1.8 wt % on dry solids, respectively. After 9 months operation the Cl concentration had stabilized at approximately 0.3 wt % on dry solids. The K concentration first went down to 1.2 and then up to 1.6 wt % on dry solids because of too low degree of purging of the liquid phase. If the purge flow is too low the K concentration in the crystallizer mother liquor reaches above the solubility limit and K partially crystallizes which results in a decrease in removal efficiency for K. [37]

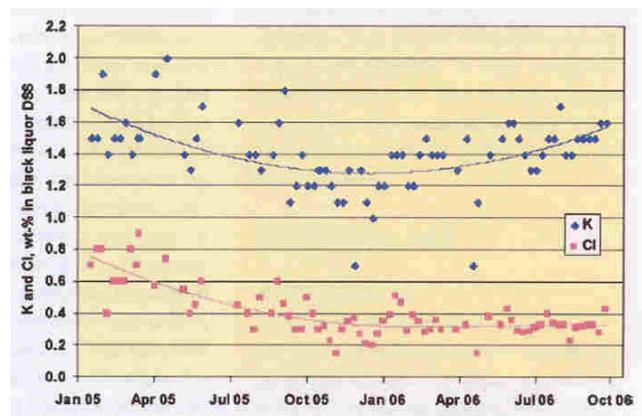


Figure 18. Change in Cl and K concentration in virgin black liquor at the Soporcel mill measured as wt % on dry solids. [37]

After 16 months of run a total recovery boiler shutdown was performed at the Soporcel mill. During the shutdown the heat exchanger areas were inspected and only in the hottest superheater regions some indications of fouling was found. The low levels of Cl and K in the recovery cycle were dedicated a major importance for the low degree of fouling. [37]

7.2.3 Eka Chemicals PDR

In Eka Chemicals PDR process ESP dust is dissolved in hot water, around 75°C. The concentration of ESP dust is set to approximately 30 % dissolved solids. The solution is pumped to a crystallizer where evaporation facilitates the crystallization of Na₂SO₄. The crystallizer operates under vacuum, about 0.33 bar, and 70°C. The formed solid phase is separated from the aqueous solution in a vacuum filter. The liquid phase is partly recirculated and partly purged depending on the levels of Cl and K. A process scheme of Eka Chemicals PDR process is shown in Figure 19.

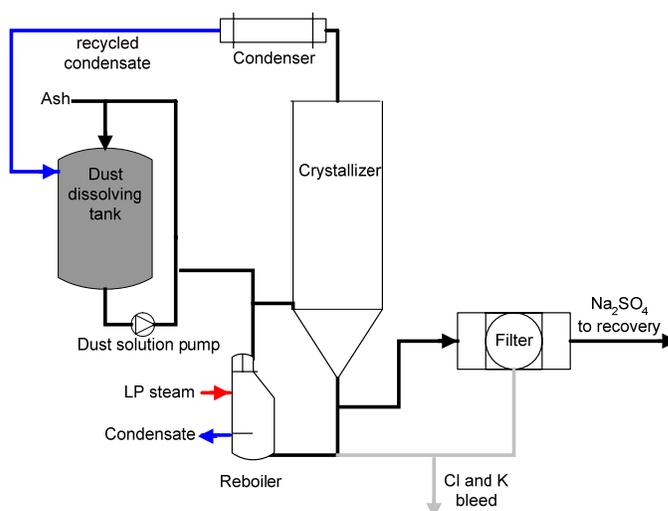


Figure 19. Process scheme for Eka Chemicals PDR process. [29]

The PDR process has not yet been commercialized but laboratory and pilot-scale testing shows a Cl and K removal efficiency of about 90 % with an approximate 80 % recovery of Na and SO₄. [17] According to sources at Eka chemicals the efforts for further research and development of the PDR process are today very limited.

7.3 Freeze Crystallization

Freeze crystallization takes advantage of the considerable decrease in solubility of sodium sulphate decahydrate (Na₂SO₄*10H₂O), also called Glauber salt, at low temperatures. Below approximately 30°C Na₂SO₄ precipitates rapidly as large Na₂SO₄*10H₂O crystals, while Cl and K remains in solution. At 40°C the solubility of Na₂SO₄*10H₂O is about 30 wt % and drops to less than 10 wt % at 10°C. As can be seen in Figure 20 there is no or very little change in solubility for NaCl and K₂SO₄ throughout that temperature range. [30] After separation of the phases purified Na₂SO₄*10H₂O crystals can be returned to the kraft liquor cycle and the solution purged to remove Cl and K.

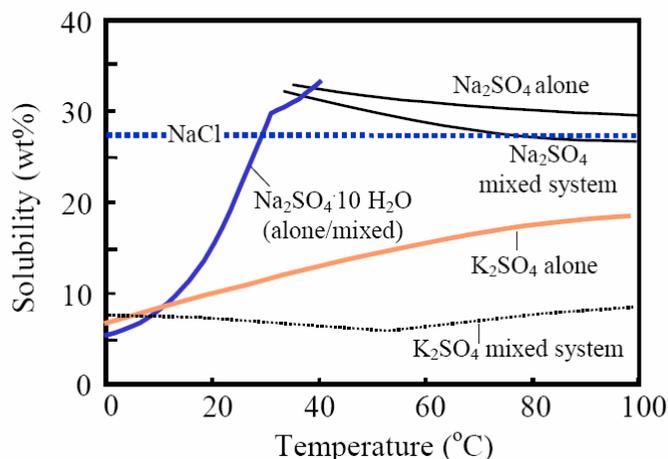


Figure 20. Solubility of the salts in the system Na_2SO_4 , K_2SO_4 and NaCl . [30]

7.3.1 Mitsubishi Freeze Crystallization process

Six Mitsubishi Freeze Crystallization systems are presently operating in Japanese pulp mills. The principal flowsheet is shown in Figure 21.

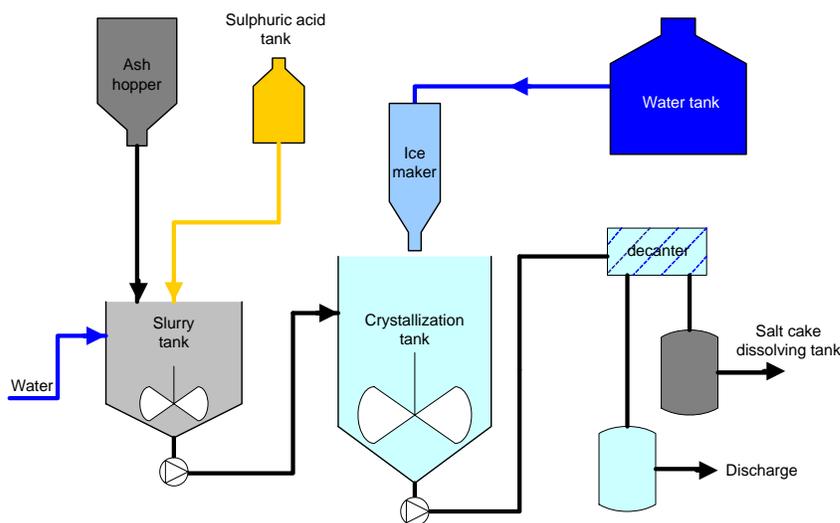


Figure 21. Schematic description of the MPR™ process. [29]

ESP dust is first mixed with water in a slurry tank. The solution temperature is kept at 40–45°C in order to facilitate maximum dissolution of K_2SO_4 and NaCl . The amount of water added must be well monitored to ensure that all K_2SO_4 and NaCl are dissolved along with a minimum of Na_2SO_4 . If the ESP dust contains a large amount of Na_2CO_3 H_2SO_4 can be added to convert the main part of Na_2CO_3 to Na_2SO_4 and thus minimize the loss of Na. However, it is not necessary to add H_2SO_4 to make the separation

process work, but Na losses will be higher if Na_2CO_3 is not converted to Na_2SO_4 . Removal of Cl and K is though not noticeably affected by the presence of carbonate.

The slurry is further transported to the precipitation tank and ice is added in order to lower the temperature to 15°C . At this temperature $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ precipitates as crystals of approximately $100\ \mu\text{m}$. The total amount of water supplied, including ice, is around 1.8-2.6 times by weight of the ash supplied to the slurry tank. A major advantage with the freeze crystallization technology is the large crystals that are formed. The large crystals can easily be separated either by decanting or centrifuge. The separated solution is purged and the solid phase is dissolved in weak black liquor and thus recirculated.

Table 8 shows some specifications for one recovery boiler and operating parameters of the Cl and K removal system at the Oji Paper Kasugai mill.

Table 8. Examples of operating parameters for one recovery boiler and the Cl and K removal system installed at Oji Paper Kasugai mill. [39]

Boiler capacity	2400 tDS/d
Steam pressure	108 bar
Steam temperature	515°C
Ash quantity treated	1.8 ton/h (About $\frac{1}{4}$ of total ash collected by EP. Max capacity 2.5 ton/h)
Slurry tank temperature	40°C
Precipitation tank temperature	15°C
Water to ESP dust ratio	2.3-2.6
Cl removal efficiency	90 %
K removal efficiency	75 %
Na recovery efficiency	70 %
SO_4 recovery efficiency	75 %

Figure 22 shows the decrease in Cl and K concentration in the ESP dust from the recovery boilers as a result of the Cl and K removal system installation. After six months of continuous operation almost no ash plugging was observed resulting in remarkable improvement in operation and maintenance of the recovery boiler. [24, 39]

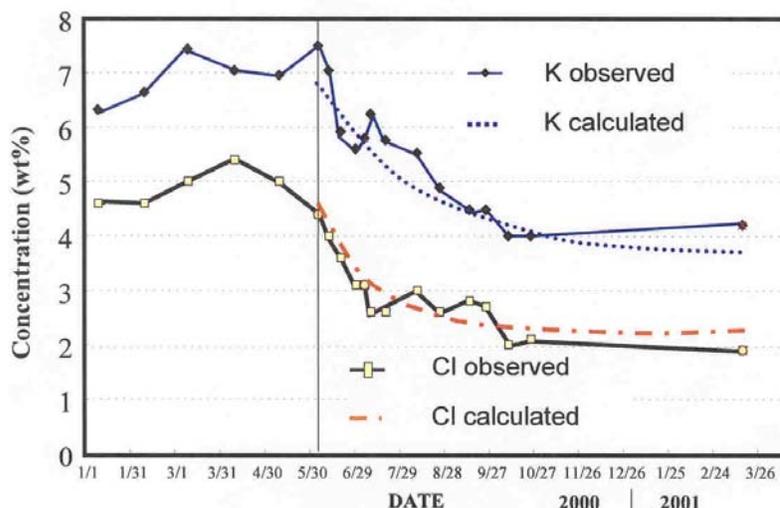


Figure 22. Cl and K concentration in ESP dust before and after the Freeze crystallization system was installed. [39]

7.4 Ion exchange

Usage of commercially available specialized ion exchange resins which contain both cation- and anion-exchange groups makes it possible to remove both Cl and K simultaneously. Since Cl ions are the only monovalent anions in the ESP dust mixture the resins will preferentially adsorb Cl instead of SO_4 and CO_3 . An ion exchange treatment system called PDP, Precipitator Dust Purification, has been developed by Eco-Tec and Paprican.

The PDP system has not yet been commercialized but a pilot plant is operating in Paprican's laboratory. Removal of Cl has been reported to be 97 % with minimal losses of Na (6 %), SO_4 (1 %). A drawback with the PDP ion exchange technology is that the Na concentration largely exceeds that of K resulting in a very low K removal in the magnitude of only 5 %. The PDP system is therefore best suited for a situation where Cl removal is far more important than K removal. [40] One major difference between the PDP process and the other described processes is that the purified Na_2SO_4 stream is returned to the liquor cycle in the form of solution. This can for some mills turn out to be a problem if they lack spare capacity in the black liquor evaporators.

Another system under development uses ion-exchange technology to remove Cl and K and takes advantage of a phenomenon called the ion-exchange isothermal super saturation effect, IXISS. The IXISS effect is observed for many ion-exchange systems where the ion-exchange system is followed by the formation of a stable supersaturated solution of soluble substances in the interstitial space of ion-exchange columns. The formed Na_2SO_4 supersaturated solution results in a rapid crystallization of Na_2SO_4 when the solution leaves the column. Promising research has shown 95 % Cl and K removal and a 98 % SO_4 recovery, but the technology is not yet commercialized. [41]

7.5 Summary of processes for removal of Cl and K from ESP dust

A summary of the efficiency for the above presented processes for removal of Cl and K is presented in Table 9. It is important to note that the efficiencies may, and in reality actually varies due to individual tuning of the processes.

Table 9. Summary of processes for removal of Cl and K from ESP dust.

Process name	Supplier	Type of process	Commercially available	Cl removal	K removal	Na recovery	SO ₄ recovery
AshLeach™	Metso	Leaching	Yes	90 %	82 %	63 %	68 %
Leaching	Andritz	Leaching	Yes	70-85 %	NR	60-80 %	NR
CRP™	US Filter / HPD	Evaporation / Crystallization	Yes	95 %	50-85 %	NR	80 %
ARC™	Andritz	Evaporation / Crystallization	Yes	85 %	85 %	77.5 %	86 %
PDR	Eka Chemicals	Evaporation / Crystallization	No (Pilot plant)	90 %	90 %	80 %	80 %
MPR	Mitsubishi	Freeze crystallization	Yes	90 %	75 %	70 %	75 %
PDP	Eco-Tec	Ion-exchange	No (Pilot plant)	97 %	5 %	94 %	99 %
“IXISS”	?	Ion-exchange	No (lab scale)	95 %	95 %	NR	98 %

7.6 Chlorine and potassium removal from green and white liquor

Because of the enrichment of Cl and K in ESP dust most efforts for removal of Cl and K have been directed towards the ESP dust. There are however suggested processes that have proved to be able to remove Cl and K from green and white liquor, but none of them are yet commercial. Two of the suggested processes will be described in brief below.

One process that has been tested in Thunder Bay, Canada, is the so called Salt-Recovery Process (SRP). In the SRP Cl ions in the white liquor are removed using evaporation/crystallization. The initial evaporation step causes crystallization of sulphates and carbonates while further evaporation facilitates crystallization of NaCl and KCl. However the method was considered too expensive since it involved evaporation of both white and black liquor. [42]

Removal of Cl and K from green liquor has been evaluated with a two step process using evaporation and freeze crystallization. The process was adapted for the Black Liquor Gasification system where there is no generation of ESP dust. The green liquor is first evaporated and then cooled to facilitate crystallization of Na_2CO_3 and NaHCO_3 . After separation of the solid phase the liquid phase, enriched in Cl and K, can be purged to remove Cl and K from the system. The method has only been tested in laboratory scale where results show that the degree of evaporation must be $\geq 70\%$ and the crystallization temperature below 20°C in order to minimize, i.e. less than 20% , the losses of CO_3 . Under those conditions more than 95% of the Cl and K could be removed. [43]

8 Background for evaluated cases

8.1 Introduction

Increased steam data in the recovery boiler generates more electricity but on the other hand require low mill levels of Cl and K in order to maintain a trouble-free operation of the recovery boiler. It is therefore fundamental to identify which levels of Cl and K that may be considered acceptable in a mill in order to uphold trouble-free operation when operating with increased steam data.

As described earlier in the Thesis it is not uncomplicated to compare different mills and thus setting fixed values for acceptable Cl and K levels for different streams will also be difficult. Many parameters, for example the enrichment ratio, are individual for each mill which further complicates a direct standardization of acceptable Cl and K levels. An extremely important aspect on the matter is also the design of the heat exchanging region in the recovery boiler where particularly the superheater and boiler section are of great importance. However, information attained from different sources [31, 37, 39, 44] has given a relatively good guideline for which Cl levels that likely will result in a trouble-free operation of the recovery boiler. It can almost be considered as common practise in the industry to direct focus towards the Cl level since Cl has greater impact on the potentially negative properties of the ESP dust. The final K concentration will consequently end up only as a secondary result and not defined as a target level initially.

From the four prerequisites in brief presented below, concerning acceptable Cl and K concentration, the target parameter for Cl concentration in the simulations was determined to be: Cl concentration in virgin black liquor should be kept below 0.30 wt % on dry solids.

- A Swedish mill that invested in a new recovery boiler with a steam temperature of 500°C and 100 bar pressure was by the supplier recommended that the concentration of Cl in virgin black liquor should be kept below 0.3 wt % on dry solids.[44]
- The recovery boiler at Oji Paper Kasugai mill in Japan operate at 515°C and 108 bar, which represents one of the highest steam data in the world. In Figure 22 concentrations of Cl and K in ESP dust from the recovery boiler at Oji Paper Kasugai mill were presented. The Cl and K concentrations in ESP dust after installation of the freeze crystallization were approximately 2 wt % and 4 wt % on dry solids, respectively. With the set conditions, enrichment ratio etc., for the reference mill a 2 wt % on dry solids concentration of Cl in ESP dust corresponds to about 0.24 wt % on dry solids content in virgin black liquor. According to the authors the recovery boiler can at those Cl and K levels be operated without any observed problems related to Cl and K. [39]
- Metso Power [31] has presented a diagram (Figure 23) that roughly shows the risk of plugging in the recovery boiler as a function of Cl and K concentration in black liquor. The diagram does not take any consideration to steam data but

anyhow gives a fairly good guideline for acceptable Cl and K concentrations. An estimated Cl concentration of 0.3 wt % with a corresponding K concentration below 2.0 wt % lies within the “Low risk of plugging area”.

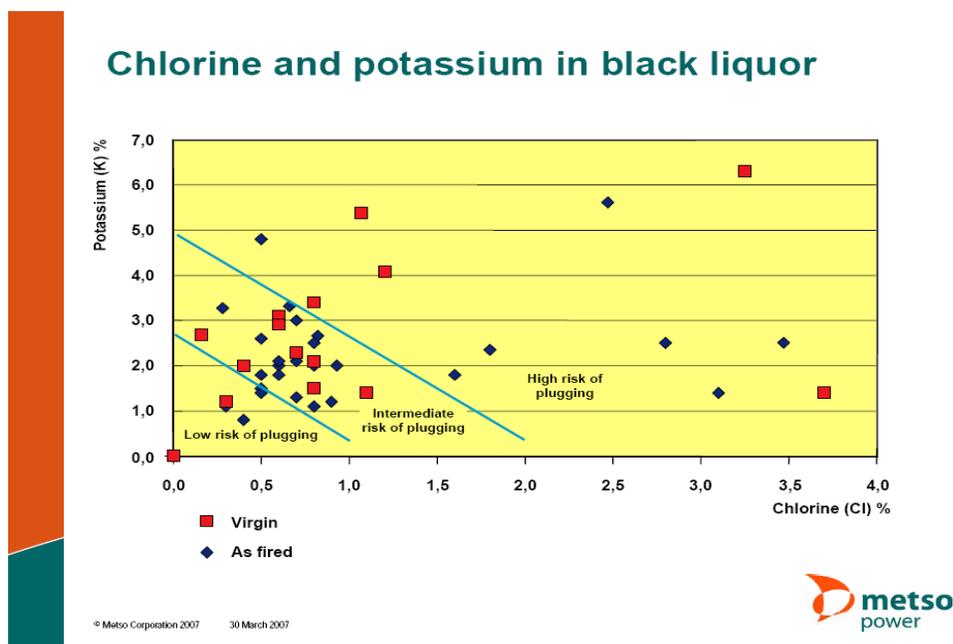


Figure 23. Risk for plugging in the recovery boiler as a function of Cl and K concentration in black liquor. Provided by Metso Power. [31]

- From Andritz installation of the ARC process at the Soporcel mill in Portugal it can from Figure 18 be read that 0.3 wt % Cl on dry solids in virgin black liquor resulted in a trouble-free operation of their recovery boiler. [37]

8.2 Cl/K and Na/S balances in the model mills

In this study the FRAM reference market pulp mill models have been used to perform simulations required for the cost benefit analysis. However, minor modifications of the models were made in order to create the desired mill conditions. In chapters 8.2.1 and 8.2.2 the initial mill balances of Cl/K and Na/S are presented to give a background of the original mill situation.

8.2.1 Softwood mill

Due to the fact that the model mills are highly closed the S level in the softwood mill have to be balanced through purging of ESP dust. In the softwood mill ESP dust is purged to maintain a sulphidity of 0.35, which represents a purge of 10.1 kg ESP dust/ADt. One important outcome of purging ESP dust is that a significant amount of Cl and K simultaneously leaves the system and thus acts as an important output for Cl and K. The Cl and K input levels with wood, net intake of Cl from the bleach plant (to the chemical recovery cycle), Cl and K concentrations in virgin black liquor and ESP dust are presented in Table 10.

Table 10. Important inputs and concentration levels of Cl and K in the FRAM reference softwood market pulp mill. [2]

	Cl	K
Input with wood (g/ADt)	124	829
Net intake from bleach plant (g/ADt)	200	-
Concentration in virgin black liquor (wt % on ds)	0.44	1.36
Concentration in ESP dust (wt % on ds)	1.94	3.83

In Figure 24 the inputs and outputs of Cl and K for the softwood mill are shown in an illustrative diagram. The upper curve is the input streams and the lower curve represents the output streams. Only the net intake/output from the bleach plant is presented since the totally dominating part of the Cl enters the mill with the bleaching chemicals but leaves with the bleach plant filtrate and thus never enters the chemical recovery cycle. It is noteworthy that the only input for K is wood while Cl enters the chemical recovery cycle as bleach plant filtrate, which is used as wash liquor on the last wash press in the brown stock, but also with wood. The dominating output of Cl and K is with the ESP dust.

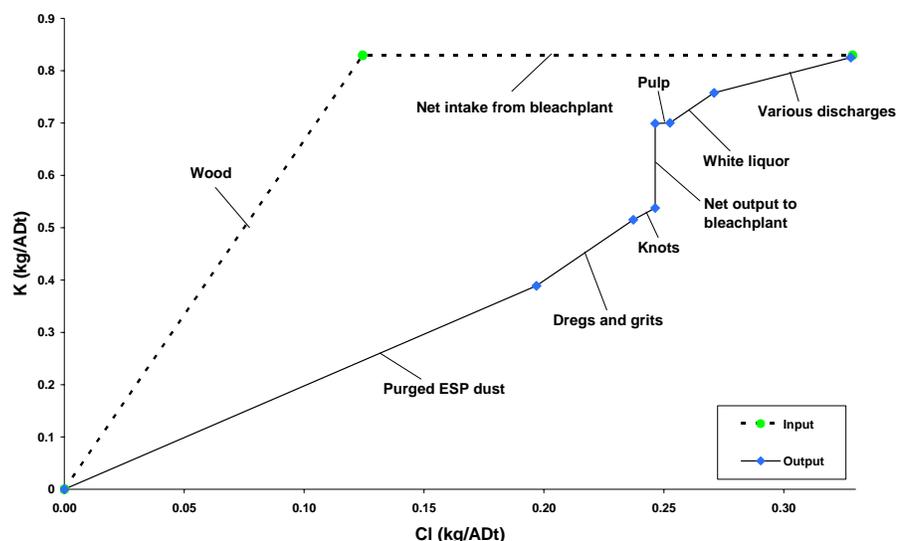


Figure 24. Inputs and outputs of Cl and K for the FRAM reference softwood market pulp mill. [2]

The S and Na balance of the mill are also of great importance in this investigation since they represent the expensive cooking chemicals that are desirable to keep in the process. A corresponding input and output diagram shown for Cl and K in Figure 24 is presented for Na and S in Figure 25. It is worth noticing that the major part of the S enters the mill with the by-product from the ClO₂ production which is used in the talloil production.

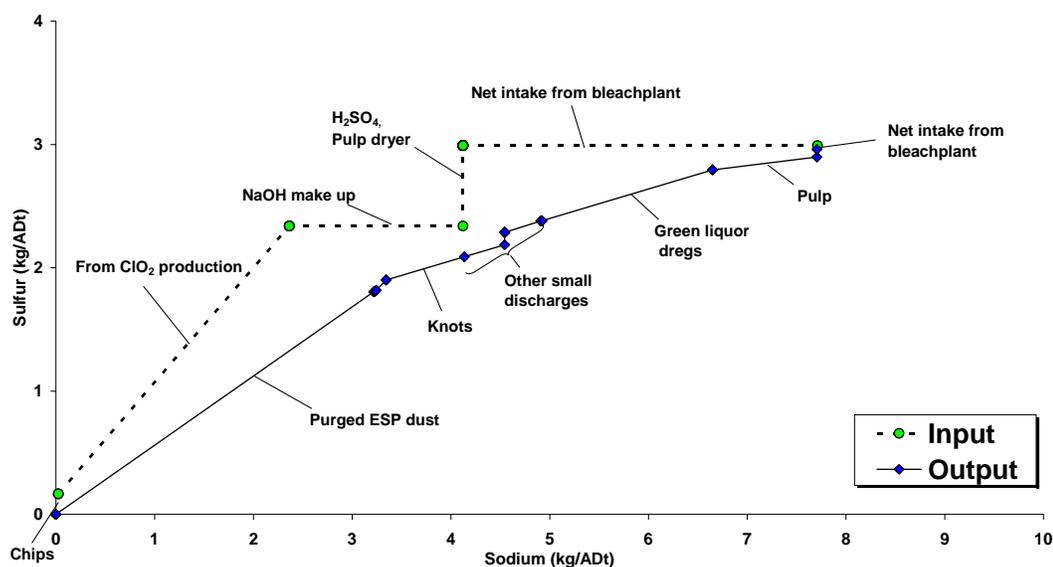


Figure 25. S and Na balance for the FRAM reference softwood market pulp mill. [2]

8.2.2 Hardwood mill

The hardwood mill is to a very large extent similar to the softwood mill. However, one difference of great importance for this study is that a hardwood mill does not have a talloil preparation plant. The overall situation resembled with the hardwood mill in this Thesis is a mill that has a deficit of S and for that reason will not purge ESP dust to maintain the sulphidity, but on the contrary initially needs to provide make-up S. It is also important to point out that hardwood generally contains a higher amount of Cl and K compared to softwood. Another possible reason that could contribute to a mill situation with a deficit of S in the process is if the bleaching sequence is TCF (Totally Chlorine Free). TCF bleaching does not generate the salt cake by-product from ClO_2 production commonly utilized as S make-up.

In the hardwood mill ESP dust is purged in order to regulate the Cl and K level. The amount of purged ESP dust is 13.0 kg ESP dust/ADt in the initial state. The Cl and K input levels with wood, net intake of Cl from the bleach plant (to the chemical recovery cycle), and Cl and K concentrations in virgin black liquor and ESP dust are presented in Table 11.

Table 11. Important inputs and concentration levels of Cl and K in the initial state for the FRAM reference hardwood market pulp mill. [2]

	Cl	K
Input with wood (g/ADt)	277	830
Net intake from bleach plant (g/ADt)	216	-
Concentration in virgin black liquor (wt % on ds)	0.68	1.33
Concentration in ESP dust (wt % on ds)	2.88	3.59

In Figure 26 and Figure 27 the Cl/K and Na/S diagrams for the modified FRAM reference hardwood market pulp mill are shown. The Cl/K balance for the hardwood mill shows a similar pattern as the softwood mill with the difference that the intake with wood is larger for the hardwood mill.

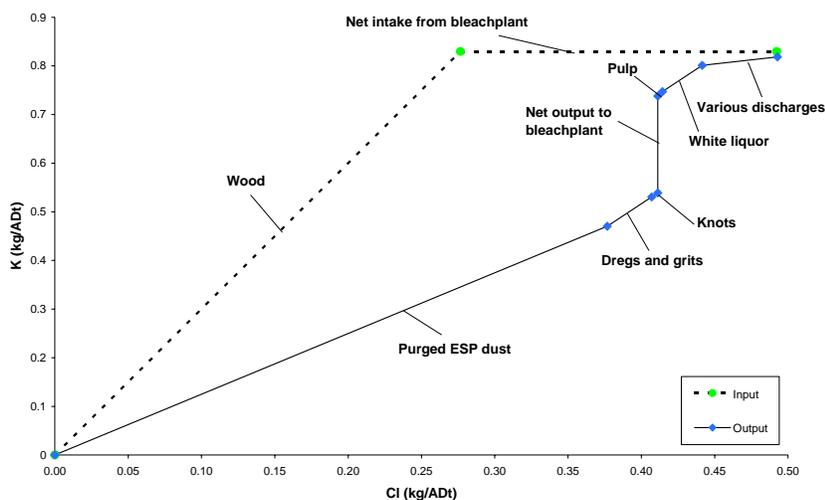


Figure 26. Inputs and outputs of Cl and K for the modified FRAM reference hardwood market pulp mill.

In Figure 27 it is essential to note that no by-product from ClO_2 production is provided to the hardwood mill.

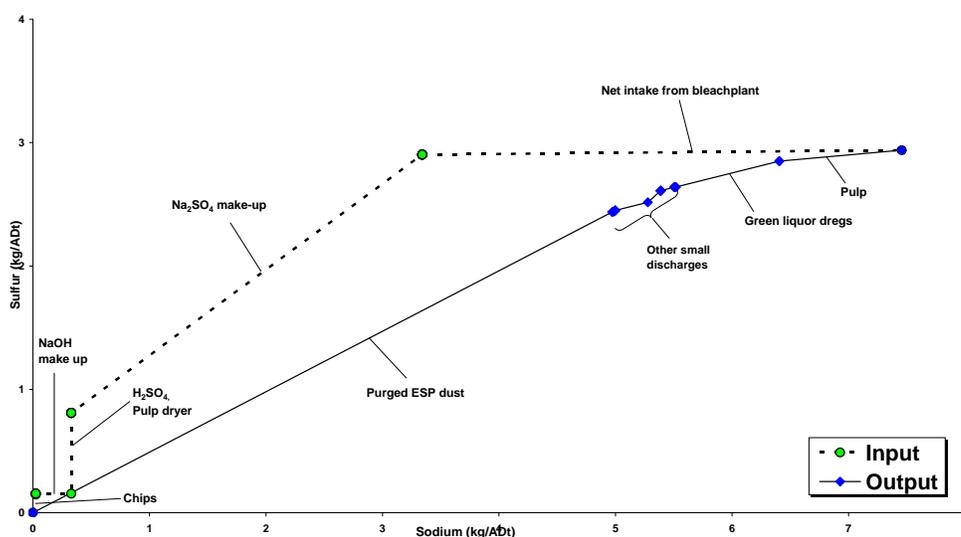


Figure 27. S and Na balance for the modified FRAM reference hardwood market pulp mill.

9 Results

9.1 Introduction

In the evaluated cases steam data in the recovery boiler was raised from 490°C and 81 bar to 510°C and 100 bar. Simultaneously the levels of Cl and K were varied. For the softwood mill Cl levels ranging between 0.3-0.96 wt % on dry solids Cl in virgin black liquor were evaluated, and the corresponding Cl range for the hardwood mill were 0.3-0.95. The mill levels of Cl and K were in the simulated cases changed by simply varying the amount of intake with wood, and the levels were chosen to represent a set of realistic figures. Higher steam data resulted in an increased electricity production, but in addition required low mill levels of Cl and K. Three different alternatives of lowering the levels of Cl and K to acceptable levels were evaluated and compared by computer simulations.

Case 1 represented a scenario where the Cl and K levels in the softwood mill were assumed to be at such low levels that they likely would not affect the recovery boiler operation. Three different steam data levels, 470°C and 70 bar, 490°C and 81 bar, 510°C and 100 bar respectively, were evaluated in order to highlight the estimated magnitude of the increased income from sold electricity when steam data was raised.

Case 2 represented an investigation of the softwood mill while **Case 3** corresponded to an evaluation of the hardwood mill. Case 2 and Case 3 were then divided into index a, b and c according to the description that follows below.

Index a represented the possibility of lowering Cl and K levels by simply purging ESP dust. The purging alternative is a very simple and effective way to lower the levels of Cl and K and there is no investment cost. The major economical drawback with purging ESP dust is that it mainly consists of useful process chemicals that have to be replaced with make-up chemicals. There is also a possibility that it in the future will be prohibited to purge ESP dust to the surrounding area.

Index b evaluated the option of implementing a leaching unit to lower the Cl and K levels. The leaching technology is reasonably simple and proven, but is also considered to be a comparatively unselective method. Since the Metso AshLeach system has been installed at a number of pulp mills and the results are fairly well documented the leaching model was built as the Metso AshLeach process.

Index c investigated an evaporation/crystallization process which in this study represented a more selective process than the leaching alternative. Evaporation/crystallization is on the contrary a somewhat more complicated process that also consumes more energy compared to leaching. The model for the evaporation/crystallization unit was chosen to be Andritz ARC process (Ash ReCrystallization process) that has been installed at the Soporcel mill in Portugal.

9.1.1 Metso AshLeach model

From data published concerning the AshLeach unit, and particularly the first unit at Aracruz, the operating data and component splitting factors in the model were preset according to Table 12. Unfortunately no information about how carbonate is split in the AshLeach could be acquired. Therefore CO_3 was treated as a dissolved solid and consequently CO_3 simply followed the water split, with the result that about 34 % of the incoming CO_3 was recirculated back to the mixtank. The schematic flowsheet of the AshLeach was shown earlier in the Thesis in Figure 14.

Table 12. Operating data and component splitting factors for the AshLeach model. [31, 33, 34, 45]

Temperature in leaching tank ($^{\circ}\text{C}$)	~90
Ash-to-water ratio	1.25:1
Cl removal (%)	90
K removal (%)	82
Na recovery (%)	63
S recovery (%)	68
Dry solids content after centrifuge (%)	85
Electricity consumption (kWh/ton ESP dust)	9

In Figure 28 the WinGEMS model flowsheet for the AshLeach unit is shown. For the softwood mill that possesses a S surplus it was necessary to implement an ESP dust purge stream (stream 12) in order to adjust sulphidity when necessary. In reality it would likely not be necessary to purge ESP dust but instead change the operating parameters of the AshLeach or take some other course of action. However, it was in this study important to keep all parameters constant to be able to perform a good comparison. The incoming water, that had an initial temperature of 60°C , was taken from the pulp dryer. When the incoming water was mixed with the ESP dust, which in the model has a rather high temperature, the resulting temperature in the leaching tank was about 90°C . In reality the ESP dust probably would have a much lower temperature and consequently it should be necessary to increase the water temperature by 30°C . However, the combination of a comparatively small water flow and the rather modest temperature increase was in this study calculated to give rise to a neglectable heat energy loss.

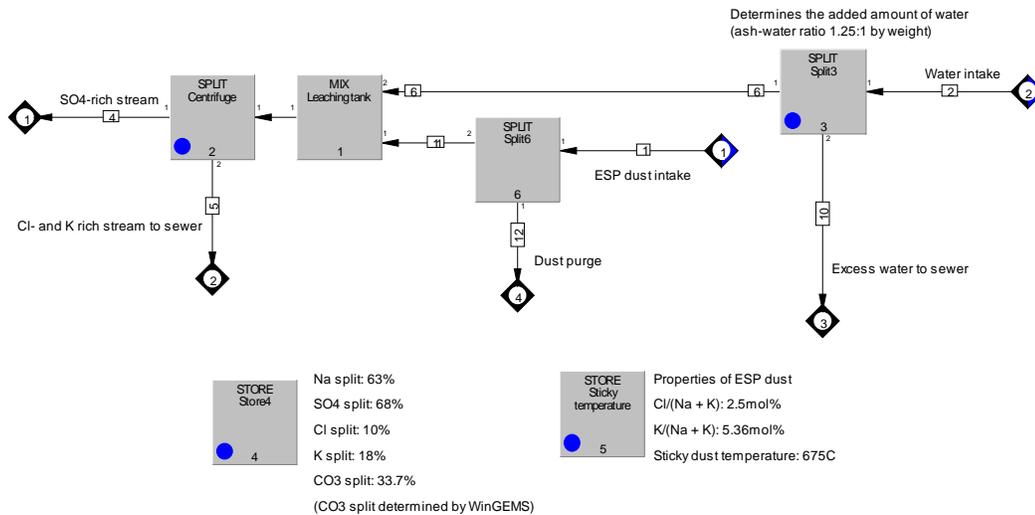


Figure 28. WinGEMS flowsheet for the Metso AshLeach unit which was implemented in Cases with index b.

Metso Power estimated that the investment cost for a Metso AshLeach process with a capacity of 80 ton ESP dust/d would amount to about 20 MSEK. [45]

9.1.2 Andritz ARC model

Through contact with Andritz and published material concerning the ARC process the evaporation/crystallization unit was built in WinGEMS. In Table 13 operating parameters and component split factors for the evaporation/crystallization unit are presented. The unit was built with a 2 effect evaporator system and it was assumed that 0.5 kg LP steam/kg evaporated water needed to be fed to the evaporator/crystallizer process. The LP steam would otherwise have been utilised in the condensing turbine to produce electricity, and therefore a minor loss in electricity production occurred when the evaporator/crystallizer process was implemented.

Table 13. Operating data and component splitting factors for the Andritz ARC model. [29, 37, 38]

Ash-to-water ratio in dissolving tank	1:2.5
Evaporated amount of water (kg water/kg dissolved ESP dust)	2
Cl removal (%)	85
K removal (%)	85
Na recovery (%)	77.5
S recovery (%)	86
CO ₃ recovery (%)	56
Dry solids content after centrifuge (%)	85
Electricity consumption (kWh/ton ESP dust)	29

In Figure 29 the WinGEMS model flowsheet for the ARC unit is shown. For the softwood mill that possesses a S surplus it was necessary to implement a possible ESP dust purge stream (stream 14) in order to adjust sulphidity when necessary. In reality it would likely not be necessary to purge any ESP dust but instead change the parameters of the ARC process or take some other course of action. However, it was in this study important to keep all parameters constant to be able to perform a good comparison.

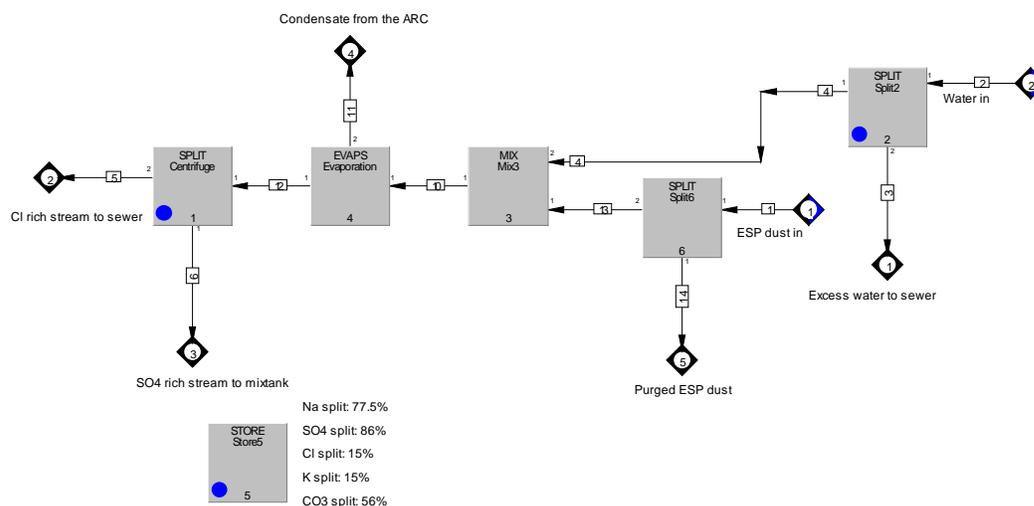


Figure 29. WinGEMS flowsheet for the Andritz ARC unit which was implemented in Cases with index c.

The investment cost for an Andritz ARC system with a capacity of 80 ton ESP dust/d was by Andritz estimated to be approximately 21 MSEK. [38]

9.2 Case 1. Low concentrations of Cl and K and three different levels of steam data.

In Case 1 the concentrations of Cl and K were assumed to be at such low levels that they most likely would not cause any problems in the recovery boiler despite the fact that steam temperature and pressure were increased. The steam data levels were chosen to represent an estimate of traditional, modern and future levels. Traditional steam data in Swedish recovery boilers is about 470°C and 70 bar, the reference mill is operating with modern steam data, 490°C and 81 bar, and finally the future energy efficient pulp mill was in this study exemplified by 510°C and 100 bar.

The main purpose of Case 1 was to highlight the magnitude of the increased income from sold electricity when steam data in the recovery boiler is raised. The figures presented are taken from simulations of the softwood market pulp mill.

The specific energy production and consumption for the different steam data levels are presented in Table 14. The process steam consumption (digester, bleaching, evaporation etc.) was kept at the same level as in the reference mill, 10.6 GJ/ADt.

Table 14. Specific energy production and consumption at three levels of steam data.

Specific energy production (GJ/ADt)			
Steam data	(470°C, 70 bar)	(490°C, 81 bar)	(510°C, 100 bar)
Recovery boiler	17.95	17.96	17.96
Secondary heat	0.60	0.59	0.59
Total production	18.55	18.55	18.55

Specific energy consumption (GJ/ADt)			
Steam data	(470°C, 70 bar)	(490°C, 81 bar)	(510°C, 100 bar)
Back-pressure turbine	2.65	2.89	3.13
Condensing turbine	5.33	5.09	4.85
Process consumption	10.57	10.57	10.57
Total consumption	18.55	18.55	18.55

The specific power production, consumption and amount of sold electricity for the different steam data levels are presented in Table 15. The process power demand was kept at 716 kWh/ADt, according to the reference mill.

Table 15. Specific production, consumption and sold amount of power at three different steam data levels.

Specific power production, consumption and sold amount (kWh/ADt)			
Steam data	(470°C, 70 bar)	(490°C, 81 bar)	(510°C, 100 bar)
Back-pressure turbine	719	774	842
Condensing turbine	525	504	492
Total power production	1244	1278	1334
Process power demand	716	716	716
Sold electricity	528	562	618

The calculated income for sold electricity is presented in Table 16. The economic outcome of the different steam data levels are presented relative to the traditional level (470°C, 70 bars). It was assumed that the mill has 355 operating days per year and an availability of 92 % which resulted in a yearly production of 653 200 ADt/year. It can from Table 16 be read that the increase from traditional to high steam data results in about 17 % increase in sold electricity while modern to future levels amounts to a little more than 10 %. The increase in steam pressure requires extra power to the feedwater pumps and the extra power consumption was within the FRAM programme estimated to reduce the incremental income with approximately 1 % unit. [2]

Table 16. Incremental income (MSEK/year) from sold electricity and green certificates for three different steam data levels.

Steam data	470°C, 70 bar	490°C, 81 bar	510°C, 100 bar
Electricity (280 SEK/MWh)	97	103	113
Green certificates (200 SEK/MWh)	68	73	81
Total incremental income (MSEK/year)	-	11	29
Increase from base case (%)	-	6.5	17.2

The electricity price has naturally a great impact on the annual income from net electricity sold. In Figure 30 a comparison between the income from sold electricity at three different levels of the electricity price, 350, 480 and 600 SEK/MWh, is shown. It is obvious that the electricity price variations actually have a greater impact on the magnitude of net electricity sold than the investigated changes in steam data.

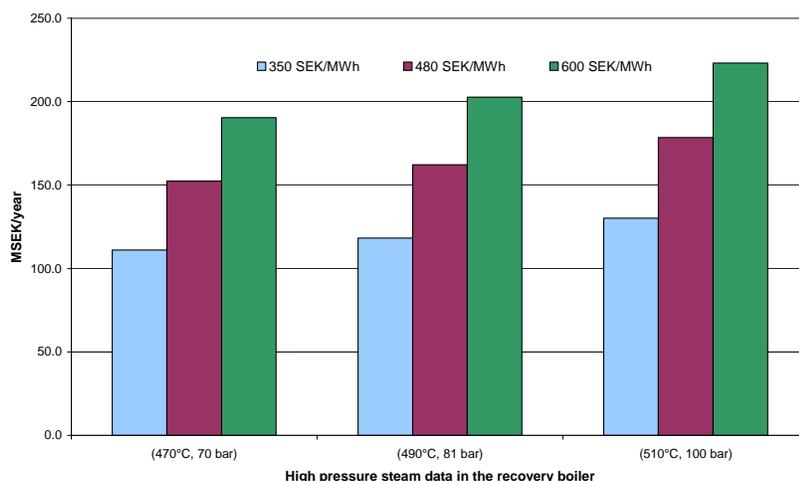


Figure 30. Income from sold electricity for the softwood reference market pulp mill at three different electricity prices.

9.3 Case 2 - Softwood mill

9.3.1 Case 2a – Purge

The amounts of ESP dust that needed to be purged and the quantity of provided make-up chemicals for each Cl level for the softwood mill Case 2a – Purge, are presented in Table 17.

The purged amounts of ESP dust are rather substantial and on a yearly basis it would for the highest Cl concentrations likely become untenable. The amount of provided make-up NaOH increases from 3 to 7 kg/ADt, while the corresponding Na₂SO₄ addition ranges from 0 to about 30 kg/ADt.

Table 17. Amounts of purged ESP dust and provided make-up chemicals for the softwood mill Case 2a - Purge.

Cl-concentration in virgin black liquor (wt % on ds)	Purged ESP dust		Amount of provided make-up chemicals	
	Ton/d	kg/ADt	NaOH (kg/ADt)	Na ₂ SO ₄ (kg/ADt)
0.3 (Base case)	20.2	10.1	3.0	-
0.44	34.7	17.3	4.1	3.8
0.55	47.1	23.5	4.6	7.2
0.72	65.4	32.7	5.7	18.2
0.96	94.1	47.0	7.2	29.8

9.3.2 Case 2b – Leaching

In this case ESP dust needed to be purged, in addition to the leaching process, for the two lowest Cl levels. The purged amounts were though minimized by optimization in WinGEMS. In Table 18 the amounts of treated ESP dust, provided make-up chemicals and purged ESP dust for Case 2b – Leaching, are listed.

The amount of treated ESP dust determined the capacity of the AshLeach process. The two largest capacity demands in the study represented a reasonable size although Metso has delivered AshLeach systems with more than twice as large capacity. On the other hand the two smallest capacities are comparatively small and would probably not constitute a realistic investment for a mill with the model mills magnitude of pulp production. It is noteworthy that no Na₂SO₄ needed to be provided for the three lowest Cl concentrations.

Table 18. Amounts of treated ESP dust, provided make-up chemicals and purged ESP dust for the softwood mill Case 2b - Leaching.

Cl-concentration in virgin black liquor (wt % on ds)	Treated ESP dust		Amount of provided make-up chemicals		Purged ESP dust
	Ton/d	kg/ADt	NaOH (kg/ADt)	Na ₂ SO ₄ (kg/ADt)	Ton/d
0.3 (Base case)	-	-	3.0	-	20.2
0.44	26.5	13.3	3.4	-	10.8
0.55	46.4	23.2	3.9	-	5.8
0.72	72.8	36.4	4.4	1.2	-
0.96	104.4	52.2	5.2	5.7	-

9.3.3 Case 2c – Evaporation/crystallization

For Case 2c ESP dust needed to be purged, in addition to the evaporation/crystallization process, for all Cl levels but the purged amounts were minimized by optimization in WinGEMS. In Table 19 the amounts of treated ESP dust, provided make-up chemicals and purged ESP dust for Case 2c – Evaporation/crystallization, are presented.

The amount of treated ESP dust determined the capacity of the ARC process. The ARC system installed at Soporcel has a capacity of 167 ton/d which means that all needed capacities in this study were significantly smaller. Especially the two smallest capacities would probably not constitute a realistic investment for a mill with the model mills magnitude of pulp production. It is essential to note that no Na₂SO₄ needed to be provided even for the highest Cl concentrations.

Table 19. Amounts of treated ESP dust, provided make-up chemicals and amounts of purged ESP dust for the hardwood mill Case 2c – Evaporation/crystallization.

Cl-concentration in virgin black liquor (wt% on ds)	Treated ESP dust		Amount of added make-up chemicals		Purged ESP dust
	Ton/d	kg/ADt	NaOH (kg/ADt)	Na ₂ SO ₄ (kg/ADt)	Ton/d
0.3 (Base case)	-	-	3.0	-	20.2
0.44	18.2	9.1	3.7	-	18.3
0.55	37.9	19.0	4.0	-	14.4
0.72	64.7	32.3	4.6	-	10.5
0.96	103.7	51.9	5.7	-	6.2

9.3.4 Comparison Case 2a-c

In Figure 31 and Figure 32 a comparison between the softwood mill Case 2a-c for the amounts of provided make-up chemicals, NaOH and Na₂SO₄, are shown.

From Figure 31 it can be stated that the purging alternative gave rise to a significantly higher amount of provided NaOH compared to leaching and evaporation/crystallization, which showed almost similar figures. Though, evaporation/crystallization required a slightly larger amount of provided NaOH compared to leaching.

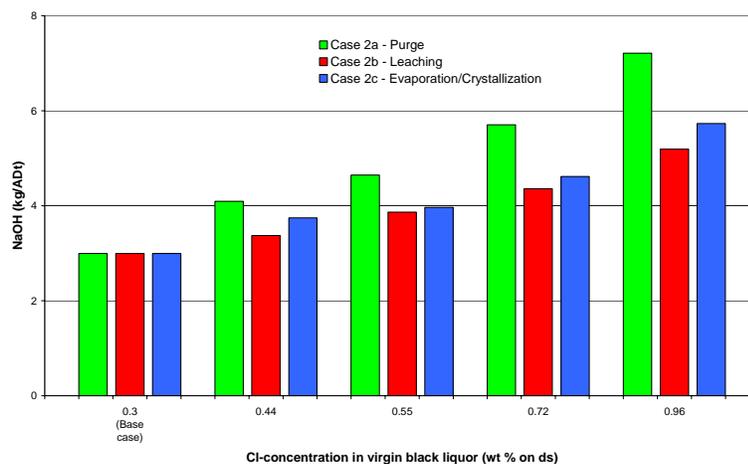


Figure 31. Amounts of provided make-up NaOH for the softwood Case 2a-c.

In Figure 32 it is obvious that the purging alternative required a substantial addition of Na₂SO₄ make-up. The leaching process resulted in a fairly low addition of Na₂SO₄ for the two highest Cl levels, while the evaporation/crystallization system gave the result that no Na₂SO₄ had to be provided.

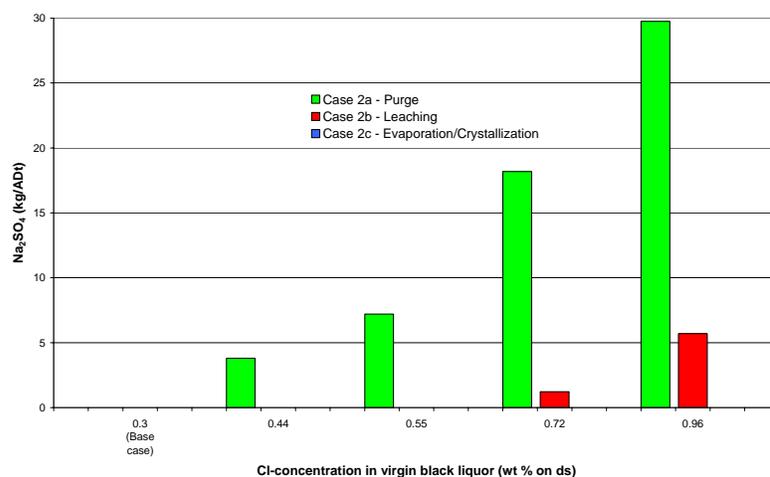


Figure 32. Amounts of provided make-up Na₂SO₄ for the softwood Case 2a-c.

9.4 Case 3 – Hardwood mill

9.4.1 Case 3a – Purge

The amounts of ESP dust that needed to be purged for each Cl level for the hardwood mill Case 3a – Purge, are presented in Table 20.

The purged amounts of ESP dust correspond to very high figures that for the highest Cl concentrations presumably would become untenable. For the purging alternative the provided amount of NaOH make-up rises 10 times from the base case to the highest Cl level, while the corresponding figure for Na₂SO₄ was an approximate 4 time increase. It is notable that the amount of provided NaOH make-up for the hardwood base case is significantly low when compared to the softwood base case. This is due to the addition of Na₂SO₄ make-up already for the hardwood base case.

Table 20. Amounts of purged ESP dust and provided make-up chemicals for the hardwood mill Case 3a - Purge.

Cl-concentration in virgin black liquor (wt % on ds)	Purged ESP dust		Amount of added make-up chemicals	
	Ton/d	kg/ADt	NaOH (kg/ADt)	Na ₂ SO ₄ (kg/ADt)
0.30 (Base case)	26.1	13.0	0.5	6.2
0.69	69.1	34.6	3.3	18.3
0.95	93.8	46.9	5.0	24.8

9.4.2 Case 3b – Leaching

The amounts of ESP dust that needed to be treated for each Cl level and provided make-up chemicals for the hardwood mill Case 3b - Leaching are presented in Table 21.

The amount of treated ESP dust determined the capacity of the AshLeach process. The two largest capacity demands in the study represented a reasonable size although Metso has delivered AshLeach systems with more than twice as large capacity. The smallest

capacity would most likely not represent a realistic investment for a mill with the model mills magnitude of pulp production. The amounts of provided make-up chemicals are found at fairly low levels and it is noteworthy that no ESP dust needed to be purged in addition to leaching in the hardwood case.

Table 21. Amounts of treated ESP dust and provided make-up chemicals for the hardwood mill Case 3b - Leaching.

Cl-concentration in virgin black liquor (wt % on ds)	Treated ESP dust		Amount of provided make-up chemicals	
	Ton/d	kg/ADt	NaOH (kg/ADt)	Na ₂ SO ₄ (kg/ADt)
0.30	30.0	15.0	0.2	2.2
0.72	76.9	38.4	1.7	6.1
0.96	104.4	52.2	2.7	8.4

9.4.3 Case 3c – Evaporation/crystallization

The amounts of ESP dust that needed to be treated for each Cl level and provided make-up chemicals for the hardwood mill Case 3c – Evaporation/crystallization are presented in Table 22.

The amount of treated ESP dust determined the capacity of the ARC process. The ARC system installed at Soporcel has a capacity of 167 ton/d which means that all capacities in this study were significantly smaller. Particularly the smallest capacity would most likely not represent a realistic investment for a mill with the model mills magnitude of pulp production. The amounts of provided make-up chemicals are found at fairly low levels and no ESP dust needed to be purged in this case.

Table 22. Amounts of treated ESP dust and provided make-up chemicals for the hardwood mill Case 3c – Evaporation/crystallization.

Cl-concentration in virgin black liquor (wt % on ds)	Treated ESP dust		Amount of added make-up chemicals	
	Ton/d	kg/ADt	NaOH (kg/ADt)	Na ₂ SO ₄ (kg/ADt)
0.30	32.8	16.4	0.2	0.8
0.72	81.5	40.8	1.8	2.5
0.96	110.5	55.3	2.6	3.9

9.4.4 Comparison Case 3a-c

In Figure 33 and Figure 34 a comparison between Case 3a-c for the amounts of provided make-up chemicals, NaOH and Na₂SO₄, are shown.

From Figure 33 it is assured that the purging alternative meant that the amount of provided NaOH was evidently higher compared to leaching and evaporation/crystallization, which showed almost identical figures. The addition of NaOH make-up proved to be clearly lower for the hardwood mill compared to the softwood mill, due to the rather extensive addition of Na₂SO₄ to the hardwood mill. An addition of Na₂SO₄ implies that 2 Na is provided to the mill for each added S and consequently the need for NaOH make-up was reduced for the hardwood mill.

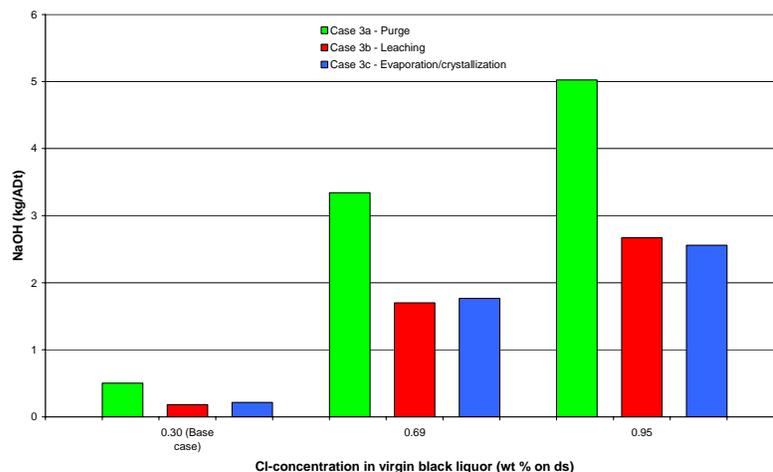


Figure 33. Amounts of provided make-up NaOH for the hardwood Case 3a-c.

In Figure 34 it is apparent that the purging case involved a considerable addition of Na_2SO_4 make-up. The leaching alternative gave rise to a moderately low amount of added Na_2SO_4 , while the evaporation/crystallization system resulted in a considerably lower provided amount of Na_2SO_4 , compared to leaching. However, it is important to point out that Na_2SO_4 make-up needed to be provided in all cases for the hardwood mill, which was not the case for the case for the softwood mill.

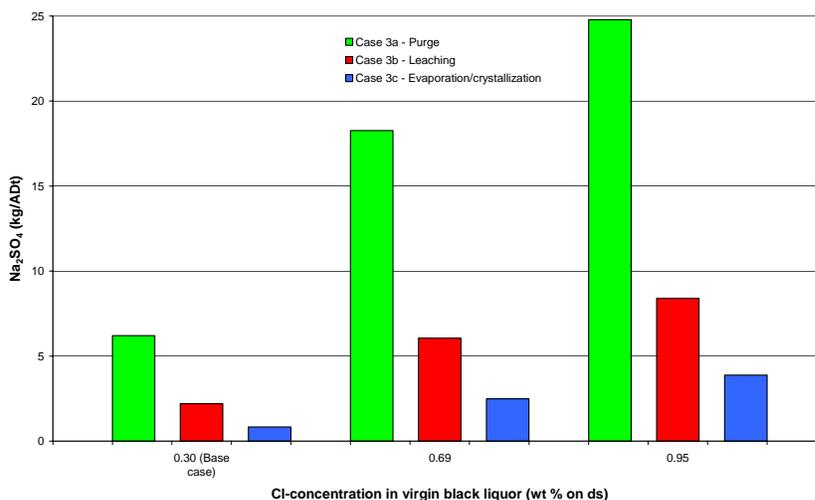


Figure 34. Amounts of provided make-up Na_2SO_4 for the hardwood Case 3a-c.

10 Cost benefit analysis

Within the FRAM programme an extensive system analysis for the reference mills was performed. The system analysis and the resulting total operating costs for the reference mills from the FRAM programme has for that reason served as a solid starting point and overall guideline for this study.

The total operating costs for the softwood reference mill was within FRAM estimated to 1407 SEK/ADt and the corresponding figures for the hardwood reference mill was 1279 SEK/ADt. Even though small modifications of the model mills were made in this study, compared to the original versions, the proposed operating costs above have been used as reference cases. In the comparative cost benefit analysis the net total benefit (= *operating benefit - operating costs - capital costs*) is used to express which alternative that proved to be the best choice from an economic point of view.

In the cost benefit analysis the following general assumptions were made:

- The different cases would not affect the load on either the external treatment or the evaporation plant.
- The only chemical charge that would be affected, and thereby changed, by the different cases was the addition of the make-up chemicals NaOH and Na₂SO₄.
- When steam data was increased from 490°C and 81 bar to 510°C and 100 bar the extra electricity consumption for the feedwater pumps would be 10 % of the incremental amount of sold electricity. The assumption was a rough estimate based on calculations performed within the FRAM programme. [2]
- The capital costs were calculated with the annuity method and the annuity factor used in this study was 0.1.
- Since the capacity of the K/Cl kidney varies with the Cl levels the investment costs had to be estimated from the given investment cost. The investment costs at different capacities were calculated according to equation 5.

$$\text{New investment cost} = \left(\frac{\text{New capacity}}{\text{Known capacity}} \right)^{0.6} \cdot \text{Known price} \quad (5)$$

- The price for sold electricity was set to be 480 SEK/MWh of which the green certificates represented 200 SEK/MWh. The purchased electricity price was kept at 280 SEK/MWh.
- The price for NaOH was assumed to be 2500 SEK/ton 100 % and the corresponding price for Na₂SO₄ was set to 2000 SEK/ton.
- Maintenance costs for the K/Cl kidney were estimated to an amount of 2 % of the total investment cost (TIC) annually.

10.1 Case 2 - Softwood mill

10.1.1 Case 2a – Purge

The purging alternative is a very simple and effective way to lower the levels of Cl and K. There is no investment cost which means that the only economical drawback is the expenses for make-up chemicals. The amounts of ESP dust that had to be purged when the Cl level was high are though significant and consequently also the quantities of provided make-up chemicals became considerable. In Table 23 the cost benefit analysis outcome for the softwood mill Case 2a – Purge, is presented. The incremental costs for make-up chemicals amount to about 70 SEK/ADt for the highest Cl level, and the costs for Na₂SO₄ make-up constitute the absolutely dominating part. It is also notable that the net total benefit at high steam data becomes negative at a Cl concentration between 0.55 and 0.72 wt % in virgin black liquor.

Table 23. Cost benefit analysis for the softwood mill Case 2a - Purge.

Cl-concentration in virgin black liquor (wt % on ds)		Normal steam data (490°C, 81 bar)					High steam data (510°C, 100 bar)				
		Base case	0.44	0.55	0.72	0.96	Base case	0.44	0.55	0.72	0.96
INVESTMENT (Total installed cost, TIC)											
Chloride kidney	MSEK	-	-	-	-	-	-	-	-	-	-
TOTAL INVESTMENT	MSEK	0	0	0	0	0	0	0	0	0	0
OPERATING COSTS											
Electricity K/Cl kidney	SEK/ADt	-	-	-	-	-	-	-	-	-	-
Extra electricity provided to feedwater pumps when steam data was increased.	SEK/ADt	-	-	-	-	-	1.58	1.58	1.58	1.58	1.58
NaOH, purchased	SEK/ADt	7.5	10.2	11.6	14.3	18.0	7.5	10.2	11.6	14.3	18.0
Na ₂ SO ₄ , purchased	SEK/ADt	0.0	7.6	14.4	36.4	59.5	0.0	7.6	14.4	36.4	59.5
Maintenance, etc.	SEK/ADt	-	-	-	-	-	-	-	-	-	-
Sold energy	SEK/ADt	-157.4	-157.4	-157.4	-157.4	-157.4	-173.3	-173.3	-173.3	-173.3	-173.3
Sold green certificate	SEK/ADt	-112.4	-112.4	-112.4	-112.4	-112.4	-123.8	-123.8	-123.8	-123.8	-123.8
All other OM costs in the mill	SEK/ADt	1530.9	1530.9	1530.9	1530.9	1530.9	1530.9	1530.9	1530.9	1530.9	1530.9
TOTAL OPERATING COSTS	SEK/ADt	1407	1417	1426	1450	1477	1381	1392	1400	1425	1452
NET TOTAL BENEFIT (Compared to base case)											
Capital costs	MSEK/year	-	-	-	-	-	-	-	-	-	-
Operating Costs	MSEK/year	-	-7	-12	-28	-46	17	10	5	-11	-29
Sum	MSEK/year	-	-7	-12	-28	-46	17	10	5	-11	-29
Sum	SEK/ADt	-	-10	-19	-43	-70	26	15	7	-18	-45

10.1.2 Case 2b – Leaching

The leaching alternative involved an initial investment cost which affected the cost benefit analysis. Also the total operating costs increased, compared to the base case, due to the electricity consumption and the additional maintenance costs related to the leaching unit. The heat energy consumption consisted of the need for hot water, about 90°C, but the amounts of heat energy was in this study calculated to account for such small quantities that they were neglected. In Table 24 the cost benefit analysis outcome for the softwood mill Case 2b – Leaching, is presented. The incremental costs for make-up chemicals by far exceed the additional operating costs that originate from the installation of the leaching unit. The net total benefit for high steam data shows positive figures in the evaluated Cl concentration range. It is important to point out that the two smallest capacities are comparatively small and therefore the estimate of the investment cost becomes very uncertain.

Table 24. Cost benefit analysis for the softwood mill Case 2b - Leaching.

		Normal steam data (490°C, 81 bar)					High steam data (510°C, 100 bar)				
Cl-concentration in virgin black liquor (wt % on ds)		Base case	0.44	0.55	0.72	0.96	Base case	0.44	0.55	0.72	0.96
INVESTMENT (Total installed cost, TIC)											
Chloride kidney	MSEK	-	10.4	14.3	18.9	23.4	-	10.4	14.3	18.9	23.4
TOTAL INVESTMENT	MSEK	0	10.4	14.3	18.9	23.4	0	10.4	14.3	18.9	23.4
OPERATING COSTS											
Electricity K/Cl kidney	SEK/ADt	-	0.03	0.06	0.09	0.13	-	0.03	0.06	0.09	0.13
Extra electricity provided to feedwater pumps when steam data was increased.	SEK/ADt	-	-	-	-	-	1.58	1.58	1.58	1.58	1.58
NaOH, purchased	SEK/ADt	7.5	8.4	9.7	10.9	13.0	7.5	8.4	9.7	10.9	13.0
Na ₂ SO ₄ , purchased	SEK/ADt	-	-	-	2.4	11.4	-	-	-	2.4	11.4
Maintenance, etc.	SEK/ADt	-	0.3	0.4	0.6	0.7	-	0.3	0.4	0.6	0.7
Sold energy	SEK/ADt	-157.4	-157.4	-157.4	-157.4	-157.4	-173.3	-173.3	-173.3	-173.3	-173.3
Sold green certificate	SEK/ADt	-112.4	-112.4	-112.4	-112.4	-112.4	-123.8	-123.8	-123.8	-123.8	-123.8
All other OM costs in the mill	SEK/ADt	1530.9	1530.9	1530.9	1530.9	1530.9	1530.9	1530.9	1530.9	1530.9	1530.9
TOTAL OPERATING COSTS	SEK/ADt	1407	1408	1410	1414	1425	1381	1383	1384	1388	1399
NET TOTAL BENEFIT (Compared to base case)											
Capital costs	MSEK/year	-	-1	-1	-2	-2	-	-1	-1	-2	-2
Operating Costs	MSEK/year	-	-1	-2	-4	-12	17	16	15	12	5
Sum	MSEK/year	-	-2	-3	-6	-14	17	15	14	11	3
Sum	SEK/ADt	-	-3	-5	-9	-21	26	23	21	16	4

10.1.3 Case 2c – Evaporation/crystallization

The evaporation/crystallization process included an investment cost which affected the cost benefit analysis. In addition the evaporation/crystallization unit consumed low pressure (LP) steam that otherwise would have been utilised to produce electricity in the

condensing turbine in the reference mill. Since the energy utilisation in the model mills is highly effective the electricity production loss for the model mills became more evident than what probably would be the case in a “real” mill. “Real” mills in most cases possess some low temperature energy streams that are not utilized and by that means such energy may in an economically advantageous way be used for the evaporation/crystallization unit. As was pointed out earlier in the Thesis Andritz ARC is operated at low temperatures which mean that secondary heat streams can be used as energy source. However, the loss in sold electricity at the most amounted to about 2 % which makes it a comparatively small factor in the cost benefit analysis. In Table 25 the cost benefit analysis outcome for the softwood mill Case 2c – Evaporation/Crystallization, is presented. As for the leaching unit the additional operating costs for the evaporation/crystallization process are comparatively small in the overall cost benefit analysis, and the net total benefit shows positive figures in the evaluated Cl concentration range. It is also once again important to point out that no Na₂SO₄ make-up needed to be provided. Also for the evaporation/crystallization process the two smallest capacities are comparatively small why the estimate of the investment cost is highly uncertain.

Table 25. Cost benefit analysis for the softwood mill Case 2c – Evaporation/Crystallization.

Cl-concentration in virgin black liquor (wt % on ds)		Normal steam data (490°C, 81 bar)					High steam data (510°C, 100 bar)				
		Base case	0.44	0.55	0.72	0.96	Base case	0.44	0.55	0.72	0.96
INVESTMENT (Total installed cost, TIC)											
Chloride kidney	MSEK	-	8.6	13.4	18.4	24.5	-	8.6	13.4	18.4	24.5
TOTAL INVESTMENT	MSEK	0	8.6	13.4	18.4	24.5	0	8.6	13.4	18.4	24.5
OPERATING COSTS											
Electricity K/Cl kidney	SEK/ADt	-	0.07	0.15	0.26	0.42	-	0.07	0.15	0.26	0.42
Extra electricity provided to feedwater pumps when steam data was increased.	SEK/ADt	-	-	-	-	-	1.58	1.58	1.58	1.58	1.58
NaOH, purchased	SEK/ADt	7.5	9.4	9.9	11.5	14.3	7.5	9.4	9.9	11.5	14.3
Na ₂ SO ₄ , purchased	SEK/ADt	-	-	-	-	-	-	-	-	-	-
Maintenance, etc.	SEK/ADt	-	0.3	0.4	0.6	0.8	-	0.3	0.4	0.6	0.8
Sold energy	SEK/ADt	-157.4	-156.9	-156.4	-155.0	-153.7	-173.0	-172.5	-171.2	-169.8	-169.8
Sold green certificate	SEK/ADt	-112.4	-112.1	-111.7	-110.7	-109.8	-123.6	-123.2	-122.3	-121.3	-121.3
All other OM costs in the mill	SEK/ADt	1530.9	1530.9	1530.9	1530.9	1530.9	1530.9	1530.9	1530.9	1530.9	1530.9
TOTAL OPERATING COSTS	SEK/ADt	1407	1410	1412	1416	1421	1381	1384	1386	1390	1395
NET TOTAL BENEFIT (Compared to base case)											
Capital costs	MSEK/year	-	-1	-1	-2	-2	-	-1	-1	-2	-2
Operating Costs	MSEK/year	-	-2	-3	-6	-9	17	15	14	11	8
Sum	MSEK/year	-	-3	-4	-8	-12	17	14	13	9	5
Sum	SEK/ADt	-	-4	-7	-12	-18	26	22	19	14	8

10.1.4 Comparison Case 2a-c

In Figure 35 and Figure 36 a comparison of the costs for provided make-up chemicals for the softwood mill Case 2a-c are shown. From Figure 35 it is clear that the expenses for make-up chemicals became considerable for the purging alternative already at low Cl concentrations. For the highest Cl level the expenses amounted to about 55 MSEK/year for the softwood mill, which is about 3 times more than the leaching process and approximately 5 times more than the evaporation/crystallization system. At high Cl levels the evaporation/crystallization process was slightly more advantageous compared to leaching due to the increasing costs for Na₂SO₄ for the leaching process.

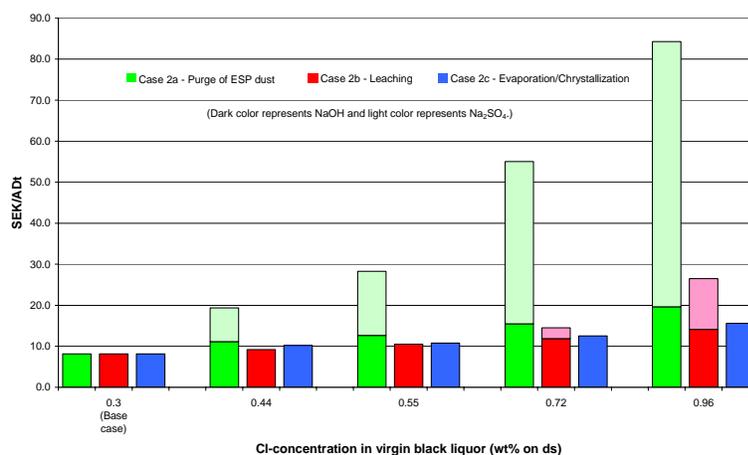


Figure 35. Costs for provided amounts of make-up chemicals for the softwood mill Case 2a-c(SEK/ADT).

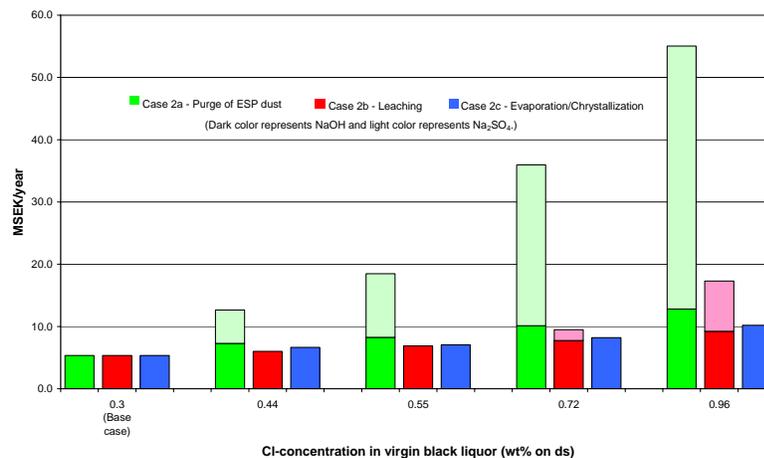


Figure 36. Costs for provided amounts of make-up chemicals for the softwood mill Case 2a-c (MSEK/year).

In Figure 37 and Figure 38 the comparative result of the net total benefit for the softwood mill Case 2a-c are shown. From Figure 37 and Figure 38 one conclusion was that leaching and evaporation/crystallization already at low Cl concentrations showed a great advantage compared to the purging alternative. Nevertheless, the leaching and evaporation/crystallization capacities becomes very small at low Cl levels why it is

difficult to give a realistic estimate of the investment cost and the actual probability of installing such a small unit. Leaching and evaporation/crystallization proved to have almost identical net total benefit within the evaluated Cl concentration range. However, evaporation/crystallization had a minor benefit at the highest Cl level, and the advantage would probably progress at even higher Cl levels due to the increasing costs for Na_2SO_4 for the leaching process. It is also worth mentioning that the purging alternative at high steam data showed a positive net total benefit until the Cl concentration in virgin black liquor reached 0.6 wt % on dry solids. Both leaching and evaporation/crystallization at high steam data on the other hand showed a clearly positive net total benefit within the evaluated Cl concentration range.

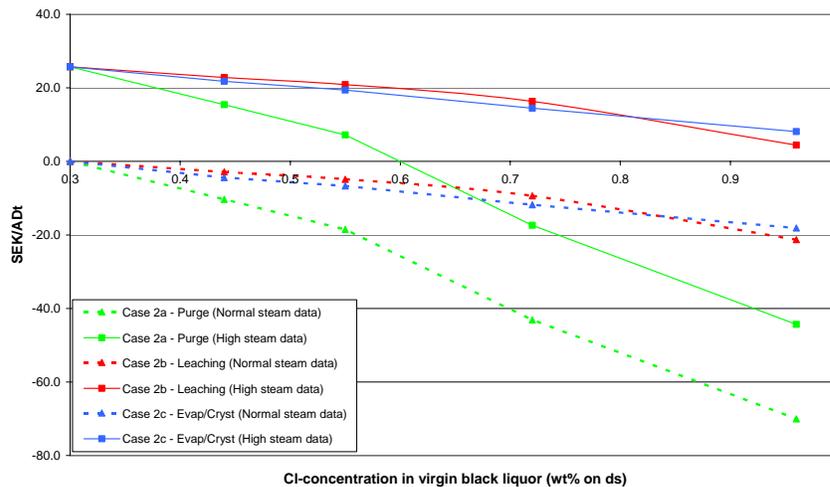


Figure 37. Net total benefit for the softwood mill Case 2a-c (SEK/ADt).

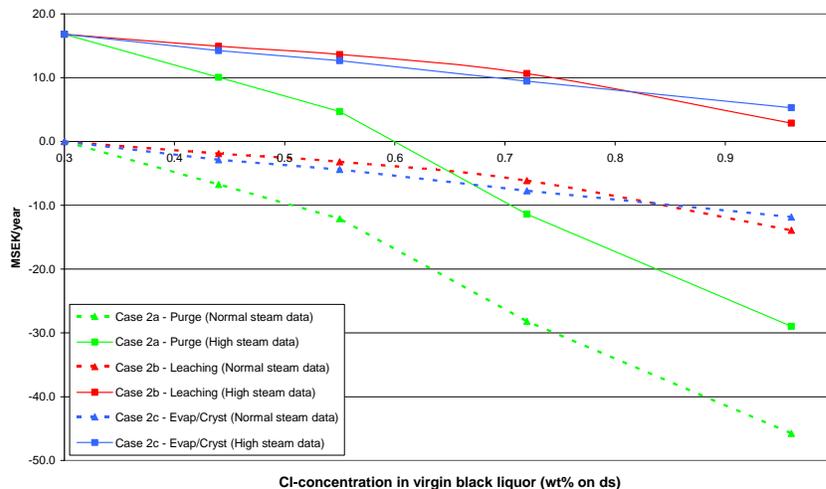


Figure 38. Net total benefit for the softwood mill Case 2a-c (MSEK/year).

The net total benefit to a great extent depended on the electricity price and therefore a sensitivity analysis was performed. In Figure 39, Figure 40 and Figure 41 the net total benefit for the softwood mill Case 2a-c (High steam data) at three different electricity prices are presented. The electricity prices included in the sensitivity analysis were 350, 480 and 630 SEK/MWh.

From Figure 39 it can be stated that the net total benefit was positive for the purging case, with high steam data, at all three electricity prices if the Cl concentration was below about 0.55 wt % on dry solids in virgin black liquor. An important aspect is that a high electricity price consequently gives a positive net total benefit at higher Cl levels.

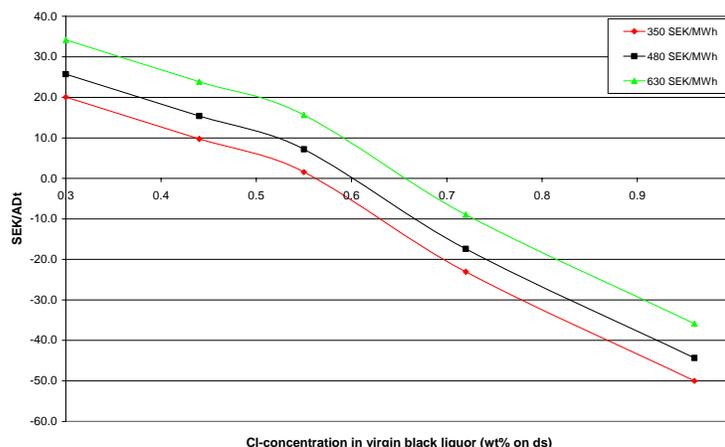


Figure 39. Net total benefit for the softwood mill Case 2a - Purge (High steam data) at three different electricity prices (SEK/ADt).

For the leaching process, at high steam data, it is in Figure 40 observed that the net total benefit was positive for all three electricity prices, if the Cl level was below about 0.9 wt % on dry solids in virgin black liquor.

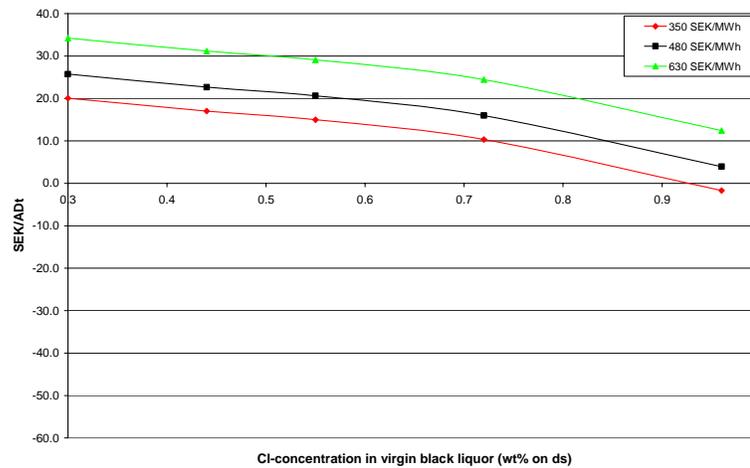


Figure 40. Net total benefit for the softwood mill Case 2b - Leaching (High steam data) at three different electricity prices (SEK/ADt).

As can be seen in Figure 41 the evaporation/crystallization system, at high steam data, showed a positive net total benefit for all three electricity prices within the entire Cl concentration range evaluated in this study.

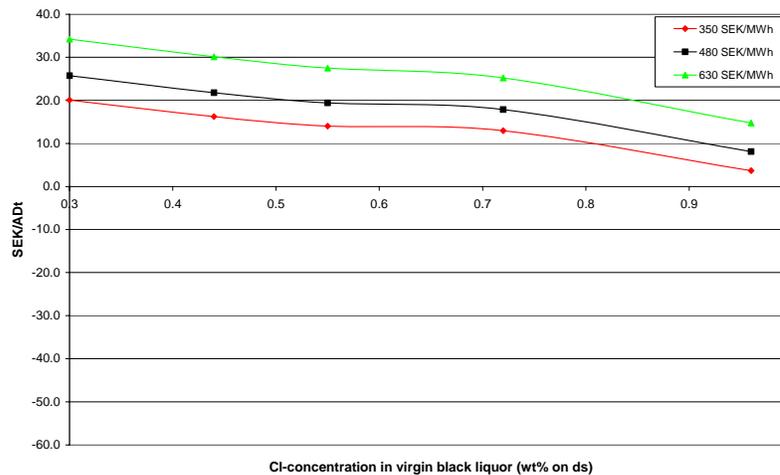


Figure 41. Net total benefit for the softwood mill Case 2c - Evaporation/Crystallization (High steam data) at three different electricity prices (SEK/ADt).

10.2 Case 3 - Hardwood mill

10.2.1 Case 3a – Purge

In Table 26 the cost benefit analysis outcome for the hardwood mill Case 3a – Purge, is presented. As for the softwood mill the purged amounts of ESP dust became huge at high Cl levels and consequently the costs for make-up chemicals rose to substantial figures. The incremental costs for make-up chemicals were 48 SEK/ADt for the highest Cl level of which the costs for Na₂SO₄ are dominating. Compared to the softwood mill the incremental costs for make-up chemicals are somewhat lower for the hardwood mill since Na₂SO₄ make-up is provided to the hardwood mill already in the base case.

Table 26. Cost benefit analysis for the hardwood mill Case 3a - Purge.

		Normal steam data (490°C, 81 bar)			High steam data (510°C, 100 bar)		
Cl-concentration in virgin black liquor (wt % on ds)		Base case	0.69	0.95	Base case	0.69	0.95
INVESTMENT (Total installed cost, TIC)							
Chloride kidney	MSEK	-	-	-	-	-	-
TOTAL INVESTMENT	MSEK	0	0	0	0	0	0
OPERATING COSTS							
Electricity K/Cl kidney	SEK/ADt	-	-	-	-	-	-
Extra electricity provided to feedwater pumps when steam data is increased.	SEK/ADt	-	-	-	1.34	1.34	1.34
NaOH, purchased	SEK/ADt	1.3	8.4	12.6	1.3	8.4	12.6
Na ₂ SO ₄ , purchased	SEK/ADt	12.4	36.5	49.6	12.4	36.5	49.6
Maintenance, etc.	SEK/ADt	-	-	-	-	-	-
Sold energy	SEK/ADt	-109.1	-109.1	-109.1	-122.6	-122.6	-122.6
Sold green certificate	SEK/ADt	-78.0	-78.0	-78.0	-87.5	-87.5	-87.5
All other OM costs in the mill	SEK/ADt	1362.3	1362.3	1362.3	1362.3	1362.3	1362.3
TOTAL OPERATING COSTS	SEK/ADt	1279	1310	1327	1257	1289	1306
NET TOTAL BENEFIT (Compared to base case)							
Capital costs	MSEK/year	-	-	-	-	-	-
Operating Costs	MSEK/year	-	-20	-32	14	-6	-18
Sum	MSEK/year	-	-20	-32	14	-6	-18
Sum	SEK/ADt	-	-31	-48	22	-10	-27

10.2.2 Case 3b – Leaching

In Table 27 the cost benefit analysis outcome for the hardwood mill Case 3b – Leaching, is presented. In Case 3b it is interesting that the net total benefit proves to be positive for the leaching unit already at really low Cl concentrations, due to the high costs for Na₂SO₄ make-up in the base case. However, the smallest capacity is very small which makes the estimated investment cost extremely uncertain. The net total benefit at high steam data is positive in the evaluated Cl concentration range.

Table 27. Cost benefit analysis for the hardwood mill Case 3b - Leaching.

		Normal steam data (490°C, 81 bar)				High steam data (510°C, 100 bar)			
		Base case	0.3	0.69	0.95	Base case	0.3	0.69	0.95
Cl-concentration in virgin black liquor (wt % on ds)									
INVESTMENT (Total installed cost, TIC)									
Chloride kidney	MSEK	-	11.1	19.5	23.4	-	11.1	19.5	23.4
TOTAL INVESTMENT	MSEK	0	11.1	19.5	23.4	0	11.1	19.5	23.4
OPERATING COSTS									
Electricity K/Cl kidney	SEK/ADt	-	0.04	0.10	0.13	-	0.04	0.10	0.13
Extra electricity provided to feedwater pumps when steam data was increased.	SEK/ADt	-	-	-	-	1.34	1.34	1.34	1.34
NaOH, purchased	SEK/ADt	1.3	0.5	4.3	6.7	1.3	0.5	4.3	6.7
Na ₂ SO ₄ , purchased	SEK/ADt	12.4	4.4	12.1	16.8	12.4	4.4	12.1	16.8
Maintenance, etc.	SEK/ADt	-	0.3	0.6	0.7	-	0.3	0.6	0.7
Sold energy	SEK/ADt	-109.1	-109.1	-109.1	-109.1	-122.6	-122.6	-122.6	-122.6
Sold green certificate	SEK/ADt	-78.0	-78.0	-78.0	-78.0	-87.5	-87.5	-87.5	-87.5
All other OM costs in the mill	SEK/ADt	1362.3	1362.3	1362.3	1362.3	1362.3	1362.3	1362.3	1362.3
TOTAL OPERATING COSTS	SEK/ADt	1279	1271	1282	1290	1257	1249	1261	1268
NET TOTAL BENEFIT (Compared to base case)									
Capital costs	MSEK/year	-	-1	-2	-2	-	-1	-2	-2
Operating Costs	MSEK/year	-	6	-2	-7	14	20	12	7
Sum	MSEK/year	-	4	-4	-9	14	19	10	5
Sum	SEK/ADt	-	7	-6	-14	22	28	15	7

10.2.3 Case 3c – Evaporation/crystallization

In Table 28 the cost benefit analysis outcome for the hardwood mill Case 3c – Evaporation/Crystallization is presented. The net total benefit is positive already for the lowest Cl levels, as for leaching, because of the high costs for Na₂SO₄ make-up in the base case. As for the leaching process the smallest capacity of the evaporation/crystallization process becomes comparatively small which makes the calculated investment cost particularly uncertain. At high steam data the net total benefit is positive in the evaluated Cl concentration range.

Table 28. Cost benefit analysis for the hardwood mill Case 3c – Evaporation/Crystallization.

		Normal steam data (490°C, 81 bar)				High steam data (510°C, 100 bar)			
Cl-concentration in virgin black liquor (wt % on ds)		Base case	0.3	0.69	0.95	Base case	0.3	0.69	0.95
INVESTMENT (Total installed cost, TIC)									
Chloride kidney	MSEK	-	12.3	21.2	25.5	-	12.3	21.2	25.5
TOTAL INVESTMENT	MSEK	0	12.3	21.2	25.5	0	12.3	21.2	25.5
OPERATING COSTS									
Electricity K/Cl kidney	SEK/ADt	-	0.13	0.33	0.45	-	0.13	0.33	0.45
Extra electricity provided to feedwater pumps when steam data was increased.	SEK/ADt	-	-	-	-	1.34	1.34	1.34	1.34
NaOH, purchased	SEK/ADt	1.3	0.5	4.4	6.4	1.3	0.5	4.4	6.4
Na ₂ SO ₄ , purchased	SEK/ADt	12.4	1.7	5.0	7.8	12.4	1.7	5.0	7.8
Maintenance, etc.	SEK/ADt	-	0.4	0.7	0.8	-	0.4	0.7	0.8
Sold energy	SEK/ADt	-109.1	-108.4	-107.8	-107.0	-122.6	-121.8	-121.1	-120.1
Sold green certificate	SEK/ADt	-78.0	-77.5	-77.0	-76.4	-87.5	-87.0	-86.5	-85.8
All other OM costs in the mill	SEK/ADt	1362.3	1362.3	1362.3	1362.3	1362.3	1362.3	1362.3	1362.3
TOTAL OPERATING COSTS	SEK/ADt	1279	1269	1278	1284	1257	1248	1257	1263
NET TOTAL BENEFIT (Compared to base case)									
Capital costs	MSEK/year	-	-1	-2	-3	-	-1	-2	-3
Operating Costs	MSEK/year	-	6	1	-4	14	20	15	10
Sum	MSEK/year	-	5	-1	-6	14	19	13	8
Sum	SEK/ADt	-	8	-2	-9	22	29	19	12

10.2.4 Comparison Case 3a-c

In Figure 42 and Figure 43 the costs for provided make-up chemicals for the hardwood mill Case 3a-c are shown. From Figure 42 it can be concluded that the expenses for make-up chemicals became substantial for the purging alternative at high Cl concentrations. For the highest Cl level the expenses amounted to about 45 MSEK/year which was about 2.5 times more than the leaching process and approximately 4 times more than the evaporation/crystallization system. At high Cl levels the evaporation/crystallization process was clearly more advantageous compared to leaching due to the rising costs for Na₂SO₄ for the leaching process. It is also clear that already for the base case the expenses for make-up chemicals were significantly higher for the purging alternative compared to both leaching and evaporation/crystallization.

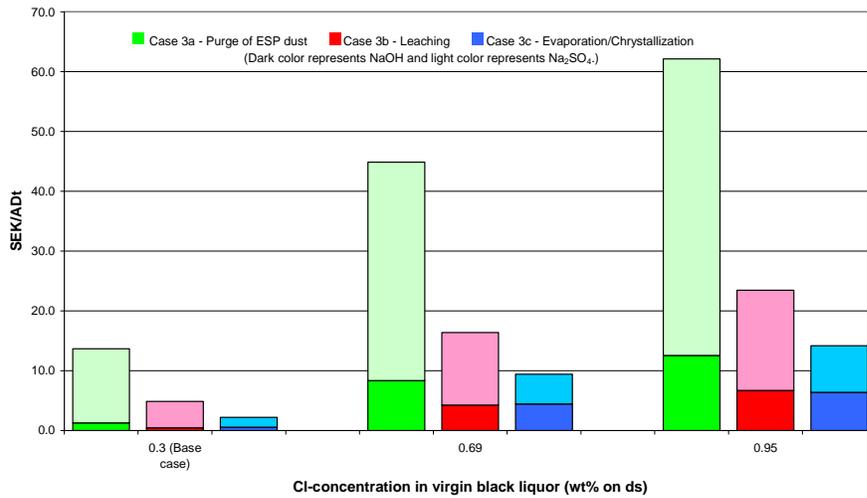


Figure 42. Costs for provided make-up chemicals for the hardwood mill Case 3a-c (SEK/ADt).

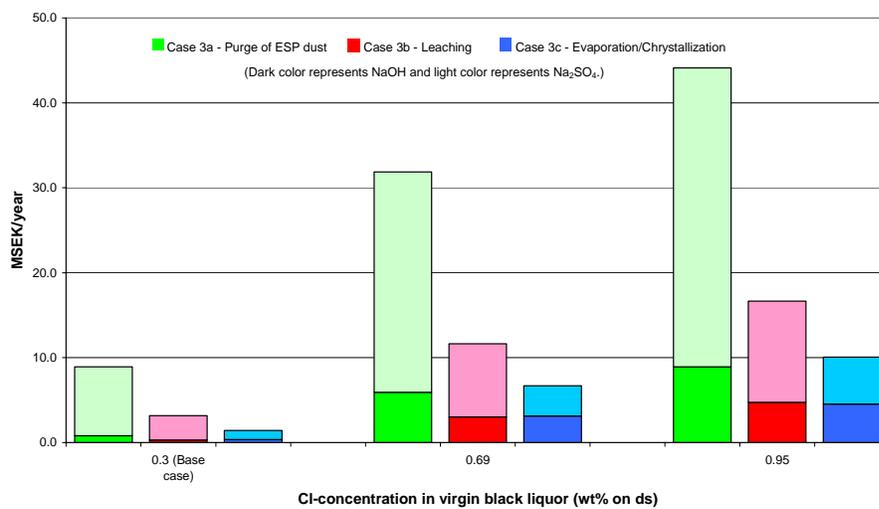


Figure 43. Costs for provided make-up chemicals for the hardwood mill Case 3a-c (MSEK/year).

In Figure 44 and Figure 45 the overall net total benefit result for the hardwood mill Case 3a-c are shown. From Figure 44 and Figure 45 it can be stated that leaching and evaporation/crystallization already at low Cl concentrations showed a substantial advantage compared to the purging alternative. Evaporation/crystallization proved to have a small, but clearly, advantageous net total benefit compared to leaching in the evaluated Cl concentration range. It is also important to note that the evaporation/crystallization benefit grew with increasing Cl concentration, due to the ascending costs for Na₂SO₄ for the leaching process. For the highest Cl level the evaporation/crystallization benefit, compared to leaching, amounted to about

3 MSEK/year. It is also notable that the purging alternative at high steam data showed a positive net total benefit until the Cl concentration in virgin black liquor reached about 0.55 wt % on dry solids. Leaching and evaporation/crystallization at high steam data on the other hand showed a positive net total benefit within the entire Cl concentration range.

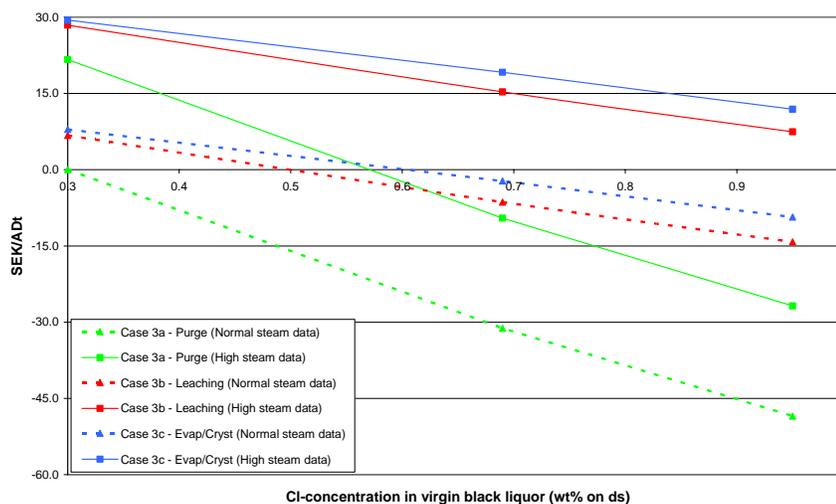


Figure 44. Net total benefit for the hardwood mill Case 3a-c (SEK/ADt).

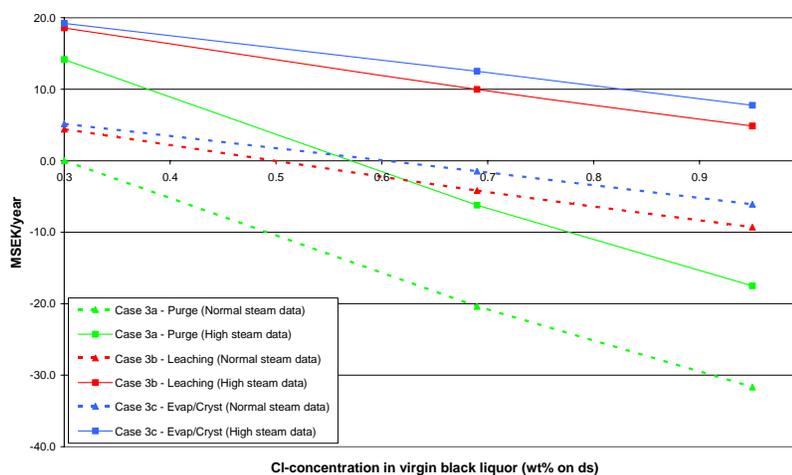


Figure 45. Net total benefit for the hardwood mill Case 3a-c (MSEK/year).

Since the resulting net total benefit to a large extent depended on the electricity price a sensitivity analysis was performed. In Figure 46, Figure 47 and Figure 48 the net total benefit for the hardwood mill Case 3a-c (High steam data) at three different electricity prices are presented. The electricity prices included in the sensitivity analysis were 350, 480 and 630 SEK/MWh. In Figure 46 it is evident that the net total benefit was positive for the purging case, with high steam data, at all three electricity prices if the Cl concentration was below about 0.5 wt % on dry solids in virgin black liquor.

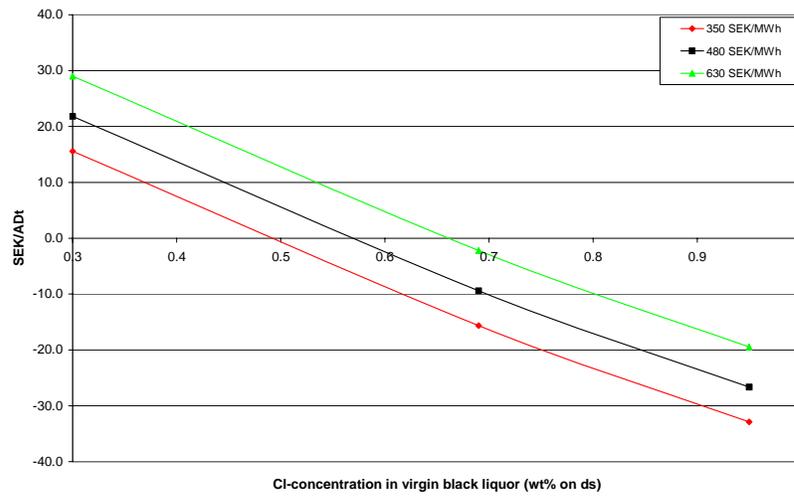


Figure 46. Net total benefit for the hardwood mill Case 3a - Purge (High steam data) at three different electricity prices (SEK/ADt).

The leaching process, at high steam data, showed a positive net total benefit for all three electricity prices within the evaluated Cl concentration range studied in this Thesis.

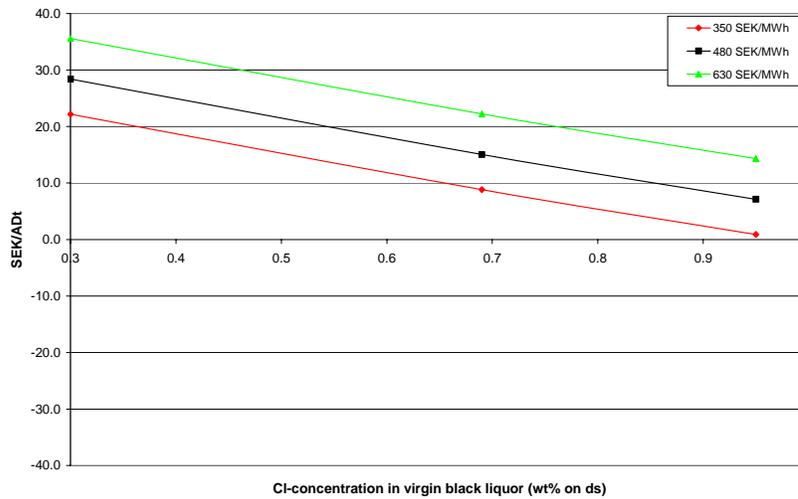


Figure 47. Net total benefit for the hardwood mill Case 3b - Leaching (High steam data) at three different electricity prices (SEK/ADt).

The results in Figure 48 show that the evaporation/crystallization system, at high steam data, gave a positive net total benefit within the evaluated Cl concentration range.

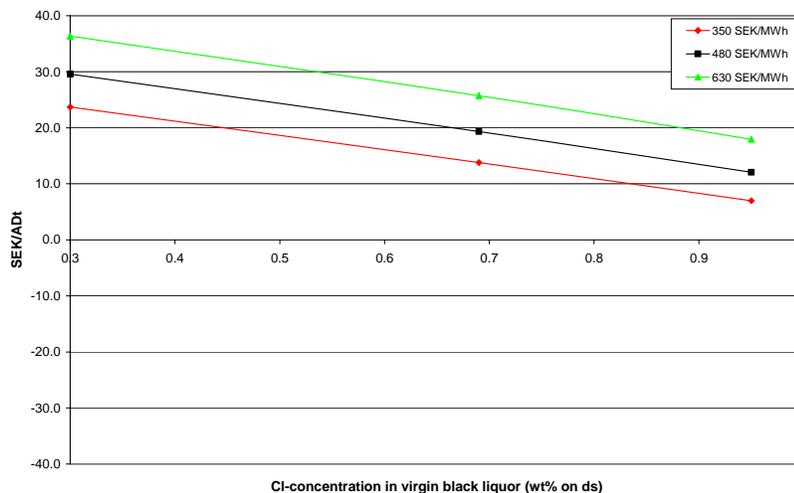


Figure 48. . Net total benefit for the hardwood mill Case 3c – Evaporation/Crystallization (High steam data) at three different electricity prices (SEK/ADt).

11 Discussion

Focus in this Thesis was directed towards the future energy effective recovery boilers that operate with high steam data and hence most likely have to keep K/Cl levels in the mill at low concentrations. Nevertheless, if a pulp mill experience problems related to K and Cl that lower the availability of the recovery boiler and by that means acts as a bottleneck for pulp production, the costs for the shut down time could in severe cases amount to huge figures. For example, if a total shutdown of the recovery boiler is assumed to take 3 days the resulting decrease in pulp production for the model mills studied in this Thesis, with a daily production of 2 000 ADt, would be 6 000 ADt. Assuming a benefit of 2100 SEK/ADt pulp the reduced income related to the recovery boiler shutdown amounts to about 12.6 MSEK. Thereby the cases in this study may naturally also serve as a guideline for mills that operate with low steam data, but anyhow need to regulate the K and Cl levels in the mill. It is though very important to do an initial analysis of the individual mills Na/S balance since it to a large extent determines how the mill should handle the K/Cl problems in the economically most beneficial way.

In this study the results clearly indicate an economic advantage for the chosen K/Cl kidneys compared to purging ESP dust, if a mill intends to lower the levels of K and Cl. However, the best choice of K/Cl separation process is somewhat more difficult to interpret. Despite the resulting net total benefit and costs for make-up chemicals one very important aspect concerning the choice of K/Cl kidney is naturally the initial investment cost. In this study information from the suppliers of the evaluated kidneys resulted in investment costs that were almost identical. The evaporation/crystallization system though proved to be somewhat more expensive and also needed to have a slightly larger capacity. The parameter that determined the capacity of the K/Cl kidneys, at different Cl levels, was the Cl removal efficiency. In this Thesis the leaching system had a minor advantage in Cl removal efficiency, compared to evaporation/crystallization, which meant that the capacity of the evaporation/crystallization process needed to be somewhat larger. Nevertheless, the difference in capacity demand between the two K/Cl separation processes only amounted to a few percent. Since the smallest capacities in the Thesis represent very small units for Cl levels lower than ~0.6 wt% on dry solids in virgin black liquor it is very important to point out that the estimated investment costs are highly uncertain for those processes. Furthermore it is interesting to note that the impact from the investment cost on the net total benefit in this study proved to be comparatively small in the cost benefit analysis. One major advantage for the leaching process is that the number of full scale installations by far exceeds those of the evaporation/crystallization system. On the other hand the evaporation/crystallization process in this Thesis had the disadvantage of consuming LP steam that otherwise would have been utilized in the condensing turbine. In a real mill probably some unused low energy stream could be used for the evaporation/crystallization process and thereby no loss in electricity production would occur.

The choice of make-up chemicals, NaOH and Na₂SO₄, was naturally a key parameter in this study and consequently the prices for the make-up chemicals were extremely decisive. Particularly the price for Na₂SO₄ to a large extent determined the difference in economical benefit between the investigated methods of lowering the K and Cl levels. Unfortunately it was difficult to obtain a somewhat fixed price from the suppliers since the price fluctuates. However, prices that should be fairly adjusted to the conditions on the market situation at the time of writing were used in this study. Even though the price for Na₂SO₄ should be much lower than what was assumed in this Thesis the pattern of the results would be the same.

As mentioned earlier in the report it is possible that it in the future, because of environmental reasons, will be prohibited to purge ESP dust. A legal restriction could consequently force the pulp and paper industry to take other courses of action to lower the mill levels of K/Cl, which further motivates an installation of a K/Cl kidney.

From a wider environmental point of view an increased electricity production in a pulp mill would mean that a market pulp mill could serve as an important supplier of green electricity. By that means the pulp- and paper industry can contribute to the intended lowering of fossil CO₂ emissions in society.

Unfortunately not much was found in literature concerning the cadmium emissions from the two investigated K/Cl kidneys. It is though most likely so that an installation of a K/Cl kidney would result in a significant lowering of the cadmium emissions with the effluent.

12 Conclusions

From the results of this Thesis the following main conclusions can be presented:

In the first part of the Thesis three levels of steam data were evaluated in order to highlight the magnitude of the increase in sold electricity when steam data is raised. It was concluded that a significant economic benefit is expected when the recovery boiler is operated with high steam data. The increase in sold electricity for the softwood reference mill, with an annual pulp production of 653 000 ADt, when comparing traditional (470°C, 70 bar) and future (510°C, 100 bar) steam data amounted to about 17 % (29 MSEK/year), while the increase in sold electricity between modern (490°C, 81 bar) and future steam data was calculated to approximately 10 % (11 MSEK/year). If a Swedish kraft pulp mill is planning to invest in a new recovery boiler it should most likely be profitable to invest in a recovery boiler that operates with high steam data. Both figures calculated in Case 1 represent a rather substantial increase in sold electricity that in this study was assumed to be achieved with a relatively minor increase in investment cost. It is on the contrary most probably so that the Cl and K mill levels somehow have to be balanced in order to maintain trouble-free operation of the recovery boiler. The lowering of the Cl and K concentrations should naturally be performed in the economically and environmentally most beneficial way.

For the softwood mill, with a surplus of S in the mill, the leaching and evaporation/crystallisation processes in this study showed almost identical net total benefit figures in the evaluated Cl concentration range (0.3-0.96 wt % Cl on dry solids in virgin black liquor). The purging alternative involved dumping massive amounts of ESP dust at high Cl levels, and the expenses for make-up chemicals consequently came up to huge figures already at fairly low Cl concentrations. When the Cl concentration reached high levels (~0.9 wt % Cl in virgin black liquor) a minor advantage in net total benefit for evaporation/crystallization was observed, due to the more effective recycling of Na and S. High prices for make-up chemicals would further increase the advantage for the more selective evaporation/crystallization process, while low prices instead would decrease it.

For the hardwood mill, that purged ESP dust to control the levels of K and Cl and also has an initial deficit of S in the mill, it was in this study already in the base case more profitable to install one of the proposed K/Cl kidneys, instead of purging ESP dust. As for the softwood mill the purging alternative became very expensive already at low Cl levels. Despite the fact that an installation of a K/Cl kidney proved to be more profitable for the base case it would be unlikely that a kidney with such small capacity in reality would be installed. For the hardwood mill the more selective evaporation/crystallization unit showed a small, but clearly, more favourable net total benefit compared to the leaching process, in the evaluated Cl concentration range. As for the softwood mill high prices for make-up chemicals would further increase the advantage for the evaporation/crystallization process while low prices would decrease it.

13 Future work

Since the suppliers of the leaching and evaporation/crystallization processes were exceptionally helpful during the literature study it would be very interesting to discuss the final Thesis with them. There are probably assumptions in this study that could be made in other ways but due to time limitations these discussions have not taken place yet.

It would also be interesting to perform a similar thorough investigation of a “real” mill in order to see if the theoretical model mill used in this Thesis in a good way can reflect a “real” mill situation.

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