Handläggare
Fredrik Öhman
Lennart Delin

Tel 010-505 40 72
Mobil 072-225 45 28
Fax 010-505 0010
fredrik.ohman@afconsult.com

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Electrolysis of sodium sulphate – efficient use of saltcake and ESP dust in pulp mills

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ÅF INDUSTRY AB
Forest Industry

Fredrik Öhman Lennart Delin

Akzo Nobel Pulp and Performance Chemicals AB

Nina Simic Kalle Pelin

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1 Summary

1.1 Summary

The pulp mill of today is very efficient with low losses of chemicals and an effective chemical recovery system. The high degree of closure is positive for the mill economy, water consumption and environmental impact, but also brings negative aspects. In a closed system the Na/S balance and build-up of K and Cl in the mill process streams has to be controlled. The chemical balances are today normally controlled by purging ESP dust (or ESP dust treated to obtain a more concentrated purge) and compensating with make-up chemicals to maintain the Na/S ratio at the desired level. This is costly and leads to the release of salt to the environment.

One option to solve/minimize the above mentioned problem is electrolysis of sodium sulphate, either in the form of pre-treated ESP dust or saltcake from ClO_2 production (more or less pure Na_2SO_4), to caustic and sulphuric acid. The current state-of-the-art, used extensively in the chlor-alkali industry, is a two compartment electrolyzer that produces pure caustic and a mix of H_2SO_4 and Na_2SO_4. This project aims to evaluate how electrolysis can be integrated in two model mills (a softwood market pulp kraft mill located in Scandinavia and a eucalyptus market pulp kraft mill located in South America. Effects on both Na/S and K/Cl levels were taken into account.

Electrolytic split of sodium sulphate can effectively reduce make-up chemicals consumption in the closed part of the mill. In five out of seven electrolysis cases NaOH can be produced to cover part of the bleaching plants need as well, i.e. no external NaOH at all is needed for the closed part. The reduction is more substantial in softwood mills due to a higher internal sulphuric acid consumption. Salt emissions from the closed mill are reduced by 65-~100%. The levels of potassium and chloride in the mill can be controlled with only minor losses of Na and S. The kidney function for K requires that alkaline filtrates from the bleaching plant are not recycled. If the acid stream is used in the ClO_2 plant it requires significant additional filter and evaporation capacity (almost double capacity). Power consumption for the electrolysis increased by between 55-206 kWh/adt (an increase of 8-30% compared to the normal mill consumption).

The total savings were found to be between 20-60 MSEK/y and are most dependent on price for NaOH, electricity and in some of the eucalyptus cases, Na_2SO_4. A deposit/handling cost for ESP dust would significantly improve the process economy. CAPEX was estimated to between 120-220 MSEK depending on case, divided between pre-treatment (only in the case of ESP dust treated), electrolysis and re-building the ClO_2-plant. This gave straight pay-back times between 3-9 yrs depending on case. Despite larger savings in chemicals for the softwood cases, the eucalyptus cases still show better pay-back times due to the higher price level for chemicals and electricity in South America.

1.2 Executive summary

Definition of problem

The pulp mill of today is very efficient with low losses of chemicals and an effective chemical recovery system. The high degree of closure is positive for the mill economy, water consumption and environmental impact, but also has negative sides:

- The Na/S-ratio that determines the composition of the pulping chemicals has to be on the desired level. If an ingoing stream has a different Na/S-ratio it will disturb the chemical balance. In a softwood pulp mill there is generally a sulphur surplus intake which normally is handled by purging electrostatic precipitator (ESP) dust mainly composed of sodium sulphate from the system. The lost sodium must then be replaced, usually by expensive NaOH.
- The high degree of closure accumulates non-process elements (NPE's) in the mill. K and Cl can cause corrosion- and plugging problem in the recovery boiler if the concentrations are too high. These are enriched in the ESP dust, which can be purged to reduce the levels of K and Cl. Then input of chemicals is needed to make up for the lost Na and S. There are ash treatment processes that purge K and Cl in more concentrated form, but the losses in chemicals are still significant.

These problems cause substantial costs for the mill in make-up chemicals (mainly NaOH since required Na_2SO_4 is normally available internally from the ClO_2-plant). In addition, a large amount of salt is purged to the environment. This can be an important future issue with more stringent environmental regulations that can lead to e.g. limited emission rights of salts.

Electrolysis of sodium sulphate

One option to solve/minimize the above mentioned problem is electrolysis of sodium sulphate in the form of ESP dust and/or saltcake from ClO_2 production to caustic and sulphuric acid (see **Figure 1.1**).

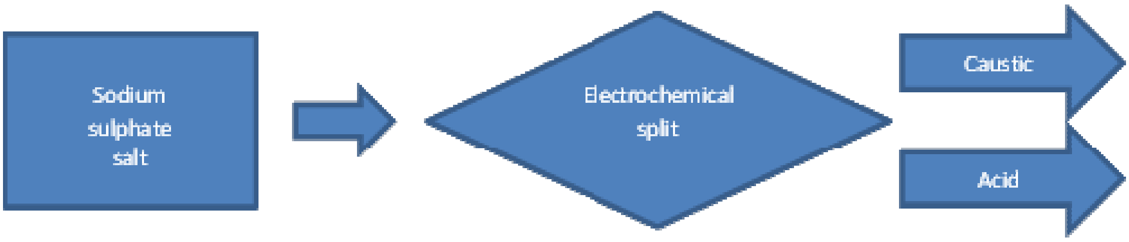

Figure 1.1. Electrochemical split of sodium sulphate.

The split of sodium and sulphur in different streams leads to an increased flexibility in the Na/S-balance (internal sulphuric acid generation). There is also a potential to purge K and/or Cl from the system with minimal losses of chemicals. One advantage for the mill is reduced make-up chemical consumption. Another advantage is that the amount of salts is reduced.

Electrolysis of sodium sulphate has been studied for a long time but has this far not been profitable. The drivers may be stronger now due to:

- Problems with Na/S and K/Cl-levels that lead to high costs for make-up chemicals.
- Development of new processes for the pulp mill that leads to higher sulphur inputs and greater disturbances (e.g. LignoBoost)
- Demands on more extensive closure of mills and reduced environmental impact, including the questioning of release of salts from the mill.
- Risk for increasing chemical prices.
- Technical development of the electrolysis process by broad application in the chlor-alkali industry

Project scope

In this project electrolysis saltcake from ClO_2-production and ESP dust is studied. A process for upgrading ESP dust to the purity demands for electrolysis is suggested. The integration of an electrolysis process with two model mills (bleach kraft from softwood in Scandinavia and bleached kraft from eucalyptus in South America, both mills producing 2000 adt/d bleached pulp) is evaluated with Na/S and K/Cl balances as boundary conditions.

Results

Sodium sulphate can be electrolysed using either two or three compartment systems. Hydrogen and oxygen gas streams are by-products from the electrolysis. The hydrogen stream is pure and can be used to fuel the lime kiln, replacing fossil oil. The oxygen stream can contain chlorine gas if there are chlorides in the sodium sulphate fed to the electrolysis process. This work focuses the two compartment electrolyzer which is extensively proven technically in the chlor-alkali industry. From this system a 50/50 mole-% of H_2SO_4/ Na_2SO_4 mix and a pure alkali stream is obtained. If ESP dust is used as feed, the alkali stream is a mix of K/NaOH.

A process for upgrading recovery boiler dust to the demands required for electrolysis is suggested where multivalent metal ions, chloride and carbonate are reduced to manageable levels. All process steps are individually proven in industrial scale. Saltcake can be fed directly to electrolysis after minor processing.

The integration of an electrolysis process (two compartment) in the model mills was studied with Na/S and K/Cl balances as boundary conditions. A number of potentially interesting cases[1] were treated with different feed to the electrolysis, see **Table 1.1**:

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[1] A complete summary of the cases are given in Chapter 8, page 49

Table 1.1. Studied cases.

Case	Feed to electrolysis	Purpose
1a, b-d	No electrolysis	Reference to Cases 2-5
2a, c-d	Saltcake	Acid demand to ClO_2-plant supplied.
3a,b	Saltcake and current purge of ESP dust.	Acid demand to ClO_2-plant supplied. Additional acid to bleach plant.
4b	ESP dust	Acid demand to ClO_2-plant supplied.
5a	Saltcake and ESP dust	Internal acid demand supplied (tall oil and ClO_2)
6a,b	No electrolysis + LignoBoost	Reference to Case 7
7a,b	ESP dust and (for euca) saltcake	H_2SO_4 demand in closed part supplied (ClO_2, LignoBoost and for SW tall oil plant)

Savings in chemicals, oil to the lime kiln and the reduction in severed salts are shown in **Table 1.2**. The savings in chemicals are generally larger for the softwood cases. The severed amount of salt is substantially reduced (65-~100 %). The electricity consumption is between 55-206 kWh/adt. This is a significant increase of 8-30% from the normal mill consumption.

Table 1.2. Savings (kton/y) in make-up chemicals consumption, oil consumption in lime kiln and severed amount of salts (compared to corresponding reference case). A negative number means that more chemicals have to be bought.

Case		**2a**	**2c**	**2d**	**3a**	**3b**	**4b**	**5a**	**7a**	**7b**
Savings in:										
H2SO4	(kton/y)	9.0	8.0	6.7	10.2	11.7	8.0	13.5	24.2	10.7
NaOH	(kton/y)	9.2	6.8	6.4	10.8	11.1	8.2	13.5	24.4	10.9
Na2SO4	(kton/y)	0.0	-9.5	-7.4	-0.1	-12.1	0.2	-2.3	-2.2	0.0
Purchased oil to lime kiln	(kton/y)	0.6	0.6	0.6	0.8	1.0	0.9	1.1	2.4	1.2
Purged dust	(kton/y)	16.2	10.8	11.8	16.2	0.6	15.7	21.9	41.2	20.0

Economic evaluation

Operating costs were estimated using the costs of consumables given in **Table 1.3**. The estimated CAPEX was adjusted for size using so called scaling factors. The investment was estimated to 120-240 MSEK of which 75-140 MSEK is the electrolysis process.

Table 1.3. Costs used in the economic assessment.

		Cost	
	Unit	**Scandinavia**	**South America**
NaOH	SEK/ton	3 120	5 560
H_2SO_4	SEK/ton	790	1 660
Na_2SO_4	SEK/ton	1 800	2 000
Electricity	SEK/MWh	412	308
Steam	SEK/ton	60	60
Deposit cost	SEK/ton	0	0
Oil price	SEK/MWh	450	450

The result was straight pay-back times between 3-9.5 years. The eucalyptus cases show better economy than the softwood cases even though more chemicals are saved in the latter. This is due to the price difference of chemicals and electricity between South America and Scandinavia.

A deposit cost would give a significantly better process economy. Already a cost of 500 SEK/ton would give pay-back times below 5 years for all cases.

Conclusions

Conclusions from the work can be summarised as:

Integration to the mill

- Using electrolysis to split sodium sulphate to sodium hydroxide and sulphuric acid can effectively reduce make-up chemicals consumption and severed amount of salts.
- The total chemicals consumption is reduced more in softwood mills where the higher sulphuric acid consumption in the closed mill cycle leads to a purge of more ESP dust and the need for more make-up chemicals.
- Electrolysis of ESP dust can be an efficient kidney for K and Cl removing 52-56% of the K and 85-90% of the Cl fed to the electrolysis process. The potassium kidney function requires that the K/NaOH stream is used in e.g. the open part of the bleaching process and that the fresh NaOH used there is taken into the mill as replacement instead.
- The power consumption for electrolysis varied between 55 and 206 kWh/adt. This means a significant increase in power consumption with 8-30% compared to the model mill.
- Using the two-compartment cell set up produces a diluted H_2SO_4-stream with 50 mole-% Na_2SO_4. If this stream is used to feed the ClO_2 plant significant additional filter and evaporation capacity is required. An extensive rebuild of the ClO_2-plant may be necessary.

Economic evaluation

- CAPEX was estimated to between 120-220 MSEK depending on case. The yearly savings was estimated to between 20-60 MSEK which gave straight pay-back times between 3-9 yrs depending on case.
- Price for NaOH, electricity and in some of the eucalyptus cases, Na_2SO_4 were found important in terms of operational costs. Deposit costs for ESP dust would significantly improve the process economy.
- Despite larger savings in chemicals for the softwood cases, the eucalyptus cases still show better pay-back times due to the higher price level for chemicals in South America (Brazil).

1.3 Exekutiv sammanfattning

Problemställning

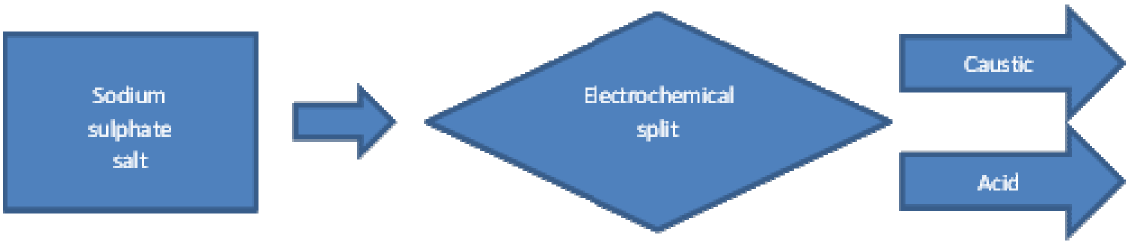
Dagens massabruk är mycket effektivt med låga förluster av kokkemikalier och ett effektivt återvinningssystem. Den höga slutningsgraden är positiv för brukets ekonomi, vattenförbrukning och miljöpåverkan men för också med sig nackdelar:

- Na/S-förhållandet som bestämmer sammansättningen på kokluten måste hållas på önskad nivå. Om en inström har ett annat Na/S förhållande kommer den att störa kemikaliebalansen. I ett barrmassabruk råder vanligen ett svavelöverskott in i processen som måste hanteras genom att ta ut motsvarande mängd svavel från systemet. Detta görs genom att blöda ut sodapannestoft (bestående till största delen av natriumsulfat). Då fås en förlust av natrium som normalt ersätts med dyr lut.
- Med hög slutningsgrad ackumuleras processfrämmande grundämnen (PFG) i bruket. K och Cl kan orsaka korrosions- och igensättningsproblem i sodapannan om nivåerna blir för höga. Dessa anrikas i stoftet från sodapannans elektrofilter och, om behov finns, blöds sodapannestoft ut för att minska halterna vilket leder till kemikalieförluster. För att minska dessa förluster finns askbehandlings-processer som blöder ut K och Cl i mer koncentrerad form, men kemikalieförlusterna är fortfarande signifikanta.

Dessa problem medför stora kostnader för bruket i form av makeup kemikalier (främst NaOH då behovet av Na_2SO_4 kan tillgodoses internt från ClO_2-processen) och dessutom utstötning av en stor mängd salter till recipienten, vilket kan vara av stor vikt då miljökraven kan bli strängare med exempelvis begränsningar i emissionsrätten som följd.

Elektrolys av natriumsulfat

Ett förslag för att lösa/minska ovanstående problem är elektrolys av natriumsulfat (elektrokemisk saltsplit), antingen i form av sodapannestoft eller biprodukter från klordioxid (ClO_2)-tillverkningen, till svavelsyra och natriumhydroxid (se **Figur1.2**).



Figur 1.2. Elektrolys av natriumsulfat.

Uppdelningen av natrium och svavel i separata strömmar leder till ökad flexibilitet gällande Na/S-balansen (intern svavelsyratillverkning). K och/eller Cl kan blödas ut från systemet med minimala kemikalieförluster. En fördel för bruket är minskade kemikaliekostnader. En annan fördel är minskade utsläpp av salt.

Elektrolys av natriumsulfat har studerats länge men hittills inte visat sig lönsamt. Drivkrafterna kan ha blivit starkare på grund av:

- Problem med Na/S och K/Cl-nivåer som leder till höga kostnader för ersättningskemikalier
- Utveckling av nya processer för massabruket som leder till ytterligare svavelsyraintag (t.ex. LignoBoost).
- Krav på slutning och minskad miljöpåverkan, inklusive ifrågasättande av utsläpp av salter från bruket.
- Risk för ökande kemikaliepriser.
- Teknisk utveckling av elektrolysprocessen genom bred tillämpning i klor-alkaliprocessen.

Projektomfattning

I projektet studeras elektrolys av både saltkaka och sodapannestoft. En process för att uppgradera sodapannestoftets renhet till den nivå som krävs för elektrolys föreslås. Integrationen av en elektrolysprocess med två modellbruk studeras (blekt sulfat från barr i Sverige samt blekt sulfat från eukalyptus i Sydamerika, båda 2000 adt/d blekt massa) med Na/S- och K/Cl-balansen som randvillkor.

Resultat

Elektrolys av natriumsulfat till NaOH och svavelsyra kan utföras med två- eller tre-kammarsystem. Som biprodukt fås vät- och syrgasströmmar. Vätgasströmmen är ren och kan användas som bränsle till mesaugnen. Syrgasströmmen kan innehålla klorgas om klorider finns i natriumsulfatet som går in i elektrolysen. Fokus i arbetet är tvåkammarsystemet som är mest beprövat tekniskt. Det ger en blandning av H_2SO_4 och Na_2SO_4 som syraprodukt (ca. 50/50 mol-%). Om sodapannestoft elektrolyseras fås K/NaOH som alkaliström.

En process för att rena sodapannestoft till de krav som ställs för elektrolys har tagits fram där multivalenta metalljoner, klorider och karbonat reduceras till hanterbara nivåer. Alla processteg är var för sig beprövade i industriell skala. Enda tillsatsen är vatten motsvarande 8.4 m^3/ton behandlat sodapannestoft. Motsvarande process för att hantera biprodukter från ClO_2-tillverkning är betydligt enklare.

Integration av ett elektrolyssystem (två kammare) med modellbruken har studerats med Na/S- och K/Cl-balansen som randvillkor. Ett antal potentiellt intressanta fall[2] behandlades med olika inflöde till elektrolysen, se **Tabell 1.4**.

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[2] För en komplett summering av fallen, se Kapitel 8, sid 49.

Tabell 1.4. Studerade fall.

Fall	Inström till elektrolys	Syfte
1a, b-d	Ingen elektrolys	Referens till Case 1-5.
2a, c-d	Saltkaka	Leverera syrabehovet till ClO_2-anläggningen
3a,b	Saltkaka och nuvarande mängd utstött sodapannestoft	Leverera syrabehovet till ClO_2-anläggningen. Syra utöver det till blekeriet.
4b	Sodapannestoft	Leverera syrabehovet till ClO_2-anläggningen.
5a	Saltkaka och sodapannestoft	Internt syrabehov tillgodosett (tallolja och ClO_2)
6a,b	Ingen elektrolys + LignoBoost	Referens till Case 7
7a,b	Sodapannestoft och (för euca) saltkaka	H_2SO_4 behov i slutna delen tillgodosett (ClO_2, LignoBoost och för SW talloljekokerit)

Besparingar i kemikalieförbrukning, olja till mesaugnen samt mängden salt till avlopp visas i **Tabell 1.5**. Minskningen i kemikalieförbrukning är generellt större i SW-fallen. Mängden salt till avlopp från slutna delen minskar betydligt i de flesta fall (65-~100 %). Elektricitetsförbrukningen är mellan 55-206 kWh/adt. Det motsvarar en betydande ökning i brukets elektricitetsbehov med 8-30%.

Tabell 1.5. Besparingar (kton/år) i kemikalieförbrukning, oljeförbrukning i mesaugnens och salt till avlopp (jämfört med motsvarande referensfall). Ett negativt tal betyder att mer kemikalier måste köpas in.

Fall		2a	2c	2d	3a	3b	4b	5a	7a	7b
Besparingar i:										
H2SO4	(kton/år)	9.0	8.0	6.7	10.2	11.7	8.0	13.5	24.2	10.7
NaOH	(kton/år)	9.2	6.8	6.4	10.8	11.1	8.2	13.5	24.4	10.9
Na2SO4	(kton/år)	0.0	-9.5	-7.4	-0.1	-12.1	0.2	-2.3	-2.2	0.0
Olja till mesaugnen	(kton/år)	0.6	0.6	0.6	0.8	1.0	0.9	1.1	2.4	1.2
Salt till avlopp	(kton/år)	16.2	10.8	11.8	16.2	0.6	15.7	21.9	41.2	20.0

Ekonomisk utvärdering

Driftskostnader uppskattades utgående från priser i **Tabell 1.5**. Den uppskattade investeringen justerades för storlek med hjälp av s.k. skalfaktorer. Investeringen ligger i storleksordningen 120-240 MSEK varav 75-140 MSEK är själva elektrolys-anläggningen.

Tabell 1.5. Kostnader använda i studien.

		Kostnad	
	Enhet	**Skandinavien**	**Sydamerika**
NaOH	SEK/ton	3 120	5 560
H_2SO_4	SEK/ton	790	1 660
Na_2SO_4	SEK/ton	1 800	2 000
Elektricitet	SEK/MWh	412	308
Ånga	SEK/ton	60	60
Depositions-/hanteringskostnad	SEK/ton	0	0
Oljepris	SEK/MWh	450	450

Resultatet visar raka återbetalningstider mellan 3-9.5 år. Eukalyptusfallen visar bättre ekonomi än barrvedsfallen trots att mer kemikalier sparas i SW-fabriken. Detta beror på prisskillnaden på kemikalier och elektricitet mellan Sydamerika och Skandinavien.

En tillkommande deponi-/hanteringskostnad skulle leda till betydligt bättre totalekonomi. Redan en kostnad på 500 SEK/ton ger återbetalningstider under 5 år för samtliga fall.

Slutsatser

Slutsatserna från arbetet kan sammanfattas som:

Integration med bruket

- Elektrolys för split av natriumsulfat till NaOH och H_2SO_4 kan effektivt minska brukets kemikalieförbrukning och utsläpp av salter.
- Totala kemikalieförbrukningen minskar mer i barrvedsfabriker där störningarna i Na/S-balansen genom den större H_2SO_4-förbrukningen i slutna delen leder till en stor mängd utstött sodapannestoft och höga kemikaliekostnader.
- Elektrolys av sodapannestoft är en effektiv njure för K och Cl där 52-56% av K och 85-90% av Cl av mängden in till elektrolysprocessen kan stötas ut. Njurfunktionen för K kräver att den producerade K/NaOH strömmen används i t.ex. den öppna delen av blekeriet och färska lut tas in i slutna delen som ersättning ("lutväxling").
- Elförbrukningen varierade mellan 55 och 206 kWh/adt i studerade fall. Det betyder en signifikant ökning i elförbrukning med 8-30% jämfört med brukets normala elbehov.
- Med tvåkammarelektrolysen produceras en utspädd H_2SO_4 med 50 mol-% Na_2SO_4. Om denna ström används som feed till ClO_2-anläggningen krävs en signifikant ökad filteryta och indunstningskapacitet. Om kapaciteten inte finns krävs en omfattande ombyggnad.

Ekonomisk utvärdering

- CAPEX uppskattades till mellan 120-220 MSEK beroende på fall. Årliga besparingar uppskattades till 20-60 MSEK vilket gav raka återbetalningstider mellan 3-9 år beroende på fall.
- Priset på NaOH, elektricitet och, i vissa eukalyptusfall, Na_2SO_4 har störst effekt på de rörliga kostnaderna. En depositionsavgift för sodapannestoft skulle ha en signifikant effekt på processekonomin.
- Trots större kemikaliebesparingar i SW-fallen visar eukalyptusfallen fortfarande bättre återbetalningstider, beroende på det högre kostnadsläget för kemikalier i Sydamerika.

2 Introduction and aims

2.1 Background

The kraft pulp mill of today is very efficient with low losses of pulping chemicals and an efficient chemical recovery system. In general the mill system has a high degree of system closure of the brown side (pulping, pulp wash, oxygen bleaching, chemical recovery) with low levels of both input and output chemicals compared to older mills. The bleach plant is for most mills still open, which means that all added chemicals together with the organic effluent must be handled in an external treatment before release to recipient. Some mills recirculate alkaline filtrate to the closed system, thereby closing a part of the bleach plant. The pulp mill is shown schematically in Figure 2.1 with the closed system inside the dotted box (note that only in- and output streams related to the Na/S balance are included).

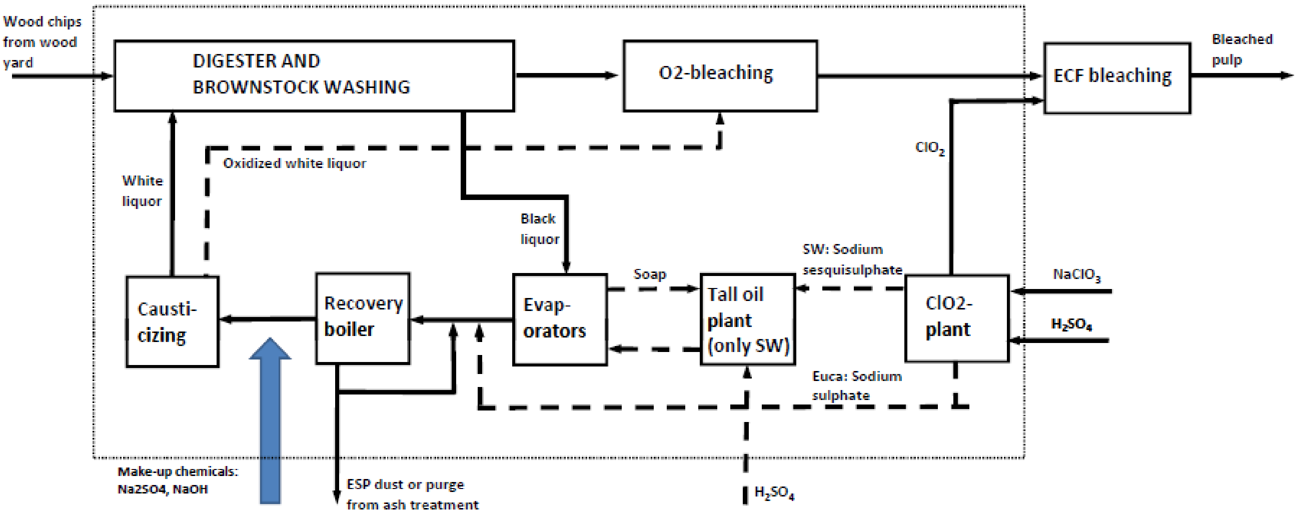

Figure 2.1. Block scheme of a kraft pulp mill with in- and outgoing streams related to the Na/S balance shown.

The high degree of system closure is overall very advantageous in terms of mill economy, impact on the environment, water consumption and energy recovery. However, it also brings difficulties.

Input and output of process chemicals must be in balance in a closed system. Of particular importance is the Na/S-ratio which controls the composition of the pulping liquor and must be maintained at the desired level. If an input stream contains a different ratio of Na/S, e.g. sulphuric acid to the tall oil plant in a softwood kraft pulp mill, it will disrupt the chemical balance and the additional sulphur input has to be purged. This is normally done by purging a part of the electrostatic precipitator dust (ESP dust) from the recovery boiler. ESP dust consists mainly of Na_2SO_4 which leads to a significant amount of lost sodium together with the sulphur. This sodium has to be replaced by a sulphur free make-up chemical which is normally expensive NaOH. In addition, a significant amount of Na_2SO_4 together with other salts and trace components is released to the recipient with the purged recovery boiler dust. This is of particular importance for softwood mills where sulphuric acid is normally added to the closed mill system.

Another problem is the accumulation of so called non-process elements (NPE) in the closed system. There are several “kidneys” where many elements (e.g. Ca, Al, Mn, etc.) are purged from the closed system, e.g. with the pulp, purge of lime, lime dust and green liquor dregs. Potassium and chloride are enriched in the ESP dust and, if the levels are high enough, cause problems with plugging and corrosion of the heat recovery system in the recovery boiler. These elements are normally controlled by either a purge of recovery dust or by treatment of ESP dust to obtain a more concentrated purge of K and Cl (e.g. Valmet AshLeach or Andritz ALE). The purge, even from ash treatment processes, contains sodium and sulphur which has to be replaced. Accumulation of K and Cl is a more important question in eucalyptus kraft pulp mills where the input mainly with the wood is larger.

Most mills are ECF mills with a ClO_2-generator which produces saltcake as a by-product. The ClO_2-plant is in a modern mill normally well-integrated in the control of the Na/S-balance. Without the ClO_2-plant the amount of external make-up chemicals needed would often, in particular for eucalyptus mills, increase. If the saltcake is returned to the recovery cycle it can be seen (in terms of Na/S) as a part of the closed cycle. In softwood mills the acidic sesquisulphate from SVP-LITE/R8 plants can be used to partly replace the fresh sulphuric acid addition to the tall oil plant. For eucalyptus mills, where the saltcake often is Na_2SO_4 it can be returned to the mill as make-up for purged ESP dust that is contaminated with K and Cl-

Thus, in a modern kraft pulp mill there are two processes generating a saltcake with sodium sulphate as main component. The most common manufacturing methods of ClO_2 in pulp mills with ECF bleaching produce sodium sulphate or sodium sesquisulphate. Electrostatic precipitator catch (ESP dust) from the recovery boiler contains mainly sodium sulphate but also other components. Often a significant amount of Na_2SO_4 is emitted to recipient. Could this by-product be recycled in an efficient way?

A method for splitting Na and S in separate streams from saltcake and/or ESP dust would be beneficial for the mill since it would allow a better control of the Na/S-balance of the mill and, at the same time produce chemicals needed in the pulp mill (NaOH and H_2SO_4). The ClO_2-plant would become even better integrated with internal sulphuric acid generation and the added sodium converted to caustic. There is also an opportunity to use the split as a kidney for K and Cl (as a complement or instead of ash leaching) depending on how the streams are handled. One option is electrolysis. Electrolytic production of NaOH and sulphuric acid from saltcake has been studied for more than 20 years (e.g. Thompson et al 1995, Cloutier 1999, Cloutier 2008a, and 2008b, Cloutier 2009). However, the concept is not in commercial use today due to weak economic and environmental drivers.

There is reason to believe that the incentives may have changed in modern pulp mills with several drivers to take into account:

- Continuously increased demands on water closure and environmental performance, e.g. limitations in water use, limited allowed discharge of salt into recipients and concerns about trace elements in ESP dust.
- Accumulation of non-process elements (NPE) in mill cycles and the resulting need for effective methods to purge NPE's from the closed system, for example K and Cl that are enriched in ESP dust and cause plugging and corrosion problems in the recovery boiler heat transfer areas. Current methods of controlling K and Cl levels are costly in terms of make-up chemicals.
- Increased closure of the mills leading to a net sulphur surplus intake from ClO2 generation and, in the case of softwood tall oil separation, and the possible introduction of new processes in the pulp mill with an even higher net input of sulphur (e.g. the LignoBoost process[3]) leads to a requirement for new means to control the sodium/sulphur balance.
- Controlling the sulphur balance today involves purging of ESP dust and the corresponding need for make-up sodium in form of expensive sodium hydroxide.
- Increased production costs, e.g. in form of increased chemical prices, can make it more interesting to generate chemicals on-site.
- Continued technological development, e.g. improved membranes, and more extensive experience from other electrolysis applications (e.g. the chlor-alkali membrane process).

This project is a co-operation between AkzoNobel and ÅF where AkzoNobel has state of the art knowledge for ClO_2 manufacturing and electrochemistry while ÅF Forest Industry are experts in pulp mill technology and the analysis of consequences for the mill when a new process is introduced.

2.2 Aims of the project

For two model mills (a softwood market pulp kraft mill located in Scandinavia and a eucalyptus market pulp kraft mill located in South America):

- Define a pre-treatment process for refining ESP dust to the quality demands required as feedstock for an electrolytic process.
    - Define a model ESP dust for an eucalyptus market pulp kraft mill (located in South America) and a softwood market kraft pulp mill (located in a Nordic country)
    - Define quality demands for the refined ESP dust

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[3] The LignoBoost process (owned and commercialized by Valmet, former Metso) extracts lignin from black liquor in order to de-bottleneck the recovery boiler and/or obtaining another product from the pulp mill, see e.g. Christiansen 2012.

- Establish best reasonable technique for a present installation for electrochemical production of sodium hydroxide and sulphuric acid from saltcake (either from refined ESP dust or saltcake from ClO2-production).
- Study system consequences in the pulp mill from the introduction of a process for electrolysis of sodium sulphate either from saltcake or refined ESP dust (make-up chemicals requirement, Na/S-balance, non-process elements, integration with and consequences for existing processes).
- Determine the benefits and viability of the electrolysis process by making a rough economic assessment including sensitivity analysis for the most important variables.

3 Na/S and K/Cl balances in the pulp mill

Two important aspects to consider in the pulp mill is maintaining the Na/S balance and keeping K and Cl amounts at safe levels. Current options for controlling these impacts the amount of make-up chemicals needed in the mill, which has a significant impact on the mill economy.

3.1 Na/S balance

In order to maintain the sulphidity of the mill it is necessary to ensure that the input of chemicals matches the losses or intentional purging from the closed liquor system. The Na/S ratio in different parts of the liquor system is almost constant.

The losses are very small compared to the liquor stock, in particular for modern mills. A typical loss per cycle in the liquor system is 2%. This means that the chemicals circulate 50 times before leaving the system. Individual input/output therefore has a marginal momentary impact on the liquor composition. Seen in a longer perspective it is however imperative to maintain the required chemical input to obtain the desired sulphidity.

The sulphur input from H_2SO_4 to the ClO_2 plant and (in case of softwood) the tall oil plant is much higher than needed from a make-up point of view. Proposed new processes in the pulp mill, e.g. the LignoBoost process which requires sulphuric acid for lignin washing, leads to even larger sulphur inputs. Sulphur must therefore be extracted from the closed liquor system. The most efficient way of doing this is to purge precipitator dust, which consists mainly of Na_2SO_4 but Na_2CO_3 is also a significant component.

As an example the Na/S balance for the softwood base case is illustrated in the form of a vector diagram in **Figure 3.1**, where the net input of sulphur to the ClO_2 plant and the tall oil plant has to be balanced with a significant purge of precipitator dust.

The main drawback is, however, that in order to be able to extract sulphur as Na_2SO_4, the corresponding loss in Na must be provided in form of sulphur free Na-salt (the horizontal line in **Figure 3.1** denoted NaOH-makeup). Normally NaOH is used but other salts as Na_2CO_3 or HCOONa are an alternative. Thus, the disturbance of the Na/S balance by adding fresh sulphur in the form of sulphuric acid leads to significant make-up chemical costs for the mill.

One important driver for the electrolysis process studied in this project is that it provides internal generation of sulphuric acid, and thus reduces the net sulphur surplus caused by input of fresh sulphuric acid, which in the end leads to reduced costs for external make-up chemicals.

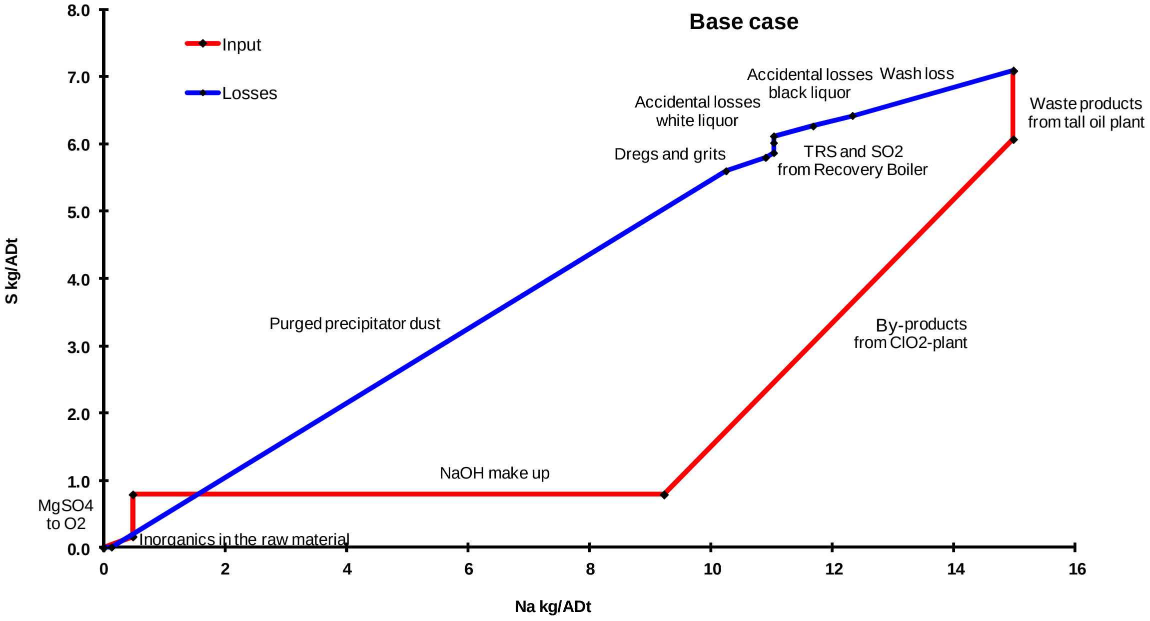

Figure 3.1. Vector diagram for the base case, i.e. the softwood model mill without an electrolysis process, showing net inputs and outputs of Na and S to and from the closed mill system.

3.2 Non-process elements K and Cl

There are several elements which can cause problems in the liquor cycle by causing scaling in different parts, such as Ca in the evaporation plant. These elements do not accumulate in the system, but cause problems directly, in the first cycle so to speak.

Elements which are soluble accumulate in the system until the concentration is so high that the losses of these together with the general losses balance. The elements causing problems are K and Cl. Both these cause problems in the recovery boiler. Cl mainly by lowering the melting point of the precipitator dust causing clogging in the main boiler tube section by forming sticky deposits. K also lowers the melting point, but the main concern here is superheater corrosion. The Cl and K content should be kept below about 2 and 6 weight% respectively to ensure reliable operation of the mill. The limiting factor (Cl or K) depends on the boiler operational data. With older boilers with moderate steam data, the main concern is clogging in the boiler bank where the tube spacing is much narrower than in the superheater. The heat uptake in the superheater is low and the temperature of the superheater surface is moderate. The flue gases enter the boiler bank at relatively high temperature and clogging is the main problem due to “sticky ash”. In this case, Cl has a relatively higher importance.

With high steam data, the temperature of the superheater surface is higher and corrosion starts as soon as some part of the dust melts. The governing factor then becomes the first melting temperature (FMT). Due to the higher heat uptake in the superheater, the flue gases are also cooler when they enter the boiler bank. In this perspective, K levels are more important than Cl-levels.

The K and Cl have earlier generally not caused any major problems, at least not in Scandinavia with pine and birch wood. In some cases there are problems with Cl where timber was floated in salt water causing high chloride levels. The main concern for chloride is presently with eucalyptus which has very high native chloride content.

3.3 Methods of controlling K and Cl

3.3.1 Purge of ESP dust

With moderate input of K and Cl together with moderate demands, K and Cl may simply be controlled by purging precipitator dust, where both K and Cl are enriched compared to the liquor. The dust consists mainly of Na_2SO_4 so the corresponding increase in make-up is also Na_2SO_4. This method is preferred e.g. in Scandinavia where the mill often have a sulphur surplus and need to purge recovery dust in any case to control the Na/S-balance.

3.3.2 Ash treatment methods

With higher inputs of K and Cl it is today standard with some sort of ash treatment plant when operating on eucalyptus wood with high K and very high Cl content. There are several processes available for treating the ash where K and Cl are removed and Na returned to the liquor system.

The most common processes, whether based on leaching (Metso/Valmet, Andritz) or recrystallization (Andritz, HPD/Veolia, Mitsubishi), purges a solution of K and Cl from the mill and returns burkeit ($2Na_2SO_4*Na_2CO_3$), and Na_2SO_4 if the carbonate content is low, to the liquor system. The main problem is however that Na and K also forms a double salt $K_3Na(SO_4)_2$ glaserite. Glaserite precipitates when the molar ratio Na/(Na+K) is below about 0.75. This unfortunately means that the purge contains at least four times as much Na as K on a mole ratio or 2.3 as kg/kg.

In some installations based on the leaching process it has been difficult to separate the burkeit (returned to the mill) from the solution (purge). A solution to the separation problems is to add sulphuric acid to the system to remove carbonates in the form of CO_2; however, this method disturbs the Na/S-balance by adding another net input source of sulphur.

To counter the separation problems, Valmet (former Metso) has developed a two-step process based on centrifuges for solid/liquid separation. On the company home page it is stated that no sulphuric acid input is needed even for ESP dust with high carbonate content.

In general, these systems provide a separation efficiency of about 80-90% for Cl and 75-85% for K while 60-80% of the Na and 65-85% of the SO4 is recovered (e.g. Johansson 2005, Lundström 2007). The specific numbers are, however, dependent on the composition of the ESP dust. Crystallization systems are more expensive in terms of installation and direct operating costs but have a slightly higher recovery of Na/S.

HPD/Veolia has proposed a two-stage system where burkeit is returned and the purge consists of glaserite plus a small amount of solution containing a high concentration of chloride which limits the losses. The separation efficiency for K is very high, up to 90-95%, Cl about 85-90% while the sodium recovery is about 87%. No such system is operating today.

NORAM offers a system based on a patented ion-exchange resin bed to achieve selective removal of the chloride from the precipitator ash with low losses of sodium. This system does not remove potassium (other than as a counter ion to the removed chloride ions in a proportion to sodium about as the same as the proportion in the ESP dust). This system is installed in at least three mills in North America and one mill in Brazil.

4 Model mills

ÅF has together with partners developed hypothetical model market pulp mills representing a design based on best available and commercially proven technology (ÅF 2011). Two of the model mills are used in this project to study process consequences of integrating electrolysis of sodium sulphate and will be described further below. The softwood mill represents a Nordic mill, while the eucalyptus mill is representative of a mill in South America, Portugal and Spain.

The design of the reference mills considers:

- high, consistent pulp quality which is competitive on the international market
- elemental chlorine free (ECF) product
- low specific consumptions of wood, chemicals, and water
- high energy efficiency
- maximized production of bio-energy, and minimal usage of fossil fuels
- low environmental emissions; on the level of newer modern mills
- cost-effective solutions

The model mills are not based on equipment from a particular supplier. In general the key process data used in the balances in this study are conservative and should not exclude any of the major pulp mill equipment suppliers.

In the original model mills alkaline filtrates from bleaching were recycled to the closed mill system. However, since most mills are not recycling alkaline bleaching filtrate today, this is not included in study, which means that the whole bleaching plant is outside the closed part of the mill.

Key process data for both model mills are summarized in **Table 4.1**.

Table 4.1. Summary of reference pulp mill key operating data.

		Softwood	Euca
Dried pulp from dryer	ADt/24 h	2 000	2 000
Operating days	d/a	355	355
Mill availability		92%	92%
Annual production	ADt/a	653 200	653 200
Wood yard			
Wood to digester	t/24 h	4 072	3 482
Bark and wood waste	t/24 h	420	583
Digester Plant			
Kappa number		30	17
Unscreened deknotted digester yield	%	47.0	54.0
Alkali charge on wood as effective alkali	NaOH,%	20.0	17.5
Sulphidity (white liquor)	mole-%	35	35
Oxygen Stage			
Kappa number after oxygen stage		12	10
Alkali charge as NaOH	kg/ADt	25	18
Oxygen charge	kg/ADt	20	14
Washing Department			
Dilution factor in the last stage	m^3/ADt unbl.	2.5	2.5
Evaporation Plant			
Weak black liquor to evaporation, excl.spill	t/h	913	733
ditto dry solids content	%	16.0	14.9
Strong black liquor, dry solids content incl. Ash	%	80	80
Total evaporation, including spill	t/h	771	638
Recovery Boiler			
Estimated higher heating value of virgin DS	MJ/kg	14.0	13.4
Strong liquor virgin solids to mixing tank	t/24 h	3 477	2 594
Net useful heat from liquor, virgin solids	MJ/kg DS	10.3	9.6
Net useful heat from liquor	MW	413	288
Causticizing and Lime Kiln			
Causticizing efficiency	mole-%	82	82
Total white liquor production	m^3/24 h	7 541	5 633
Lime kiln load	t/24 h	534	399
Active CaO in lime	%	90	90
Lime kiln fuel		Bark / wood waste	

The model mills are very energy efficient and the black liquor alone produces enough steam to satisfy the process steam consumption in each of the mills. The recovery boiler is designed to produce high pressure steam at 100 bar(g) and 505°C.

The lime kiln is fired with bark powder, or gasified bark, and the remaining bark from the woodyard and chip screening is burned in a power boiler. There is an excess of steam from the recovery and power boilers which is utilized in a condensing turbine to produce in green power which is sold.

The evaporation plant is a conventional 7-effect system utilising LP and MP steam designed to produce 80% dry solids liquor (including recovery boiler ash).

4.1 Bleached market pulp eucalyptus mill

The eucalyptus raw material consists mainly of *Globulus*. The supply is 100% as roundwood, with bark.

Continuous cooking is used (e.g. Metso Compact Cooking or Andritz DownFlow LoSolids) with 17.5% EA on wood and cooking temperature 138° C to a Kappa number of 17 and a yield of 54%.

Oxygen delignification is done in two stages without intermediate washing to a kappa number of 10. Oxidized white liquor is the primary alkali source (18 kg oxidized WL as NaOH/adt O_2 and 14 kg O_2/adt O_2).

The brown-stock wash consists of two stages of pre-oxygen washing using either wash presses or drum displacement (DD) filters can be used. Post oxygen washing is performed in a 2-stage DD washer before the oxygen bleached storage tower.

The bleaching plant is designed with the sequence D_{hot}(EPO)DP. The eucalyptus pulp is bleached to a final brightness of 90-91% ISO. Expected chemical consumption and conditions are summarized in **Table 4.2.**

Table 4.2. Expected chemical charges for the eucalyptus kraft pulp with the sequence D_{hot}(EPO)DP to 90-91%ISO brightness (kg/ADt). ClO_2 as ClO_2 and not as active Cl. Kappa number of pulp to bleaching: 10.

Stage	Temp (°C)	Time (min)	pH	ClO_2	O_2	H_2O_2	NaOH	H_2SO_4	SO_2 or $NaHSO_3$ as SO_2
D_{hot}	85-90	120	~3	6.5				6	
(EPO)	85-90	60	10.5-11		3	1	9		
D	75-80	120	3.5-4	3.5			1		0.5
P	75-80	120	~10			5	5		1 (a)

(a) After P-stage

Chlorine dioxide is generated using an AkzoNobel SVP-SCW or an Erco R10 process producing neutral saltcake (mainly Na_2SO_4).

4.2 Bleached market pulp softwood (pine) mill

The softwood raw material consists of 50% pine (*Pinus sylvestris*) and 50% spruce (*Picea abies*).

Continuous cooking is used (e.g. Metso Compact Cooking or Andritz DownFlow LoSolids) with 20.0% EA on wood and cooking temperature 143° C to a Kappa number of 30 and a yield of 47%.

Oxygen delignification is done in two stages without intermediate washing to a kappa number of 12. Oxidized white liquor is the primary alkali source (25 kg oxidized WL as NaOH/adt O_2 and 20 kg O_2/adt O_2).

The brown-stock wash consists of three stages of pre-oxygen washing using either wash presses or drum displacement (DD) filters can be used. Post oxygen washing is performed in a 2-stage DD washer before the oxygen bleached storage tower.

The bleach plant is designed using an D(EPO)DP sequence with conditions and chemical charges according to **Table 4.3.**

Table 4.3. Expected chemical charges for the SW kraft pulp with the sequence D(EPO)DP to 90%ISO brightness (kg/ADt). ClO_2 as ClO_2 and not as active Cl. Kappa number of pulp to bleaching: 12.

Stage	Temp (°C)	Time (min)	pH	ClO_2	O_2	H_2O_2	NaOH	H_2SO_4	SO_2 or $NaHSO_3$ as SO_2
D	70	60	~2,5	9				4	
(EPO)	80-85	75	10.5-11		6	1	13		
D	75-80	150	3.5-4	5			1		0.5
P	75-80	150	~10			6	6		1.5 (a)

(a) After P-stage

Chlorine dioxide is generated using an AkzoNobel SVP-LITE or an Erco R8 process. The acidic sesquisulphate produced ($Na_3H(SO_4)_2$) is used as partial supply of acid used for soap splitting, which is included in the SW model mill.

5 Electrolysis of sodium sulphate

A realistic and technically feasible process for splitting sodium sulphate is an electrochemical process electrolyzing the sodium sulphate into caustic and acid. The obvious place to start for a first installation is the saltcake from the chlorine dioxide process since it is less complex technically. In order to further reduce the need of purchased caustic and/or sulphuric acid the ESP dust, being rich in sodium sulphate may also be used as raw material. This is schematically represented in **Figure 5.1**.

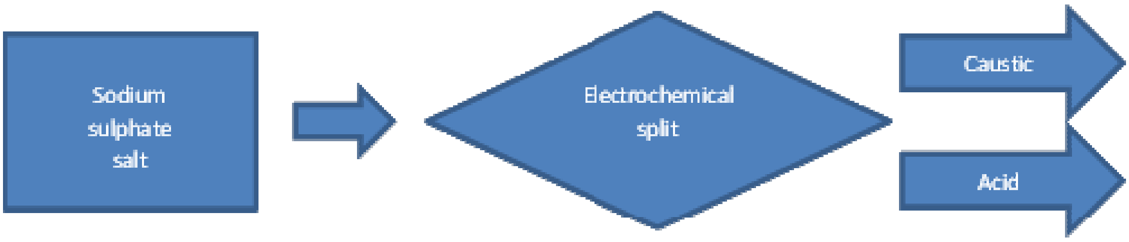

Figure 5.1. Schematic representation of splitting sodium sulphate into caustic and acid.

The main alternative configurations for electrolysing the sodium sulphate are described below. There are two main alternatives; a two compartment electrolyzer and a three compartment electrolyzer (Cloutier 1999, 2008, 2008, 2009, Oloman 1996). Further alternatives for sodium sulphate split may comprise electrodialysis, using bipolar membranes (Lundblad 2012, Oloman, 1996, Paleologou 1996, Simmrock 1996), and chemical processing (e.g. Glasson 1965, Moeck et al 1976, Ling et al 2005, Lioliou, 2006 and Amjad 1985). All of these are here considered less attractive due to that no commercial process has been realised and most of these alternative would mean high investment to relatively small conversion.

In all electrochemical processes the separation of Na and S is governed by an electrostatic field creating migration of ions over an ion exchange membrane (general reference).

5.1 Two compartment electrolyzer

The two compartment electrolyzer, **Figure 5.2** is very similar to the modern membrane based chlor-alkali electrolyzer concept and is thus technically proven for that application. The acid and the base are electrochemically generated by splitting water. On the anode side water is oxidized into oxygen and protons and on the cathode side water is reduced into hydrogen and hydroxide. By dividing the cell with a cation exchange membrane (CEM), which conducts the sodium ions but not sulphate ions, sodium may migrate from the anode (+) to the cathode (-) side of the cell. Hence, in the cathode compartment sodium hydroxide will be produced and in the anode compartment sulphuric acid mixed with sodium sulphate will be produced, see **Figure 5.2.**

The electrochemical reactions are the following;

Cathode:	$2H_2O + 2e^- \rightarrow 2OH^- + H_2$	(E^0=−0,83 V)
Anode:	$H_2O \rightarrow 2H^+ + ½O_2 + 2e^-$	(E^0=1,23 V)
Total:	$3H_2O \rightarrow 2OH^- + H_2 + 2H^+ + ½O_2$	

Including the counter ions the overall reaction is;

$$Na_2SO_4 + 3H_2O \xrightarrow{2F} 2NaOH + H_2SO_4 + H_2 + \tfrac{1}{2}O_2$$ (**Reaction 1**)

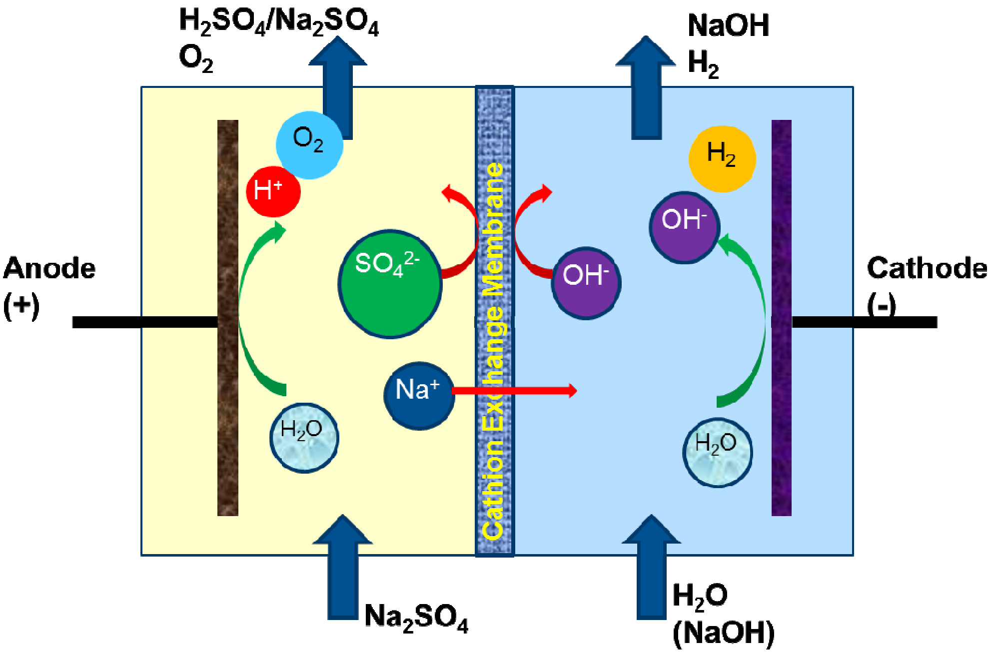

Figure 5.2 The two compartment set up.

The cell chemistry follows a simple stoichiometry where one mole of protons and hydroxide ions is formed for each mole of electrons passes through the circuit interconnecting the two electrodes, and one mole of Na^+ must be transported through the cation exchange membrane (or H^+, but that is a loss). Any back migration of hydroxide through the membrane or migration of hydrogen ions instead of sodium ions through the membrane will lead to a current efficiency loss. In addition, undesired electrode reactions lead to current efficiency losses, e.g. impurities of chlorides that will get oxidized forming chlorine instead of protons. Hence, it is the performance of the electrode reactions as well as the selectivity of the membrane that decides the current efficiency of the salt split.

If impurities that can participate in electrode reactions are kept at low levels in the electrolyte, the main contribution to loss in current efficiency is the migration of hydrogen ions through the cation exchange membrane to the cathode compartment neutralising the caustic. The loss of hydrogen ions over the membrane increases as the ration H^+/Na^+ increases in the anode compartment. Due to the limited selectivity of the CEM an economic feasibility is more likely if conversion of sodium sulphate is limited to approximately 50-60%. Consequently the product from the anode side in the two compartment set up is an acidic sodium sulphate solution ($Na_2SO_4 \cdot H_2SO_4(aq)$).

It may be considered to use an anion exchange membrane (AEM) and instead feed the sodium sulphate to the cathodic side. Then the sulphate ions will migrate over the AEM and a pure anolyte, acid, would be obtained. In this work however, when referred to a two compartment set up a CEM is considered. The reasons are several but mainly the fact that CEM are more robust and durably then AEM and that a sulphate free caustic is considered more attractive than a sodium free acid.

5.2 Three compartment electrolyzer

The limitation in conversion in the two compartment cell may be overcome by combination of a CEM and an AEM in the same electrolytic cell, **Figure 5.3**. The same chemical reactions as above occur.

The products are pure caustic and pure sulphuric acid more or less free from sodium sulphate. Thanks to the dual membrane arrangement the conversion of sodium sulphate into caustic and acid may be almost 100%. The drawback is a far more complex cell arrangement and as the distance and resistance between the electrodes increases which increases the power consumption and the operational cost. The higher power consumption is somewhat compensated by the often higher current efficiency, which gives that the power consumption per kilo of product might not differ considerably to the two compartment set up.

In addition the electrolyzer itself is more expensive and the technology not as developed as for the two compartment case. The three compartment electrolyzer is also a less established technology. The complexity of the electrolyzer is higher why the systems have not been put in practical use other than for some few applications. A second aggravating circumstance is that the anion exchange membranes are not as well-developed as cation exchange membranes.

There are however commercial electrolyzers and therefore, despite the higher cost, this solution may be more attractive than the two compartment arrangement.

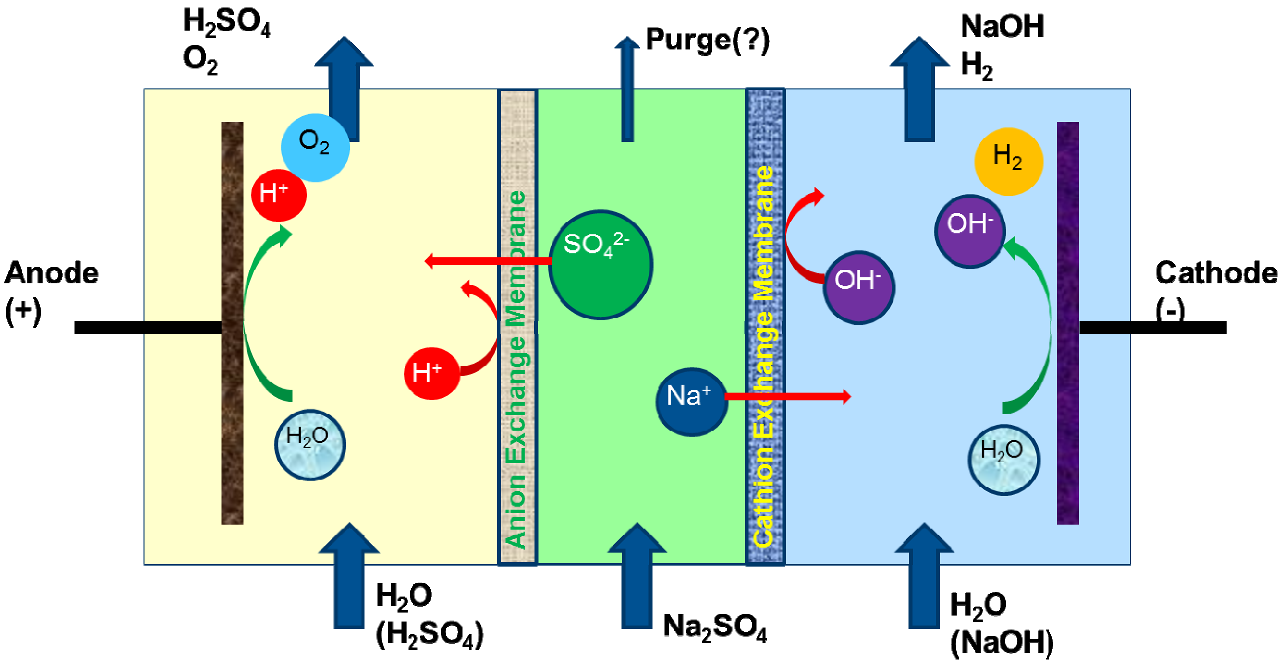

Figure 5.3 The three compartment set up.

5.3 Comparison between two and three compartment electrolyzers processes

Some parameters of the two processes are compared in **Table 5.1**.

Table 5.1 Comparison of two and three compartment electrolyzer systems for sodium sulphate splitting.

	Two compartment electrolyzer system	**Three compartment electrolyzer system**
	Figure 5.2	**Figure 5.3**
Electrolyzers available on the market	Many different suppliers of electrolyzers, the chlor-alkali market is very large industry	Few suppliers have three compartment electrolyzers available. Only a few applications exist.
Membranes	Cation exchange membranes – many different and well proven membranes exists.	Same cation exchange membranes. Needs also anion exchange membranes which are more sensitive to harsh conditions
Anode reaction	$H_2O \rightarrow 2H^+ + ½O_2 + 2e^-$	
Cathode reaction	$2H_2O + 2e^- \rightarrow 2OH^- + H_2$	
Possible conversion of sodium sulphate to acid	50-60%, limited by loss of current efficiency when proton gradient over the membrane becomes too high	Almost complete
Current efficiency	50-70%	
Cell voltage	3-6V/cell	
Operating temperature	60-80 ºC	
Current density	2-5 kA/m^2	
Energy consumption	4000 kWh/ton NaOH*	
Caustic purity	Comparably to commercial NaOH from membrane plants.	
Caustic strength	Up 10-15 wt% NaOH	
Acid purity	Contains approximately 50/50 /H_2SO_4	Pure H_2SO_4, may be very high purity.
Acid strength	Up to 20 wt% H_2SO_4, containing 30 wt% Na_2SO_4. This is equivalent to 50 wt% $NaHSO_4$	Up to 20 wt% H_2SO_4, no Na_2SO_4.
Hydrogen purity	Pure, concentrated	
Oxygen purity	Concentrated, scrubbing from Cl_2 necessary if feed Na_2SO_4 contains chloride	
Hypochlorite by-product	Depends on chloride impurity level in the feed stock	
Investment cost	Comparable to chlor-alkali plant cell rooms of the same installed electrode area.	Significantly higher due to arrangement for extra compartment (feed/outlet system and extra membrane).
Maintenance cost	Comparable to chlor-alkali plant cell rooms	Higher cost, due to mid-compartment and extra membrane.
Overall economics	Depends on integration to mill. In general it might be considered that despite the higher capital cost for the three compartment system these offers better integration to the mill and hence a better economical option.	

*Should be compared with energy consumption in the ChlorAlkali process 2200 kWh/ton NaOH
(Oloman 1996)

5.4 Brief description of the electrochemical process

The steps in the overall process are (see **Figure 5.4**):

1. Sodium sulphate feed stream
2. Pre-treatment to remove impurities
3. Anolyte system
4. Electrolyzers
5. Catholyte system
6. Post-treatment of gas streams

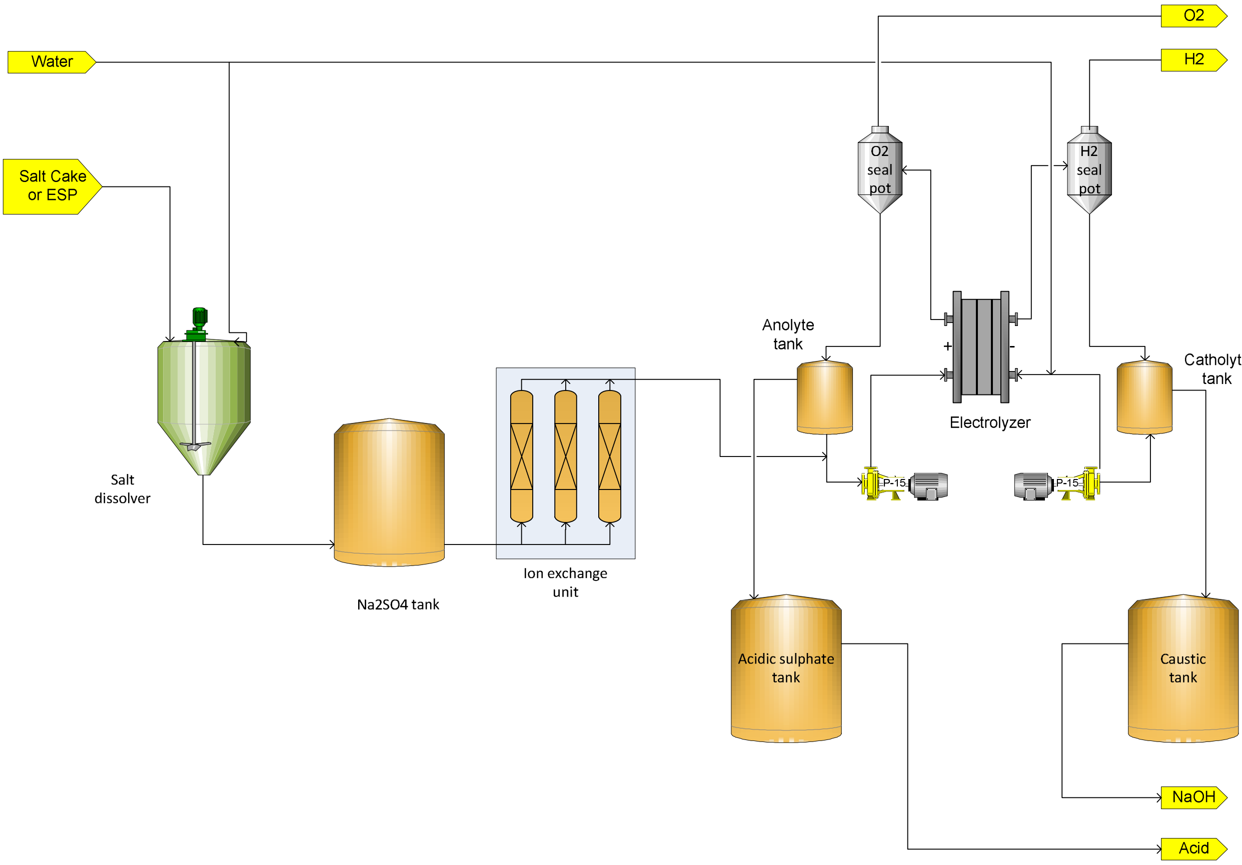

Figure 5.4 Process flow diagram

Steps 1 and 2 (dissolving and pre-treatment) are treated in **Chapter 7** and Step 6 is discussed in **Chapter 8**. Steps 3-5 which concerns the electrolysis are described below.

The two compartment electrolysis system can be divided in three parts; anolyte, catholyte and electrolyzer system. The anolyte recirculates over the anode side of the electrolyzer. The catholyte recirculates over the cathode side of the electrolyzer. The sodium sulphate solution is feed into the anolyte circulation as a makeup. The product acidic sulphate is bleed from the same circulation to the acid buffer tank. A main purpose with the anolyte tank is to separate the oxygen from the anolyte.

On the catholyte side circulation is maintained over a catholyte tank. The catholyte is the sodium hydroxide solution produced. In the catholyte tank hydrogen formed in the electrolyzer is separated from the catholyte. The hydrogen is removed for further use in e.g. the lime kiln (se Chapter 8). The catholyte is returned to the cell. The produced caustic stored in a new storage and buffer tank

The electrolyzer may be chlor-alkali type electrolyzers, preferably commercial two compartment zero gap technology membrane cells for chlor-alkali production. Each electrolyzer is made out from a larger number of cells (cf **Figure 5.2**) stacked in series, **Figure 5.5**. For sulphate splitting the anode electrodes are oxygen evolution electrodes, whilst the cathodes are standard chlor-alkali hydrogen evolution electrodes. The anolyte and catholyte compartment is separated with a cation ion exchange membrane.

The three compartment electrolysis system is very similar to the above described two compartment system. It also contains anolyte, catholyte and electrolyzer system, but in addition there is a mid-compartment system in which the sodium sulphate is added (instead of in the anolyte system). From the mid-compartment system a small purge is taken to allow control of impurities which cannot pass over the membranes.

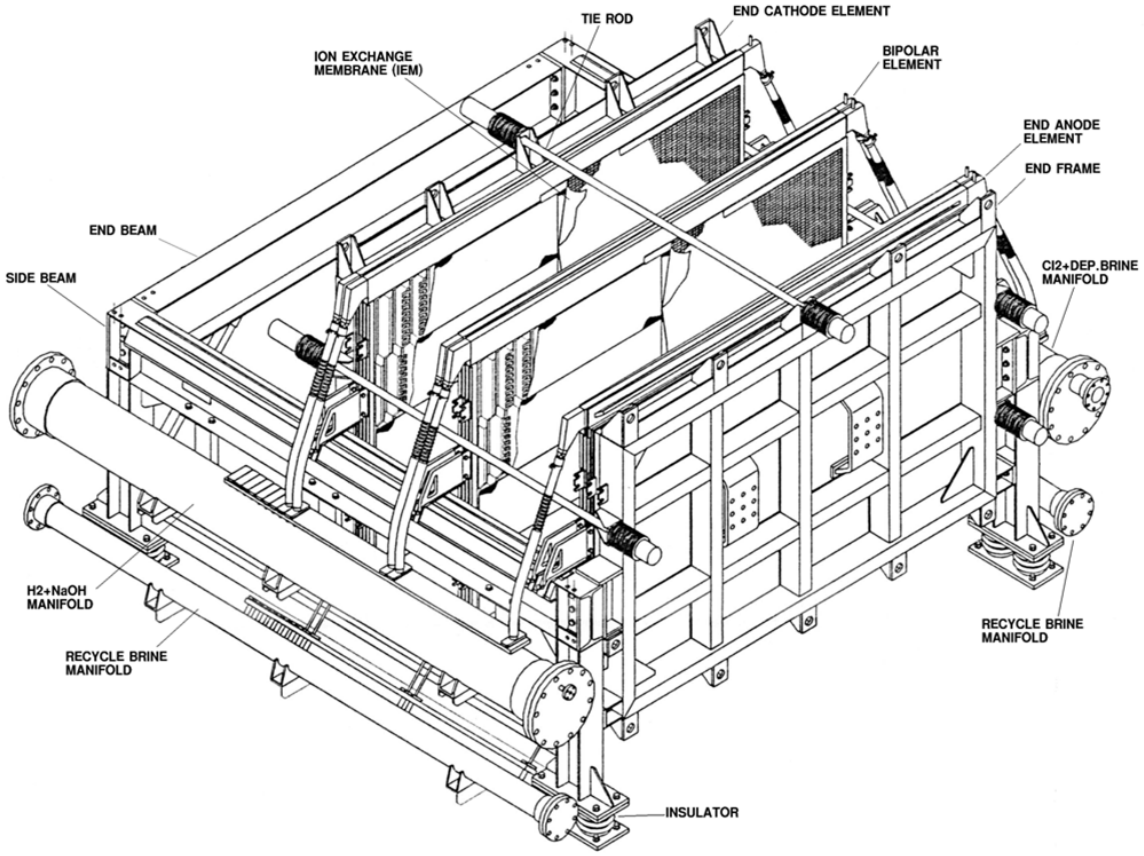

Figure 5.5 n-BiTAC Chlor alkali (two compartment) electrolyzer, picture courtesy of Permelec Electrode Ltd.

5.5 Feed sodium sulphate requirements

5.5.1 Acidic or neutral saltcake

It is beneficial to use neutral saltcake rather than acidic (sesqui) saltcake as feed material to the salt split unit. This is in order to achieve high current efficiency in the electrolyzer and to produce as much caustic as possible.
If the sodium sulphate raw material would be sesquisulphate (SVP-LITE or R8 process) or even more acidic spent acid (HP-A or Mathieson process) the protons in the sulphate raw material has to be considered. This will limit the possible conversion/the salt split; else the current efficiency will quickly erode. This is elucidated by the examples below.

Example A: A neutral sodium sulphate is fed to a two compartment salt split unit, the neutral sodium sulphate will be converted in to a mixture of sodium sulphate and sulphuric acid, with the H^+/Na^+ ratio of for instance 1/1. Stoichiometric amount of protons and caustic is produced, as described in **Reaction 1**. In addition the SCW unit will produce sulphuric acid. In the example described in **Figure 5.6**, you start with 1 mole of sodium sesquisulphate, after the metathesis reaction in the SCW process step you have two process streams; one of 0,5 mole of sulphuric acid and one of 1,5 mole of sodium sulphate. The neutral sodium sulphate is fed to the salt split unit where half of the sodium ions are going to be exchanged to hydrogen ions, hence 1,5 mole of protons need to be produced, requiring 1,5 mole of electrons. Stoichiometric amount (1,5 mole) of caustic is co-produced simultaneously. The salt mix product out of the salt split unit contains 0,75 mole of sulphuric acid mixed with 0,75 mole of sodium sulphate.

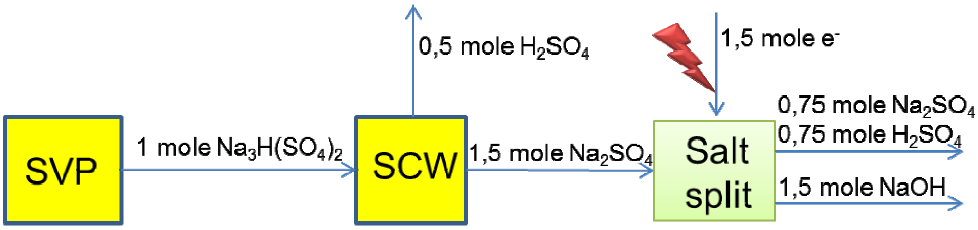

Figure 5.6 The unit operations and forms of sulphate salt in the different process steps when neutral sodium sulphate is fed to the salt split unit at a conversion of 50%, i.e. H^+/Na^+ ratio of 1/1.

Example B: The salt split unit is fed with 1 mole of sodium sesquisulphate instead and the goal is a mixture with the same conversion as in case a, i.e. 50% conversion and H^+/Na^+ ratio of 1/1, see **Figure 5.7**. The salt is already acidic, and hence less sodium ions are needed to be exchanged with hydrogen ions to reach the same conversion. To reach the conversion of 50%, one mole of protons is needed to be produced requiring 1 mole of electrons. Stoichiometric amount of caustic (1 mole) is co-produced. Hence, 33% less caustic and 20% less acid is produced in Example B compared to Example A (counting also the acid out of the SCW unit, in Example A) but also 33% less electrons are needed.

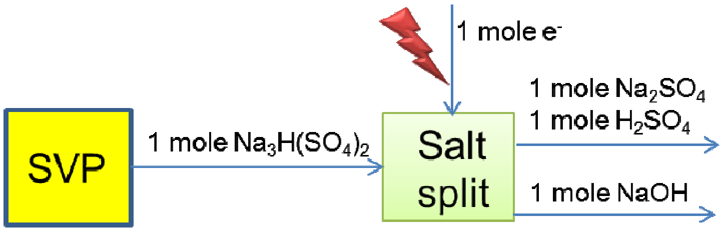

Figure 5.7 The unit operations and forms of sulphate salt in the different process steps when sodium sesquisulphate is fed to the salt split unit, at a conversion of 50%, i.e. H^+/Na^+ ratio of 1/1.

There is a possibility to produce as much caustic as in **Example A** also with the staring material of sodium sesquisulphate by going to a higher conversion i.e. a higher H^+/Na^+ ratio. In **Example C**, the starting material is 1 mole of sodium sesquisulphate fed directly to the salt split unit (**Figure 5.8**). The same amount of caustic as in **Example A** will be produced, i.e. 1,5 mole of caustic, this will require 1,5 mole of electrons and 1,5 mole of protons will be co-produced. Hence 1,5 mole of the sodium ions in the sesquisulphate will be exchanged to hydrogen ions. This will give an H^+/Na^+ ratio of 5/3 and a conversion of about 63%. Hence the acid salt product will be a mixture of 0,75 mole of sodium sulphate and 1,25 mole of sulphuric acid. The higher the conversion, the larger is the losses of protons through the membrane and the current efficiency drops. Hence, the energy consumption in **Example C** will be significantly higher than in **Example A** even if the amount of electrons required are the same. The total production of caustic and acid is the same as in **Example A** and **C**.

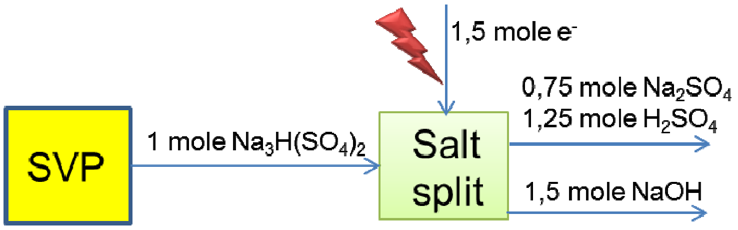

Figure 5.8. The unit operations and forms of sulphate salt in the different process steps when sodium sesquisulphate is fed to the salt split unit, at a conversion of ~63%, i.e. H^+/Na^+ ratio of 5/3.

5.5.2 Estimated purity required of the sodium sulphate

It is not fully explored what the detailed requirements for the raw material are. Impurities, such as multivalent ions, suspended material, chloride ions, carbonates and organics, need to be controlled. If not, the membrane life time may be shortened imposing significant costs for membrane exchange.

Based on literature data (O’Brien et al. 2007 and DuPont 2000), an estimate of the purity required of the sodium sulphate raw material is given in **Table 5.2**.

Failing to meet purity may result in:

- Multivalent ions precipitating inside the membrane. As the Me^{x+} ions migrate in the potential field it will encounter the high hydroxide concentration (high pH) within the membrane on the cathode side. Hence most ions will precipitate in the membrane as hydroxides or carbonates. If the precipitate is very fine as with highly insoluble material, the membrane voltage will increase. This is caused by cations with very low solubility like magnesium. If the impurity is moderately soluble it can precipitate in the membrane in crystals large enough to disrupt the polymer. This will cause a decline in current efficiency. Calcium is a common cation causing this type of failure. Eventually the conductivity and/or current efficiency will be too low and the membrane must be replaced.
- Suspended material constitutes a risk for fouling. Specifically in the three compartment system a purge will be needed.
- Chloride ions can be oxidized on the anode, creating elemental chlorine. Hence the oxygen must be treated (above mentioned scrubber system), and the resulting liquid be safely taken care of. In addition, the presence of elemental chlorine may, as always, create chloroorganics (AOX). Chlorides is finally a major parameter when it comes to controlling corrosion.
- Certain organic impurities in brine can swell the membrane, which results in a reduction of current efficiency. Organics in the sodium sulphate might in case of two compartment cells form “AOX”, see previous bullet. In the three compartment system most organics will stay in the mid-compartment system and must be purged from the system. In addition, organics might cause fouling of the membranes.
- Carbonates needs to be removed when using ESP dust as source of sodium sulphate to avoid extensive carbon dioxide gas formation upon acidification in the salt split process.

Table 5.2 Purity requirements of sodium sulphate raw material

Impurities	Typical limit $<4kA/m^2$	Typical limit $4\text{-}6kA/m^2$	Physical effects	Performance effects
Calcium	<30 ppb Combined Ca+Mg	<20 ppb Combined Ca+Mg	Precipitates in membrane	May reduce CE to 80%
Magnesium	See Ca	See Ca	Precipitates in membrane	Increases voltage
Strontium	<500 ppb	<400 ppb	Precipitates in membrane	Less severe than Ca
Barium	<1 ppm	<500 ppb	Precipitates in membrane	Less severe than Ca and Sr
Iodine	<1 ppm	<200 ppb	Is oxidized to iodate in anolyte and forms periodate in membrane. At higher conc. paraperiodate will precipitate damaging the membrane. At lower conc. iodine may precipitate with alkaline earth cations.	Reduces CE to 80-85% Less severe loss in CE
Aluminium **Silica**	Al <100 ppb SiO_2< 10ppm	Al <100 ppb SiO_2< 6ppm	Under acidic conditions aluminium will dissolve and combine with silicates and precipitate in membrane	May reduce CE to 90-93%
Sodium chlorate	$<20g/dm^3$	$<20g/dm^3$		Increases chlorate in caustic

Du Pont (2000) "Nafion® Perflourinated Membranes User's Guide"

6 Sources of sodium sulphate in the mill

There are many streams in a pulp mill containing sodium and/or sulphate. In practice however the two relevant sources are the by-product from the chlorine dioxide process, commonly referred to as “saltcake” after the filter, and the particles captured in the electrostatic precipitator on the exhaust gas from the recovery boiler (ESP dust).

Both streams are interesting as raw material for an electrochemical process splitting sodium sulphate into sulphuric acid and caustic (NaOH).

6.1 Saltcake from ClO_2-production

The amount and composition of sodium sulphate by-product from the chlorine dioxide manufacturing process depend on the type of process and how optimum this is run (Pelin et al. 2010, Pelin 2011). In practice the sulphate should be concentrated and in neutral shape (cf section 5.5.1), why the process in reality should be either SVP-SCW or R10 (or possible SVP-HP or R11).

By use of chlorine dioxide processes giving neutral sulphate, every ton of ClO_2 gives approximately 1.1 ton of sodium sulphate (or slightly less, according to stoichiometry 1.05 ton Na_2SO_4 per ton ClO_2). The neutral saltcake is preferably returned to the mill recovery system instead of severed, although it is not always needed from a Na/S-balance perspective. The saltcake however provides an advantage as it contains less contaminants than e.g. the ESP dust. If the corresponding amount of ESP dust is severed instead of the saltcake, a net reduction of K and Cl in the closed mill cycle can be achieved (see **Chapter 8.6**). This may be accomplished also with sesquisulphate, but then sulphur free make-up is required to balance the lower Na/S ratio in the saltcake.

In most softwood mills typically either a SVP-LITE or an R8 ClO_2 plant is instead installed. These processes give sodium sesquisulphate crystals, $Na_3H(SO_4)_2(s)$, as a by-product. Sesquisulphate are typically used in the mill’s tall oil plant to supply part of the acid demand. Alternatively it may be used as acid in the bleach line, however then the Na and S are emitted with the effluent. As mentioned above, sesquisulphate should preferably be first converted to neutral sulphate before electrolysis, but the conditions at each mill has to be evaluated case by case. By converting the SVP-LITE to SVP-SCW or the R8 to R10 process the acid sulphate, sodium sesquisulphate ($Na_3H(SO_4)_2$) is converted to neutral sodium sulphate and release sulphuric acid which is brought back to the chlorine dioxide reactor by the reaction:

$$2\ Na_3H(SO_4)_2 \rightarrow 3\ Na_2SO_4 + H_2SO_4$$

This so called metathesis reaction is often beneficial as the consumption of sulphuric acid for the chlorine dioxide manufacturing processes decreases by approximately 25% (Pelin 2010). It hereby offers a significant reduction of the sulphate to the total mill mass balance, why these neutral salt processes often are beneficial from a sustainability aspect (Tegstedt 2011).

In most eucalyptus mills SVP-SCW or R10 is already installed.

The Softwood mill model used in this report is based on a SVP-LITE/R8 providing a bleach line charge of 16 kg ClO_2 per ADt, why saltcake going into the mill/model is 17.8 kg/ADt.

The Eucalyptus mill model used in this report is based on a SVP-SCW/R10 providing a bleach line charge of 15 kg ClO_2 per ADt, why saltcake going into the mill/model is 16.7 kg/ADt.

The saltcake from the ClO_2-plant is significantly less contaminated than the ESP dust. Some examples of trace elements in saltcakes from both SVP-LITE and SVP-SCW processes are found in **Table 6.1** (AkzoNobel analytical data).

Table 6.1. Example of trace elements in saltcakes from different mills (AkzoNobel).

Reference		Mill A	Mill B	Mill C	Mill D	Mill E	Mill F
Location		South America	South America	Scand	Scand	Europe	South America
Process		SVP-SCW	SVP-SCW	SVP-lite	SVP-lite	SVP-lite	SVP-SCW
Al	mg/kg		0.19	0.23			
As	mg/kg		0.80				
Ba	mg/kg		0.17				
Ca	mg/kg	0.24	7.80	1.63	4.90	2.50	<0.5
Co	mg/kg						
Cr	mg/kg	6.92		1.83	2.90	2.50	7.00
Cu	mg/kg			0.19			
Fe	mg/kg	13.80	28.00	16.50	2.60	7.15	12.00
Mg	mg/kg	0.02	1.00	0.24	<0.3	0.40	<0.3
Mn	mg/kg	0.06	0.09	0.10	<0.03	0.06	0.04
Ni	mg/kg	0.20	0.13	0.35			
Si	mg/kg		1.00				
Sn	mg/kg						
Ti	mg/kg	0.49					
V	mg/kg		0.14				
Zn	mg/kg			0.67			

6.2 Recovery boiler dust (ESP dust)

An alternative source of Na_2SO_4 in the closed system for electrolysis is the ESP dust from the recovery boiler electrofilters. This is a significant amount corresponding to in the model mills 132 and 94 kg ESP dust/adt for the softwood and eucalyptus case respectively.

The ESP dust consists mainly of Na_2SO_4 but may also contain considerable amounts of Na_2CO_3 (up to 30%), chlorides and potassium. The Cl and K content must be kept below about 2 and 6 weight% respectively for reliable operation of the mill. In addition to this there is a number of other inorganic contaminants at lower concentrations. There can also be a small amount of organic carry-over from the recovery boiler, but this is normally not a problem in well-operated mills.

K is not assumed to cause any concern, but will perform similarly as Na in the electrolysis process. Chloride will however be oxidised to elemental chlorine contaminating the produced oxygen. As the pH is lowered during electrolysis, the carbonates in the ESP dust will react and form CO2, which will dilute the produced oxygen and chlorine stream. Since this reaction consumes acid it will lower the net production of H_2SO_4 from the electrolysis.

A number of different analyses of ESP dust are presented in **Table 6.2.** Most published data is from softwood mills and only one published study was found containing analyses of trace elements in ESP dust from eucalyptus pulping

Table 6.2. Composition of ESP dust from a number of mills (part 1).

Reference		Brown et al. 1998	Lundblad, 2012	Lundblad, 2012	Lundblad, 2012	Lundblad, 2012	Lundblad, 2012	Lundblad, 2012	Lundblad, 2012	Lundblad, 2012	Lundblad, 2012	Forssen et al, 2000	Forssen et al, 2000	Forssen et al, 2000
Location		Canada	Scand	Scand	Scand	Scand	Scand	Scand	Scand	Scand	Scand	Mörrum	Korsnäs SP5	Norrsundet
Feedstock		SW?	SW	SW/HW	SW/HW	SW	SW/HW	SW/HW	SW	?	?	SW/HW	SW/HW	SW
SO4	g/kg		593	540	564	398	592	578	511	588	575			
CO3	g/kg		54	74	58	219	55	86	125	47	21			
Cl	g/kg		13	20	26	9	7	12	12	11	1	20	17	4
Na	g/kg	263	294	312	303	323	291	307	313	284	255	279	279	285
K	g/kg	318	40	38	44	39	64	42	48	55	21	57	56	44
Al	mg/kg		11	15	9	10	8	4	8	7	33			
As	mg/kg													
B	mg/kg													
Ba														
Ca	mg/kg	500	63	169	79	64	64	76	32	58	850			
Cd	mg/kg		3	3	5	2	2	3	1	4	4			
Co	mg/kg													
Cr	mg/kg													
Cu	mg/kg													
Fe	mg/kg	100	8	16	10	16	30	11	39	14	77			
Mg	mg/kg		39	73	46	130	46	69	65	49	640			
Mn	mg/kg	273	38	43	32	54	47	57	37	49	70			
Mo	mg/kg													
Ni	mg/kg													
P	mg/kg													
Pb	mg/kg													
Sb	mg/kg													
Se	mg/kg													
Si	mg/kg													
Sn	mg/kg													
Ti	mg/kg													
Tl	mg/kg													
V	mg/kg													
Zn	mg/kg	68	50	110	78	53	56	59	45	49	62			
Organics	mg/kg													

*recalculated from amounts/adt to mg/kg ESP dust assuming 94 kg ESP dust/adt

Table 6.2 cont. Composition of ESP dust from a number of mills (part 2).

Reference		Forssen et al, 2000	Forssen et al, 2000	Forssen et al, 2000	Forssen et al, 2000	Forssen et al, 2000	Paleologou et al., 1996a	Paleologou et al., 1996a	Dahlbom & Wadsborn 2005	Dahlbom & Wadsborn 2005	Rapp & Pfromm 1998	Rapp & Pfromm 1998	Ek, 2014	Ek, 2014	Ek	Ferreira et al. 2004	Doldan 2011*
Location		Husum LDS	Husum HDS	Munksund	Vallvik ECF	Vallvik TCF	Non-coastal mill	Coastal mill	Frövi, Swe	Obbola, Swe	USA	USA	Kraft, Southern Sweden	Kraft, Mid Sweden	Kraft, North Sweden	Portugal	Uruguay
Feedstock		SW	SW	SW	SW	SW	SW?	SW?	SW/HW	SW	?	?	?	?	?	Euca Glob	Mixed Euca
SO4	g/kg						635	527			557	441				320-370	
CO3	g/kg						2	0			75	142				160-180	
Cl	g/kg	4	12	4	6	6	7	149	1	4	38	43				50-70	
Na	g/kg	301	306	294	29	29	300	302	304	378	263	268	307	331	338	30-40	
K	g/kg	21	20	32	53	54	33	57			110	86	60	37	23	40	
Al	mg/kg						ND	<100	1	6	6	25	6	3	1		9
As	mg/kg										3	3					
B	mg/kg										7	2					
Ba									1	1	3	4	1	1	1		
Ca	mg/kg						90	40	11	10	77	174	209	149	186		137
Cd	mg/kg										2	2	4	1	1		
Co	mg/kg										0	1					
Cr	mg/kg						20	20			<0.4	0					
Cu	mg/kg								<0.02	1	1	5	2	2	1		
Fe	mg/kg						70	600	<0.02	2	16	46	11	6	17		
Mg	mg/kg						30	20	7	20	28	41	105	71	95		46
Mn	mg/kg						30	20	1	8	24	24	48	33	42		22
Mo	mg/kg										1	2					
Ni	mg/kg										1	20					
P	mg/kg										19	65					23
Pb	mg/kg										4	9	4	1	1		
Sb	mg/kg										3	1					
Se	mg/kg										<2.2	<1.1					
Si	mg/kg								11	48							126
Sn	mg/kg										<15	<7.8					
Ti	mg/kg										1	2					
Tl	mg/kg										3	<0.59					
V	mg/kg										3	12					
Zn	mg/kg										23	78	78	62	51		
Organics	mg/kg							up t. 0.9 %-w			0.1 %-w						

*recalculated from amounts/adt to mg/kg ESP dust assuming 94 kg ESP dust/adt

6.3 Selection of model ESP dust

The composition of the major elements in the ESP dust (Na, K, Cl, SO_4, CO_3) is defined in the model mill and changes with the balance calculations. **Table 6.3** lists the levels for the SW reference case (1a) and the eucalyptus reference case (1b) with ESP purge for control of K and Cl levels. Note the low levels of K and Cl in the SW ESP dust compared to the eucalyptus ESP dust.

Since only one reference for ESP dust trace elements content from eucalyptus pulping was found and it does not deviate significantly from the softwood case, it was decided to use an average composition of all analyses for the trace elements content, **Table 6.3**. The highest and lowest value were removed before calculating the average.

Table 6.3. Composition of the ESP model dust for two reference cases without electrolysis.

ESP dust components		**SW ref case (1a)**	**Euca ref case (1b)**
Na	(%-w)	33	30
K	(%-w)	2.1	6.0
SO_4	(%-w)	56	55
CO_3	(%-w)	9	6
Cl	(%-w)	0.4	2.6
Al	(mg/kg)	9	9
Zn	(mg/kg)	45	45
Si	(mg/kg)	83	83
Ca	(mg/kg)	128	128
Mg	(mg/kg)	58	58
Mn	(mg/kg)	34	34
Ba	(mg/kg)	3	3
Fe	(mg/kg)	32	32
Cu	(mg/kg)	2	2

7 Pre-treatment before electrolysis

7.1 Demands on the pre-treatment process

Pre-treatment of the sodium sulphate stream is important for the economy and runnability of the electrolysis process. The extent and type of pre-treatment depends on what sodium sulphate source that is used, e.g. ESP dust requires significantly more pre-treatment than saltcake.

7.1.1 ESP dust

Membrane lifetime and current efficiency is affected by the purity of the ESP dust solution. In particular multivalent metal ions and organic material that can precipitate in and/or on membrane surfaces are problematic. In addition, chloride ions should be removed to avoid formation of Cl_2 during electrolysis.

The presence of carbonate in the ESP dust leads to the formation of carbon dioxide during electrolysis. Since the CO_2 would dilute the formed O_2/Cl_2-stream formed and also consume chemicals in the gas treatment system the carbonates should preferably removed before entering the electrolysis.

7.1.2 Saltcake from ClO_2-generation

Saltcake from the ClO_2-plant generally has only low levels of impurities and does not require extensive pre-treatment. In this case, ionic exchange is probably the only required step to bring impurities down to the required low level for electrolysis. To protect the ion exchange resin residual chlorine dioxide or sodium chlorate must be destructed. This may be done by addition of sodium bisulphite in the dissolving step.

7.2 Pre-treatment of ESP dust before electrolysis

A pre-treatment process of ESP dust before electrolysis, based on the commercially available PDP (Precipitator Dust Purification) process by NORAM (NORAM 2012, Jemaa et al. 1999) followed by additional steps to remove carbonates and further lower the multivalent metal ion content, is proposed according to **Figure 7.1**.

ESP dust is dissolved in water at a concentration close to saturation (Na_2SO_4). If necessary the carbonate level and/or the pH is adjusted. The remaining solids are removed using a pulse filter. Chloride ions are removed from the clear filtrate in a

Recoflo ion-exchange resin bed to the necessary level. The first steps of the pre-treatment are identical with the commercially available PDP-process marketed by NORAM which is currently installed in at least two locations in North America (**Figure 7.2**). The solution is further purified with ion exchange to remove remaining metal ions before entering the electrolysis unit.

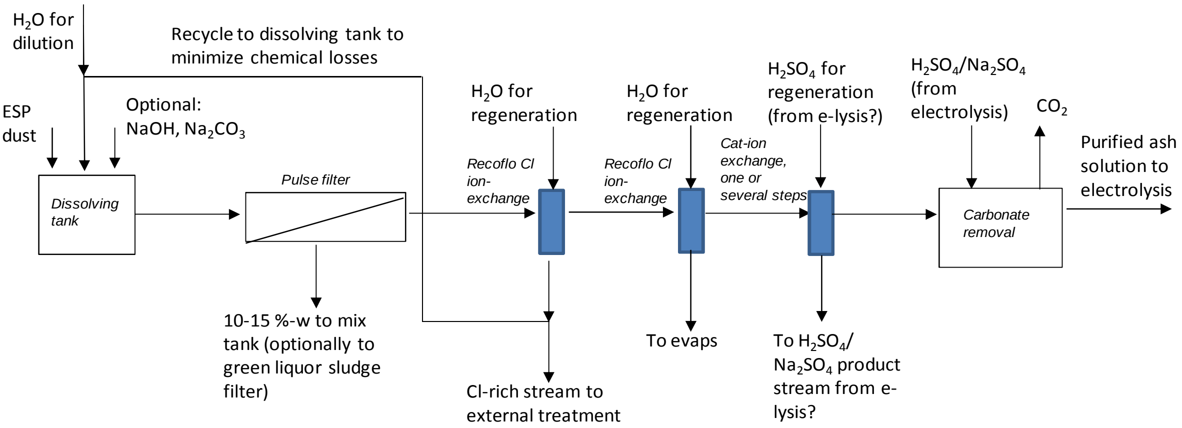

Figure 7.1. Proposed process for pre-treatment of ESP dust before electrolysis.

Figure 7.2. PDP process installation at RockTenn mill in Demopolis, USA (Mathis and Futterer 2013)

7.2.1 Dissolving in water

The first step is dissolving the ESP dust in warm water (40-60 °C) to produce a salt solution close to saturation (~30 %-w). Not all of the dust is soluble. What remains in solid phase is mainly hydrocarbon residues (unburnt material) and insoluble compounds of multi-valent metal ions (e.g. Fe, Ca, Mn, Zn), Brown et al. 1998. The resulting solids concentration in the solution is in the order of magnitude several hundred ppm.

7.2.2 Solids separation

NORAM proposes that the solids separation from the dissolved ESP dust solution is performed using a pulse filter. This filter is rather similar to the white liquor tube filters (e.g. Clarifil) used in the pulping industry. The salt solution is introduced into the tube and is filtered through polypropylene ”socks” on the tube elements. A filter cake is formed on the outside of the socks while the clear salt solution passes through and is collected at the top of the filter. When the pressure difference increases above a preset level the inlet flow is stopped and the filter tubes are backflushed with filtrate, thus removing the filter cake which then settles into the bottom of the filter. Periodically, sludge is removed from the bottom of the filter at a solids concentration of 10-20 %-w. The maintenance and cleaning requirements are very similar to the Clarifil type of filters (e.g. periodic acid wash and eventually replacement of the socks due to accumulation of acid insoluble residues and wear).

7.2.3 Removal of impurities in the solids separation step

In order to reduce e.g. the calcium content higher carbonate content in the ESP dust is beneficial (Landfors et al. 1996).Tests on ESP dust dissolved in warm water at 65 °C followed by solids separation showed that the calcium can be reduced by 88-97%, manganese almost completely and barium by 90-100% depending on carbonate concentration and pH. This study also claims that the content of aluminium and phosphate is reduced to a ”considerable extent” even though no experimental data is given. One option to optimize/maximize the metal removal could also be to adjust the pH with sodium hydroxide in order to further precipitate metals as hydroxides. In the suggested separation system

A similar approach is used by Paleologou et al. (1996b) showing reduction levels of Fe 99%, Mn 98%, Mg 98%, Cr 91% and Ni 82%. Jemaa et al. (1999) dissolved ESP dust in water and also reported high reduction levels of Al, Ca, Ba, Cu, Fe, Mg, Mn, Si and Zn. This is also in line with information from Metso where it is stated that the major part of the heavy metals stays in the solid phase in their ash leaching process (the Metso process, however, works at a different solubility level keeping most of the sodium sulphate in solid phase).

Treatment with active carbon is suggested in order to remove organic material from the solution (Paleologou et al. 1996b). Organic carryover is normally not a problem in a modern well-operated recovery boiler.

Table 7.1 shows the estimated reduction level of a number of impurities based on experimental data from the studies mentioned above.

Table 7.1. Expected reduction of undesirable elements by separation of undissolved material.

Element		**Al**	**Ba**	**Ca**	**Cr**	**Cu**	**Fe**	**Mg**	**Mn**	**Si**	**Zn**
Expected reduction level	(%)	77	49	91	91	99.5	99	82	95	77	99.5

7.2.4 Removal of chloride by ion exchange

The ”heart” of the PDP process is a Recoflo ion-exchange resin bed (patented by EcoTec) where sodium/potassium chloride is separated from the solution (**Figure 7.3**). The separation is conducted using two steps. In the first step the ESP salt solution is pumped up through the resin bed where sodium/potassium chloride is taken up by the resin. In the second step water is pumped down through the bed to regenerate the bed. To improve the efficiency, the first displaced volumes both from the ”upstroke” and ”downstroke” are collected separately and sent to the dissolving tank.

By changing the re-cycling conditions the so called SSU (Salt Separation Unit)-unit can either maximize chloride removal (at higher losses) or minimize losses (at about 20% lower chloride removal. In the conventional PDP process there is one ion-exchange step. In the pre-treatment process an additional step is proposed to further reduce the chloride level going to electrolysis to minimize Cl_2 formation.

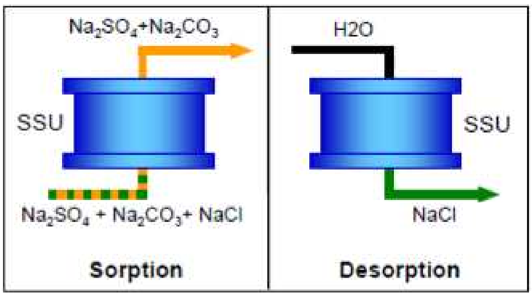

Figure 7.3. Eco-Tec ion exchange principles.

7.2.5 Cation exchange

The solution from the SSU-units is further purified in conventional cation exchange units (one or several steps, as required) to reduce the multivalent cation content to the levels required for the electrolysis process. This technology is established and well-proven for purifying salt solutions as feed to the membrane chlor-alkali process to the required levels. Ion exchange is best made at temperatures above 60°C.

Regeneration is normally made in two steps by reverting the resin to acid form with hydrochloric acid, (HCl) which eluates the multivalent metals. One option could be to use a small part of the produced sulphuric acid/sodium sulphate stream for re-generation. The resin is then neutralized with caustic and reverted to the sodium form and ready to use again.

7.2.6 Resulting salt stream after pre-treatment

Table 7.2 shows the composition of the resulting dissolved salt stream after pre-treatment according to the proposed scheme in the process as well as some intermediate streams (example from **Case 4b**). The product salt stream can be used as is (with lower membrane life/performance) or treated further with cation exchanger to the high quality demand required for chlor-alkali membranes (to get similar membrane life time/performance).

The only added component in the pre-treatment process is water (8.4 ton/ton ESP dust treated)

Table 7.2. Streams in the pre-treatment process based on 1 t ESP dust entering the process (example from **Case 4b**).

		ESP dust in	**After dissolving**	**After filter**	**After SSU-units**	**After ion exchange**	**Feed to electrolysis**
Flow	(t/h)	1.0	3.9	3.8	3.4	3.4	4.6
Na	(%-w)	30.4	8.5	8.5	7.3	7.3	6.3
K	(%-w)	5.0	1.4	1.4	1.2	1.2	1.1
SO4	(%-w)	55.7	15.3	15.3	13.9	13.9	14.5
CO3	(%-w)	7.7	2.1	2.1	1.9	1.9	0.0
Cl	(%-w)	1.2	0.7	0.7	2.0E-03	2.0E-03	1.5E-03
Al	(mg/kg)	9	2.4	0.5	0.5	3.4E-02	2.6E-02
Zn	(mg/kg)	45	10.9	0.1	0.0	3.5E-03	2.7E-03
Si	(mg/kg)	83	31.2	7.2	6.5	8.9	6.8
Ca	(mg/kg)	128	33.8	3.2	2.9	0.2	0.2
Mg	(mg/kg)	58	12.1	12.1	10.9	0.8	0.6
Mn	(mg/kg)	34	5.4	0.3	0.3	1.8E-02	1.4E-02
Ba	(mg/kg)	3	0.6	0.3	0.3	2.1E-02	1.6E-02
Fe	(mg/kg)	32	8.0	0.1	0.1	5.1E-03	3.9E-03
Cu	(mg/kg)	2	0.5	0.0	0.0	1.6E-04	1.2E-04

8 Integration of Na_2SO_4 electrolysis processes in the pulp mill

8.1 System constraints

When looking at possibilities with electrolysis of Na_2SO_4 it is necessary to include the constraints of the chemical balances:

- Balance for the closed liquor system must be maintained, in = out
- The ratio of Na/S ("sulphidity") in the mill must be maintained.
- K and Cl must be maintained at acceptable levels.

These boundary conditions were taken into account in the calculations. The maximum levels of K and Cl to ensure safe operations of the recovery boiler was set to 6 and 2 %-w of the ESP dust respectively.

Depending on the feed to the electrolysis process (saltcake or ESP dust) the effects of integrating the process with the pulp mill can be different.

8.2 Studied cases

A number of potentially interesting cases were defined and are summarized in **Table 7.1**, all using two compartment technology. In the description (a) denotes the SW mill, (b) the eucalyptus mill with ESP purge, (c) the eucalyptus mill with ash treatment system and (d) the eucalyptus mill with ash treatment system where sulphuric acid is used to remove CO_3 in the ESP dust.

The cases 2a-5a are compared to the corresponding reference mill (1a-b). Cases 7a-b are compared to the reference mill with LignoBoost included (6a-b).

Table 7.1. Studied cases.

Case		**Model mill**	**Feed to electrolysis**	**Acid**	**Caustic**	**K/Cl-handling**
1. Reference	**1a**	**SW**		-		Purge ESP dust
	1b	**Euc**		-		Purge ESP dust
	1c	**Euc**		-		Ash leaching, conventional
	1d	**Euc**		-		Ash leaching, H_2SO_4 added
2.	**2a**	**SW**	Saltcake	To ClO_2, whole demand produced	To closed part	Purge ESP dust
	2c	**Euc**	Saltcake	To ClO_2, whole demand produced	To closed part	Ash leaching, conventional
	2d	**Euc**	Saltcake	To ClO_2, whole demand produced	To closed part	Ash leaching, H_2SO_4 added
3.	**3a**	**SW**	Saltcake Purged ESP dust	To ClO_2, whole demand produced. Acid corresponding e-lysis of ESP dust to bleaching.	K/NaOH corresponding to e-lysis of ESP dust to bleaching, rest to closed part.	Electrolysis
	3b	**Euc**	Saltcake Purged ESP dust	To ClO_2, whole demand produced. Acid corresponding e-lysis of ESP dust to bleaching	K/NaOH corresponding to e-lysis of ESP dust to bleaching, rest to closed part.	Electrolysis
4.	**4b**	**Euc**	ESP dust	To ClO_2, whole demand produced.	K/NaOH to bleaching. Corresponding fresh caustic to closed part.	Electrolysis
5.	**5a**	**SW**	Saltcake ESP dust	Whole H_2SO_4 demand in closed part covered (ClO_2 and tall oil separation)	K/NaOH to bleaching. Corresponding fresh caustic to closed part.	Electrolysis
6. Reference + LignoBoost	**6a**	**SW**	-	-	-	Purge ESP dust
	6b	**Euc**	-	-	-	Purge ESP dust
7.	**7a**	**SW**	ESP dust	Whole H_2SO_4 demand in closed part covered (ClO_2 LignoBoost and tall oil separation)	K/NaOH to bleaching. Corresponding fresh caustic to closed part.	Electrolysis
	7b	**Euc**	Saltcake ESP dust	Whole H_2SO_4 demand in closed part covered (ClO_2 and LignoBoost)	K/NaOH to bleaching. Corresponding fresh caustic to closed part.	Electrolysis

8.3 Summary of balances

Flow sheets for all cases are given in **Appendix 1** while Na/S and K/Cl-balances in table form can be found in **Appendix 2**.

8.4 Electrolysis process

A summary of the expected consumption and production numbers in the electrolysis plant for the different cases is shown in **Table 8.2**.

Table 8.2. Expected consumption and production numbers in the electrolysis plant for the different cases.

Case		**1a**	**1b**	**1c**	**1d**	**2a**	**2c**	**2d**	**3a**	**3b**	**4b**	**5a**	**6a**	**6b**	**7a**	**7b**
Electrolysis unit:																
Feed electrolysis:																
-ESP dust	(kg/adt)								7.8	21.7	49.4	28.3			96.8	65.6
-Saltcake ClO_2	(kg/adt)					17.8	16.7	16.7	17.8	16.7		17.8			17.8	
Power consumption	(kWh/adt)					58.8	55.2	55.2	71.9	90.1	82.0	107.0			226.4	111.1
Produced NaOH (as 100% NaOH)	(kg/adt)					10.0	9.4	9.4	12.2	15.3	13.9	18.2			38.5	18.9
Produced H2SO4 (as 100% H2SO4)	(kg/adt)					12.3	11.5	11.5	14.1	16.7	11.5	18.8			34.7	15.3
Hydrogen production	(kg/adt)					0.3	0.2	0.2	0.3	0.4	0.4	0.5			1.0	0.5
Increased steam for evaporation demand																
-for conc. of H_2SO_4 in ClO_2 plant	(ton/adt)					0.05	0.05	0.05	0.05	0.05	0.00	0.05			0.05	0.00
- for evap of water from pre-treatment process	(ton/adt)								0.004	0.010	0.022	0.013			0.044	0.030

The power consumption for electrolysis amounts to between 55 to 206 kWh/adt, naturally dependent on how much sodium sulphate that is treated in the electrolysis plant. Since the total power consumption of the model mill is 719 kWh/adt this means an increase in power consumption with 8-30% for the mill which is highly significant. The steam consumption is comparatively low, in particular for the additional evaporation required for water from the pre-treatment process.

It should be noted that in the cases where saltcake is electrolysed the sulphuric acid production per amount of feed is higher than for cases where ESP dust is treated. The reason is the carbonate content of the ESP dust which reacts with some of the acid to form CO_2 during pre-treatment.

8.5 Effects on make-up chemicals (Na/S-balance)

The effect on the chemicals consumption in the mill is shown in **Table 8.3** (kg/adt) and **Table 8.4** (savings in chemicals, kton/y). In most of the studied cases the chemicals consumption is significantly reduced compared to the corresponding reference case. A negative number means that there is a net output of chemicals going from the closed system and used in the open part of the bleaching plant.

Note that the purged dust/CRP corresponds to the amount that is severed **directly** from the closed part of the mill. There is in many cases an outgoing stream of Na from the closed part, but instead of being severed it is sent to the bleach plant in the form of useful chemicals that will replace fresh chemicals and thereby reduce the total salt amount released to the recipient with a corresponding amount. In the cases **3a** and **3b** where H_2SO_4 is sent to the bleaching plant (mixed with Na_2SO_4), the Na_2SO_4 is an inert stream that will bypass the bleaching plant without reducing the chemical charge and should be counted as severed. The amounts are written in parenthesis in **Table 8.2.**
In one case (**3b**) where all saltcake as well as the purged amount of ESP dust is electrolysed the amount of H_2SO_4 produced is slightly larger than the consumption in the bleach plant. To compensate for the sodium and sulphur lost a significant amount of sodium sulphate make-up has to be purchased.

The reference cases where a LignoBoost plant is included (**6a** and **6b**) clearly shows the strong negative impact on the Na/S-balance from the installation. The input of both H_2SO_4 and Na_2SO_4 as well as the amount of purged dust is significantly increased compared to the references without LignoBoost (**1a** and **1b**). With the installation of an electrolysis plant, most of the chemicals needed can be produced internally. In the case **7b**, only ESP dust is electrolysed, and a similar result to **7a** would be obtained if saltcake was included as feedstock as well (the amount of ESP dust is too small to supply the LignoBoost and the ClO_2-plant with sulphuric acid).

A detailed summary of Na/S in and outputs is given in **Appendix 2**.

Table 8.3. Effects on chemicals consumption in the mill (including the H_2SO_4 demand in both the closed parts of the mill and the bleaching plant and NaOH demand in the bleaching plant for reference.

Case		**1a**	**1b**	**1c**	**1d**	**2a**	**2c**	**2d**	**3a**	**3b**	**4b**	**5a**	**6a**	**6b**	**7a**	**7b**
H2SO4	(kg/adt)	19.3	11.5	11.5	12.9	6.5	0.0	3.3	4.7	-5.2	0.0	0.0	34.6	26.8	0.0	11.5
NaOH	(kg/adt)	15.2	6.6	5.8	6.7	2.1	-3.9	-2.4	-0.1	-9.2	-5.1	-4.0	30.8	21.4	-4.0	5.9
Na2SO4	(kg/adt)	0.0	5.7	0.0	0.0	0.0	13.6	10.6	0.1	23.0	5.3	3.2	0.0	0.0	3.1	0.0
Purchased oil to lime kiln	(kg/adt)	34.9	34.9	34.9	34.9	34.0	34.1	34.1	33.8	33.5	33.7	33.3	34.9	34.9	31.4	33.2
Purged dust/CRP	(kg/adt)	31.2	22.5	15.4	16.9	8.0	0.0	0.0	(8.1)	(21.6)	0.0	0.0	58.9	43.1	0.0	14.4
H2SO4 demand, closed part	(kg/adt)	19.3	11.5	11.5	12.9											
H2SO4 demand, bleaching	(kg/adt)	4.0	5.0	5.0	5.0											
NaOH demand, bleaching	(kg/adt)	20.0	15.0	15.0	15.0											

A general conclusion is that the total chemicals consumption is reduced more in the softwood mills where the disturbances in the Na/S balance caused by the comparatively high sulphuric acid consumption in the closed mill cycle leads to high make-up chemicals consumption and a significant ESP dust purge. In eucalyptus mills where the Na/S is more or less in balance already before installing the electrolysis process, the internal generation of chemicals has to be compensated with a greater intake of make-up sodium sulphate, since sodium is removed from the system in form of NaOH to the bleaching plant.

8.6 Effects on K and Cl

Electrolysis of ESP dust can be an efficient kidney for K and Cl (see **Figure 8.1** where an example from **Case 4b** is shown) and also gives a possibility to control the sodium balance in the mill. The chloride is removed in the pre-treatment process to an extent of 85-90%. In the electrolysis, K behaves approximately the same way as Na and migrates through the membrane and forms a mixture of KOH and NaOH. If the produced K/NaOH is used in the open part of the bleach plant instead of fresh sodium hydroxide, and the corresponding amount of fresh sodium hydroxide is taken into the closed parts of the mill instead, there will be a significant purge of potassium. Approximately 52-56% of the K in the ESP dust entering the electrolysis process will be purged in form of a useful chemical in this approach (with the assumption that the membrane has the same selectivity for K as for Na).

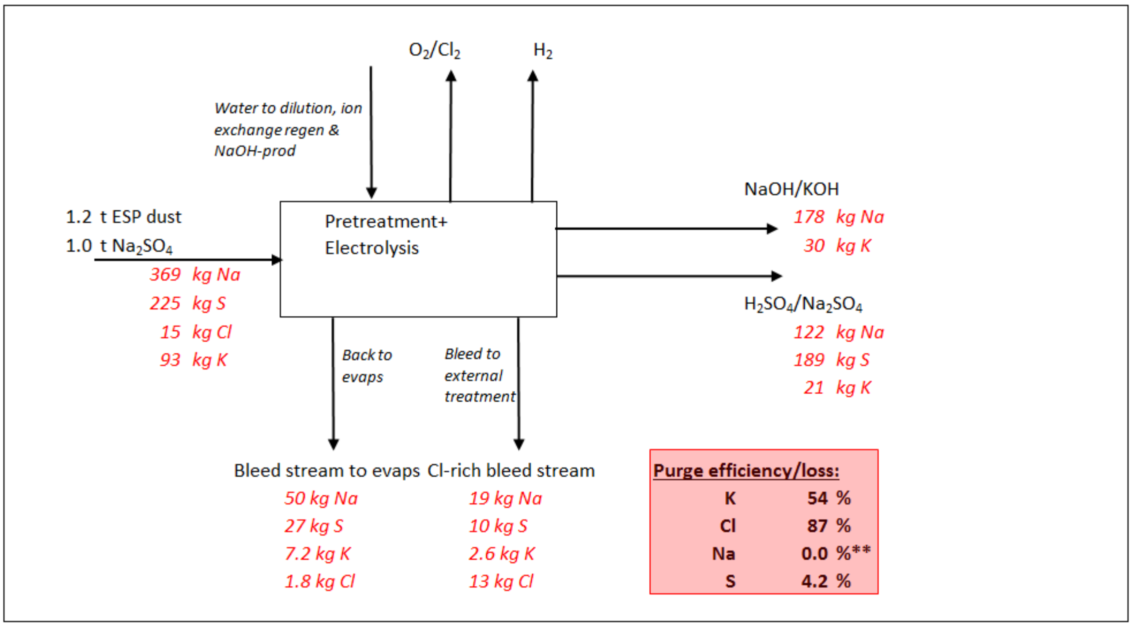

Figure 8.1. Pre-treatment and electrolysis of ESP dust as a kidney for K and Cl (example from Case 4b).

Some sodium is lost together with the chloride-rich stream in the pre-treatment plant. There is also a significant input of sodium in the $NaClO_3$ stream to the ClO_2-plant which has to be balanced by the KOH produced and by not replacing some of the NaOH sent to the bleach plant together with the KOH.

8.7 Effects on ClO_2-generation

One possible use of the acidic anolyte stream from two compartment cell concept is to replace the fresh sulphuric acid for the chlorine dioxide production. This has consequences for the ClO_2-plant since the sulphuric acid is diluted as well as contains a significant amount of Na_2SO_4.

If the feed stream from electrolysis is assumed to be closed to saturated at 60°C with a composition of approximately 45wt% water, 23 wt% H_2SO_4 and 32 wt% H_2SO_4, replaces the fresh acid in a 24 tpd SVP-SCW unit the consequences would be:

- In the alternative scenario there is 2 kg water per kg acid. Hence the steam consumption increases with about 2 kg steam per kg ClO_2 (normally almost 6 kg/kg is required so this is an increase with almost 20%). The steam is in the normal case needed to evaporate the water in the chlorate feed and water used for flushing ducts etc in the slurry system.
- The sulphate load increase to the double amount. Therefore the filter systems will have to be twice as large as if fresh acid is used. Sesquifilters, sulphate filter and all pumps and vessels needs to be either replaced or parallel capacity installed.
- The increased water balance requires the reboiler, condenser and circulation pumps to be increased. Also the generator vessel diameter needs to be increased by approximately 20%.
- Due to the increased condensate flow the latent heat going into the absorber will increased why the cooling water temperature needs to be decreased by approximately 1ºC.

Hence the 24 tpd generator system would essentially need to be replaced by a complete 50 tpd generator and salt system – which is a large part of the chlorine dioxide plant. This leads to a significant investment. In addition to the investment, the operating costs would increase, mainly for steam and cooling water. For new installations the fresh acid system still needs to be installed (and maintained) as a back-up system.

8.8 Handling of gas streams from electrolysis

8.8.1 Hydrogen gas stream as lime kiln fuel

The generated hydrogen gas can be used to partially replace other fuel in the lime kiln. In the model mill the lime kiln fuel is assumed to be bark/wood. However, it is a more common situation that the lime kiln is fuelled with mineral oil.

As an example in Case 5a where 49 kg ESP dust/adt is treated about 0.35 kg H_2/adt is generated from the electrolysis. This corresponds to 50 MJ/adt which is about 3.6% of the total fuel demand for the lime kiln (assuming 34.9 kg fuel oil/adt). The yearly savings would be about 750 t fuel oil or, if the oil price is assumed to be 650 SEK/barrel, about 3.6 MSEK/y, which can motivate a smaller investment. To fire the hydrogen gas, a separate burner would likely have to be installed together with feeding system from the electrolysis plant to the lime kiln.

Another option is to fire the produced H_2 in the recovery boiler.

8.8.2 Oxygen stream

Oxidised white liquor is commonly used as an alkali source to oxygen delignification (~18-25 kg/Adt). The oxidation is normally conducted using air although pure O_2 is also a possibility.
Electrolysis of purified ESP dust solution leads to the generation of an oxygen gas stream (~38 kg O_2/ton ESP dust treated) containing in the order of magnitude 2% Cl_2 (~0.7 kg Cl_2/ton ESP dust treated) as contaminant if no air leakage is assumed. This is a negligible amount from a mill balance perspective.

This gas stream can be utilised/purified in a white liquor scrubber (using a surplus of white liquor) to produce partially oxidised white liquor which is subsequently sent to the existing white liquor oxidation plant. With Case 5a as example, 49 kg ESP dust/adt is treated to generate an amount of oxygen that could perform approximately 10-15% of the oxidation required to supply the O_2-bleaching plant with alkali. The chlorine gas reacts with sodium hydroxide in the white liquor to form sodium hypochlorite. The hypochlorite reacts further with sulphur species in the white liquor to form thiosulphate and/or sulphate and sodium chloride.

This does not lead to any significant savings in operating costs but the capacity of the white liquor oxidation system is increased and the costs for handling the Cl_2-gas from the electrolysis would be rather small.

An alternative to the white liquor scrubber is a hypochlorite scrubber system which is standard design in the chlor-alkali process. This is a caustic scrubber with recirculating solution over a chiller. Here hypochlorite is formed by the reaction:

Chlorine hydrolysis: $Cl_2 + OH^- \rightarrow ClO^- + H^+ + Cl^-$

The released oxygen is hence free from chlorine and can be released to atmosphere or used elsewhere. Caustic is used as make up in the scrubber. Alternatively sodium bisulphite may be used.

If only saltcake is used as feed to the electrolysis the gas stream will be more or less pure O_2 which can be used in either the recovery boiler combustion air system or in the white liquor oxidation plant.

8.9 Three compartment electrolyzer (qualitative effects)

Application of three compartment cells was not treated in detail since it is further from commercialization. Using a three compartment system, however, opens new integration opportunities mainly because of the “clean split” where pure H_2SO_4 is produced instead of a mix of H_2SO_4 and Na_2SO_4. A few interesting examples are given here:

- No additional sesquifilters, sulphate filter and related pumps and vessels would be needed if pure H_2SO_4 from a three compartment process is used for ClO_2 production (which is a significant part of the additional investment required).
- The produced diluted sulphuric acid can be used in the bleaching plant (without loss of sodium) while the corresponding amount of more concentrated sulphuric acid can be used in the ClO_2-plant. If only saltcake is used for electrolysis, the sulphuric acid used in bleaching is about 40% of the total acid needed in the ClO_2-plant. This would limit the increase in evaporation capacity needed in the ClO_2-plant.
- Higher conversion of sodium sulphate to NaOH and H_2SO_4 can be achieved with a three-compartment electrolyzer, which gives more produced chemicals for the same amount of supplied salt. This is interesting in e.g. **Case 3a** and **3b** where ESP dust that is currently purged from the system is treated. More chemicals would be produced for the same amount of feedstock.
- With the higher conversion rate, the purge efficiency of potassium will improve and less ESP dust needs to be treated to achieve the same kidney function.

9 Economic evaluation

The economic evaluation is based on the two compartment set-up. It should be remembered that the assessment is made for model mills, and that each mill needs to be evaluated on a case by case basis because of differences in chemical charge, losses, background levels of NPE's, etc.

9.1 Assumptions economic evaluation

The cost for chemicals, electricity and utilities used in the study are summarised in **Table 9.1**. It should be remembered that these are estimates only and that real prices are dependent on the current state of the market, amounts, geographic location (a rough division for South America and Scandinavia was made), logistics etc. Possible deposit costs/environmental fees for purging ESP dust is not included in the primary assessment, but is treated in the parameter study (**Chapter 9.**4).

Table 9.1. Estimated costs used in the economic assessment.

Item	**Unit**	**Cost Scandinavia**	**South America**
NaOH	SEK/ton	3 120	5 560
H_2SO_4	SEK/ton	790	1 660
Na_2SO_4	SEK/ton	1 800	2 000
Electricity	SEK/MWh	412	308
Steam	SEK/ton	60	60
Deposit cost	SEK/ton	0	0
Oil price	SEK/MWh	450	450

Other estimates used are:

- 4 ton steam/ton recycled H_2SO_4 to the ClO_2 plant for evaporation.
- 3.1 ton water/ton ESP dust treated will go back to the evaporators.
- Steam consumption in the evaporators corresponds to 6.8 ton water/ton steam.
- Produced hydrogen replaces fuel oil in the lime kiln.

9.2 Estimated operating costs

Using the prices and assumptions given in 9.1 the total operating costs have been estimated (see Table **9.2**). Under the assumptions given in 9.1, all cases have a positive economy with between 20-45 MSEK/y annual savings. The reference case with LignoBoost installed has very high costs in make-up chemicals compared to the other cases.

Table 9.2. Estimated operating costs (SEK/adt and MSEK/y) and annual savings (MSEK/y).

Case		**1a**	**1b**	**1c**	**1d**	**2a**	**2c**	**2d**	**3a**	**3b**	**4b**	**5a**	**6a**	**6b**	**7a**	**7b**
NaOH	SEK/adt	47.4	36.8	32.5	37.1	6.7	-21.9	-13.4	-0.5	-51.2	-28.4	-12.6	96.0	119.3	-12.5	32.8
H_2SO_4	SEK/adt	15.3	19.0	19.0	21.4	5.1	0.0	5.5	3.7	-8.6	0.0	0.0	27.4	44.4	0.0	19.0
Na_2SO_4	SEK/adt	0.0	11.4	0.0	0.0	0.0	27.2	21.2	0.2	46.0	10.7	5.8	0.0	0.0	5.6	0.0
Deposit cost	SEK/ADt	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Evaporation:																
-ClO_2	SEK/ADt	0.0	0.0	0.0	0.0	2.9	2.8	2.8	2.9	2.8	0.0	2.9	0.0	0.0	2.9	0.0
-Pretreat	SEK/ADt	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.6	1.3	0.8	0.0	0.0	2.6	1.8
H_2	SEK/ADt	0.0	0.0	0.0	0.0	-3.9	-3.6	-3.6	-4.8	-6.0	-5.4	-7.1	0.0	0.0	-15.0	-7.3
Power	SEK/ADt	0.0	0.0	0.0	0.0	24.3	17.0	17.0	29.6	27.7	25.2	44.1	0.0	0.0	93.3	34.2
Total cost	SEK/ADt	62.7	67.2	51.5	58.5	35.1	21.4	29.4	31.5	11.3	3.5	34.0	123.4	163.7	77.0	80.4
Total cost	MSEK/y	40.9	43.9	33.6	38.2	22.9	14.0	19.2	20.6	7.4	2.3	22.2	80.6	106.9	50.3	52.5
Total saving vs. reference	MSEK/y					**18.0**	**19.7**	**19.0**	**20.4**	**36.5**	**41.6**	**18.7**			**30.3**	**54.4**
related to LignoBoost	MSEK/y														11.5	12.7

9.3 Estimated investment and pay-back times

An estimated total investment for the process divided into pre-treatment, electrolysis and ClO_2-rebuild is given in **Table 9.3**. A scaling factor (S) of 0.6 for the pre-treatment process and 0.3 for the electrolysis was used to adjust for different sizes of the plants according to the equation:

$$\mathrm{Cost}_1 = \mathrm{Cost}_2 \left(\frac{\mathrm{Capacity}_1}{\mathrm{Capacity}_2}\right)^S$$

The cost for re-building the ClO_2-plant is assumed to be constant between the cases (same amount of H_2SO_4 going in for all cases). There is high uncertainty for all the estimates (at least ±30%)

There is a significant investment involved in all cases, between 120-240 MSEK. The economy is still positive with straight pay-back times between 3.2 and 9.4 years, see **Table 9.3**. It is interesting to notice that the two best cases (under the conditions applied) are eucalyptus mills where the saltcake is not treated. In general, the eucalyptus cases (denoted b) have better pay back times than the corresponding softwood case. This is due to the higher price levels of chemicals in South America (Brazil). For the LignoBoost cases, in particular for the eucalyptus mill, the pay-back times are low.

Table 9.3. Estimated investment and pay-back times.

Case		**2a**	**2c**	**2d**	**3a**	**3b**	**4b**	**5a**	**7a**	**7b**
Investment Pre-treatment	MSEK	0	0	0	14	26	42	30	63	50
Electrolysis	MSEK	78	76	76	87	98	106	104	136	123
Rebuild ClO_2	MSEK	43	43	43	43	43	43	43	43	
Sum	MSEK	121	120	120	144	167	191	177	242	173
Total savings	MSEK/y	18.0	19.7	19.0	20.4	36.5	41.6	18.7	30.3	54.4
Pay-back time	y	6.7	6.1	6.3	7.1	4.6	4.6	9.4	8.0	3.2

9.4 Parameter study

The most important parameters in the study in terms of economy (costs for NaOH, H_2SO_4, Na_2SO_4 and electricity together with CAPEX) was varied in the range 50% to 150% of the baseline value (see **Table 9.1** and **Table 9.3**) to see impact on the pay-back times. In addition, the impact of a possible deposit cost/environmental fee between 0 to 1500 SEK/ton was evaluated. The complete results are attached in **Appendix 3**.

The NaOH price is an important variable for all cases, exemplified for **Cases 2a**, **2c** and **4b** in **Figure 9.1**, **9.2** and **9.3** respectively. The electricity price is naturally also an important factor for an electrolysis process. In some of the cases (in particular for the eucalyptus **cases 2c, 2d** and **4b**) the Na2SO4 price also has a significant impact while in other cases the effect is minimal. The H2SO4 price is of less importance in all cases.

A deposit cost/environmental fee for purge of ESP dust would be a significant driver for an electrolysis process (see **Table 9.4**). Already a cost of 500 SEK/ton would bring the pay-back time for all except one case down below 5 years. At the highest level all cases are interesting.

No additive effects etc. of several variables were treated and there are also other factors that impacts the process economy.

Table 9.4. Impact of a deposit cost/handling fee on the payback time for the different cases.

Deposit cost/fees (SEK/ton)	**Cases 2a**	**2c**	**2d**	**3a**	**3b**	**4b**	**5a**	**7a**	**7b**
	Payback time (years)								
0	6.7	6.1	6.3	7.1	4.6	3.6	9.4	8.0	3.2
500	4.7	4.8	4.9	4.7	4.1	3.0	6.1	4.9	2.6
1 000	3.7	4.0	4.0	3.5	3.8	2.6	4.5	3.5	2.2
1 500	3.0	3.4	3.4	2.8	3.5	2.3	3.6	2.8	1.9

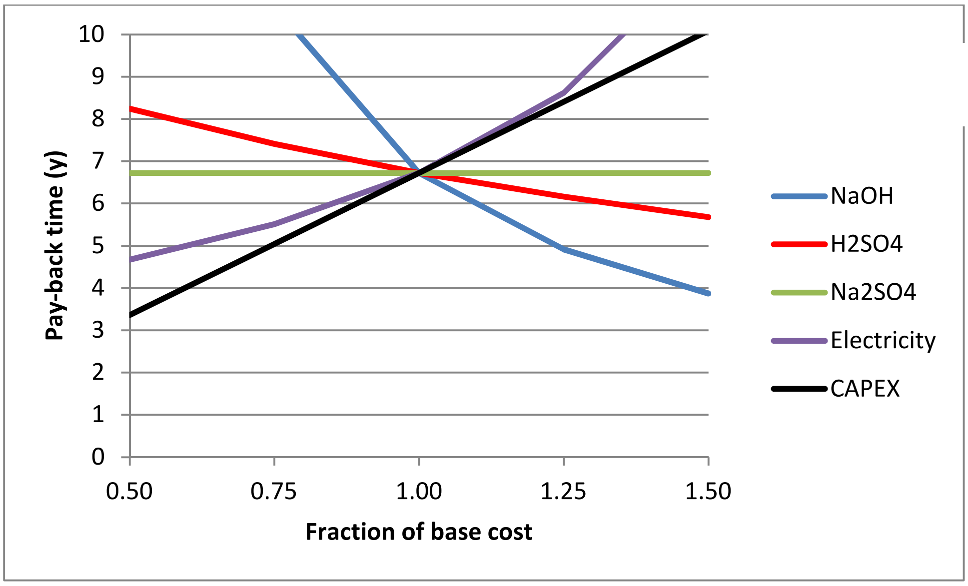

Figure 9.1 Impact of chemical prices, electricity price and CAPEX on pay-back time for Case 2a.

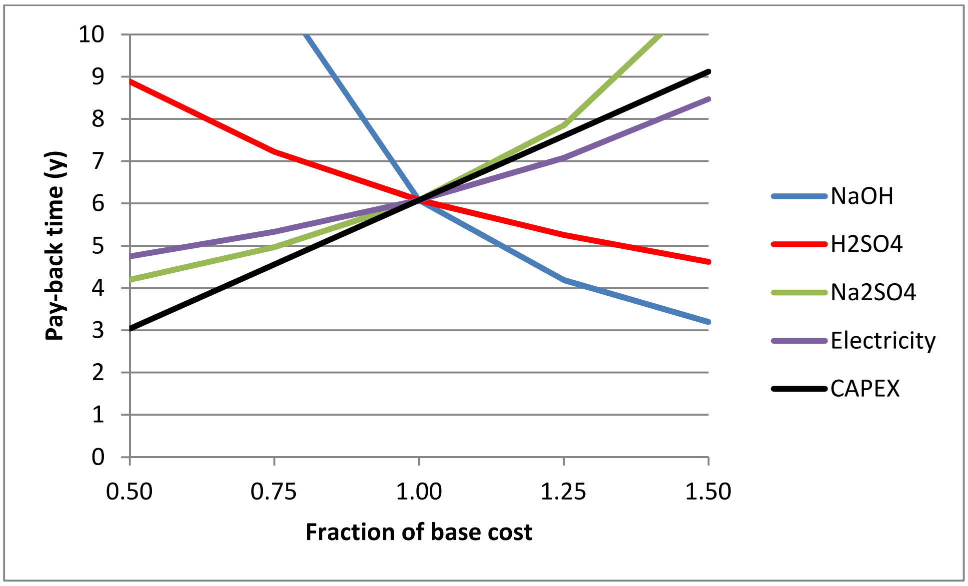

Figure 9.2 Impact of chemical prices, electricity price and CAPEX on pay-back time for Case 2b.

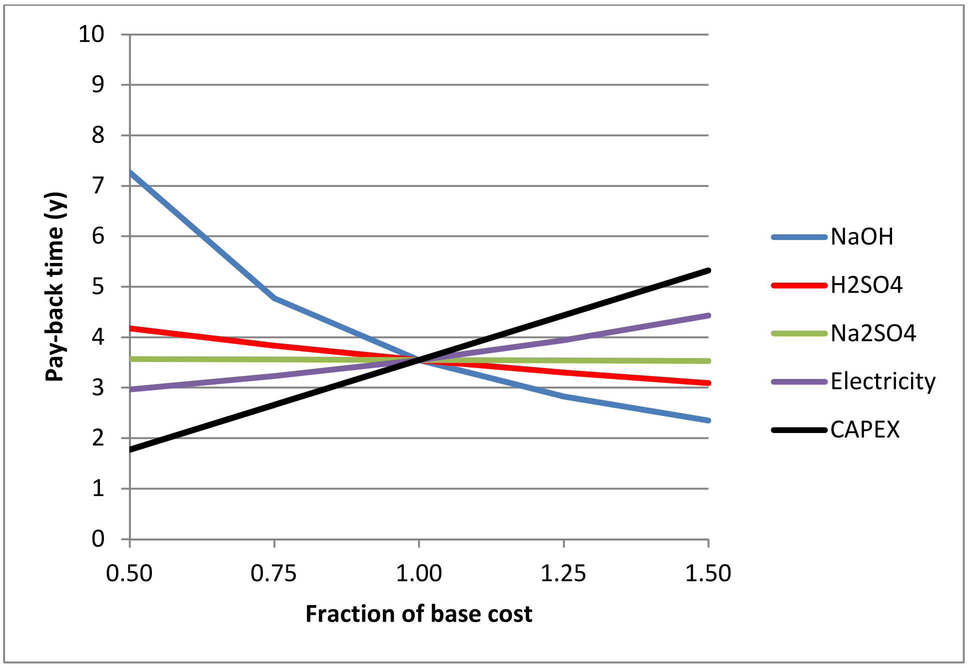

Figure 9.3 Impact of chemical prices, electricity price and CAPEX on pay-back time for Case 4b.

10 Conclusions

The most significant conclusions from this study of integrating an electrolysis process in a model mill (either SW or Euca) are:

Integration to the mill

- Using electrolysis to split sodium sulphate to sodium hydroxide and sulphuric acid can effectively reduce make-up chemicals consumption () and reduce ESP dust/salt emissions (60-~100%).
- The total chemicals consumption is reduced more in softwood mills where the disturbances in the Na/S balance caused by the comparatively high sulphuric acid consumption in the closed mill cycle leads to high make-up chemical costs and a significant ESP dust purge.
- Electrolysis of ESP dust can be an efficient kidney for K and Cl.
  - Approximately 52-56% of the K and 85-90% of the Cl (of the amounts fed to the electrolysis process) can be removed with minimal net losses of Na and S.
  - The potassium kidney function requires that the K/NaOH stream is used in e.g. the open part of the bleaching process and that the fresh NaOH used there is taken into the mill as replacement instead.
- The power consumption for electrolysis varied between 55 to 206 kWh/adt in the cases studied. Since the total power consumption of the mill is about 720 kWh/adt this means a highly significant increase in power consumption with 8-30%.
- Using the two-compartment cell set up produces a more diluted H_2SO_4-stream which also contains a considerably amount of Na_2SO_4. If the H_2SO_4-stream is used in the ClO_2 plant it requires significant additional filter and evaporation capacity. If the capacity is lacking the existing ClO_2-plant has to be extensively rebuilt.
- The electrolysis process gives two by-product gas streams:
  - The H_2 stream can be used as a lime kiln fuel. In one of the cases studied here 3% of the lime kiln fuel can be replaced for a value of about 3 MSEK/y (assuming fossil oil at 650 SEK/barrel).
  - The O_2/Cl_2-stream can be effectively treated in a white liquor scrubber, at the same time performing part of the oxidation work if OWL is used as alkali source in the mill.

Economic evaluation

- CAPEX was estimated to between 120-220 MSEK depending on case. The yearly savings was estimated to between 20-60 MSEK which gave straight pay-back times between 3-9 yrs depending on case.

- Price for NaOH, electricity and in some of the eucalyptus cases, Na_2SO_4 were found important in terms of operational costs. In addition, a deposit cost for ESP dust would significantly improve the process economy.
- Despite larger savings in chemicals for the softwood cases, the eucalyptus cases still show better pay-back times due to the higher price level for chemicals in South America (Brazil).

Electrolysis process

- A two-compartment electrolysis process was chosen as the main focus since it is well-proven technically in the chlor-alkali industry and many well-proven cation exchange membranes are available.
- A process, based on proven technology, where ESP dust is treated to reach purity levels required for a successful electrolysis has been proposed and evaluated.
- The three-compartment cell set up technology compares to the two-compartment variant as:
  - Increased technical uncertainty (less proven process).
  - Smaller rebuild of the ClO_2-plant required (evaporation capacity but not filter area).
  - More freedom in use of the produced H_2SO_4-stream which can be sent to e.g. the open part of the bleaching process if the Na/S-balance allows this.
  - A “clean” split of sodium and sulphur which allows even better control of the Na/S-balance.

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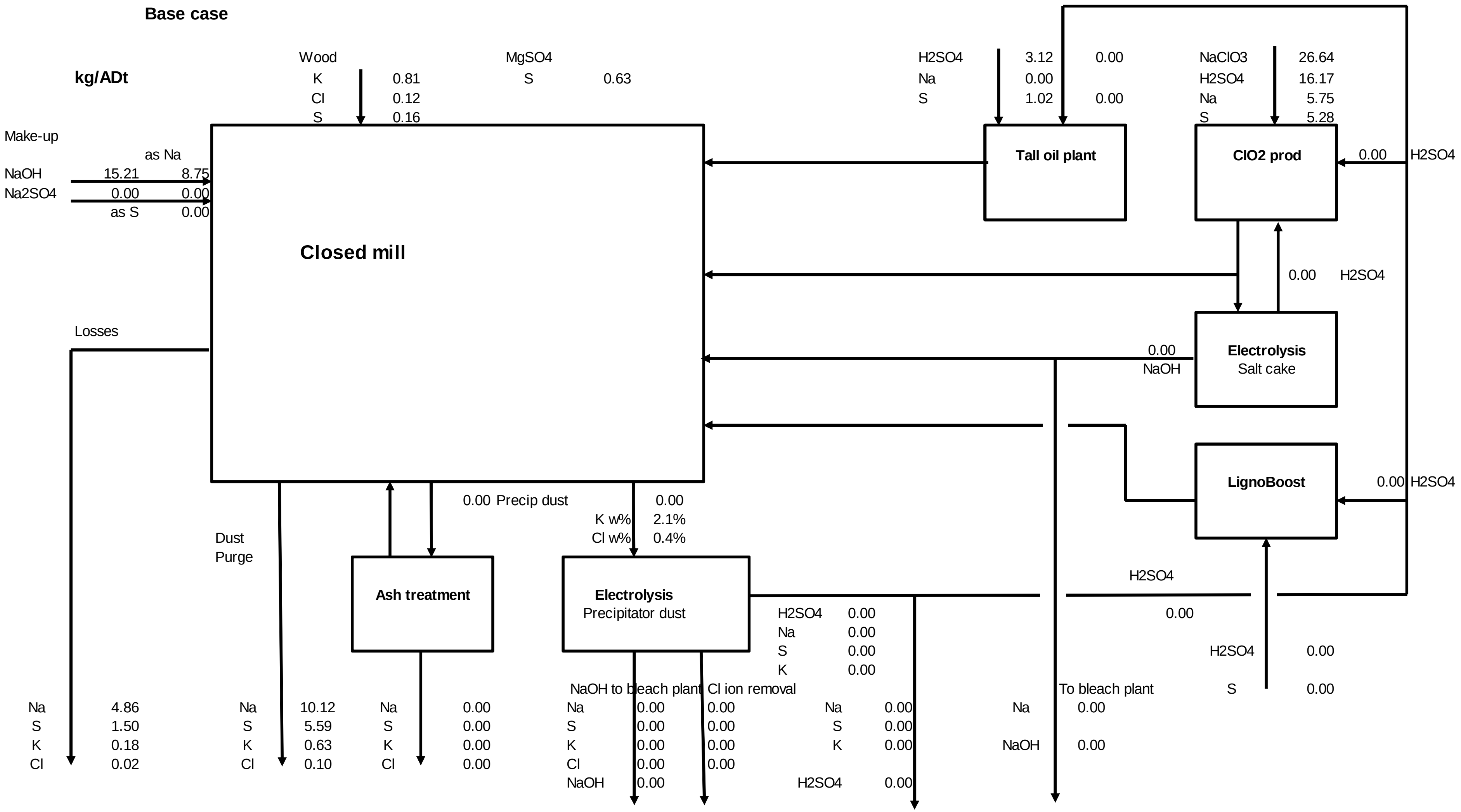
APPENDIX 1. FLOW SCHEMES FOR EVALUATED CASES.

Shown figures for Na include K calculated as Na

Case 1a **Softwood**

Base case

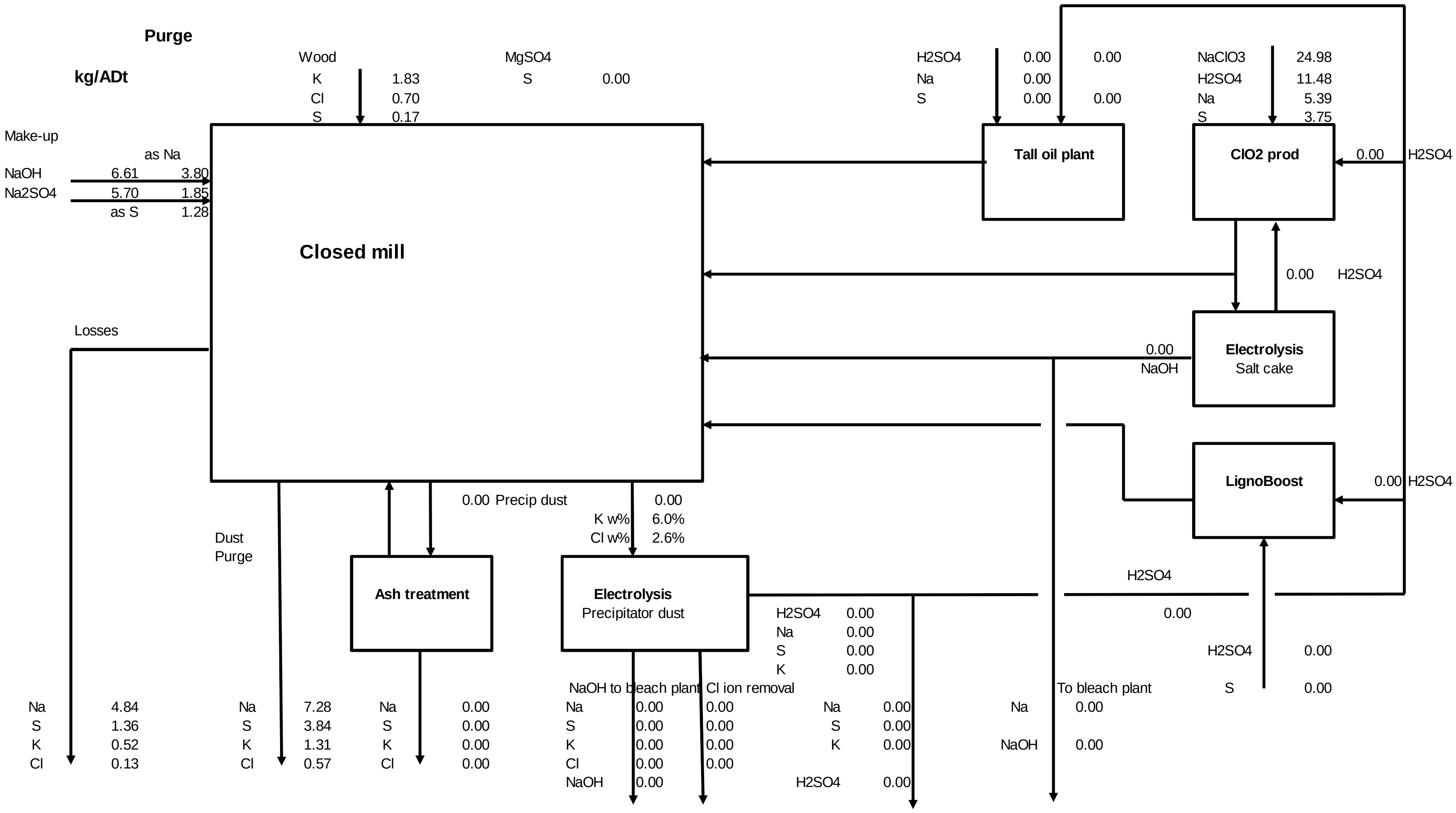


Case 1b

Euca

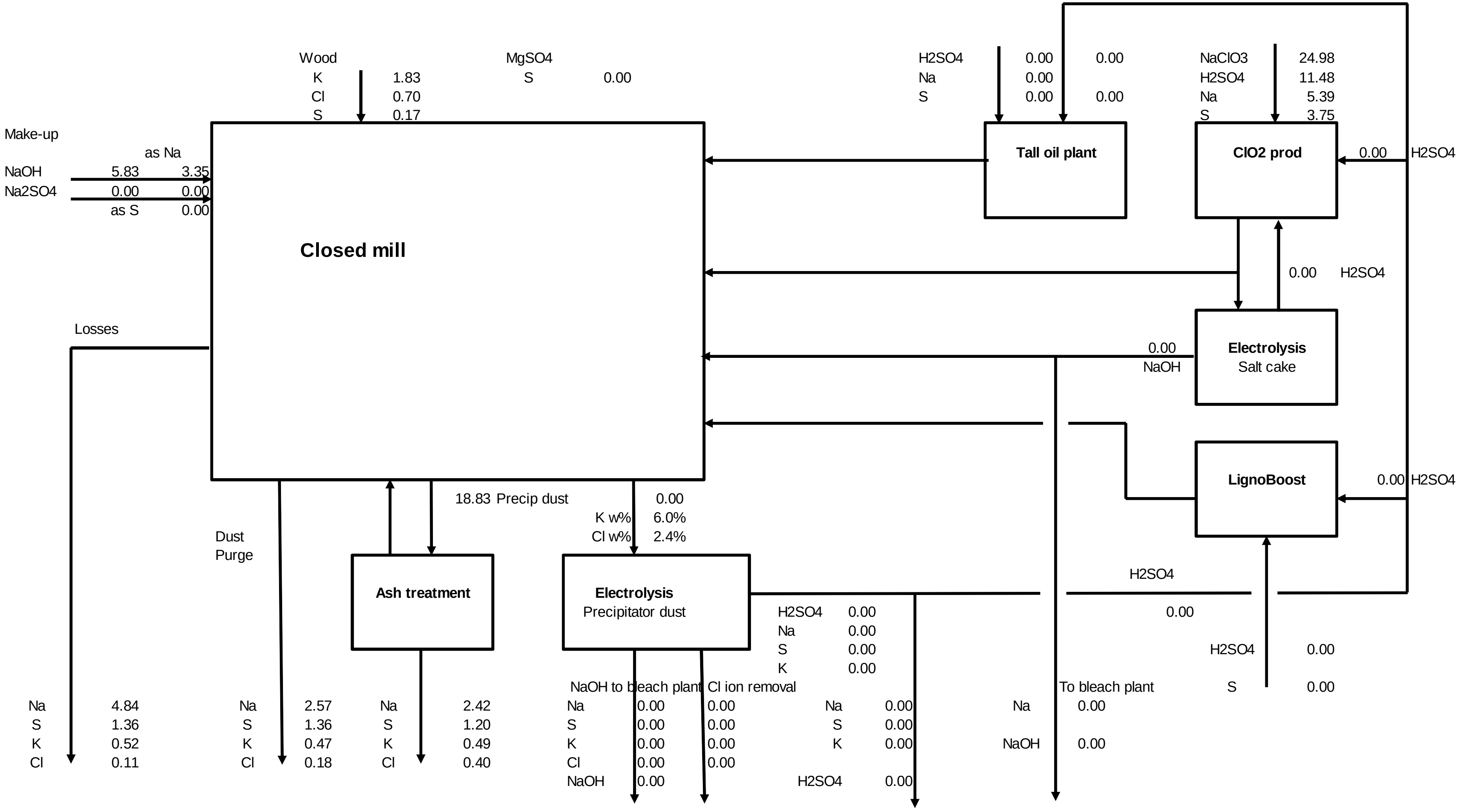
Purge

kg/ADt



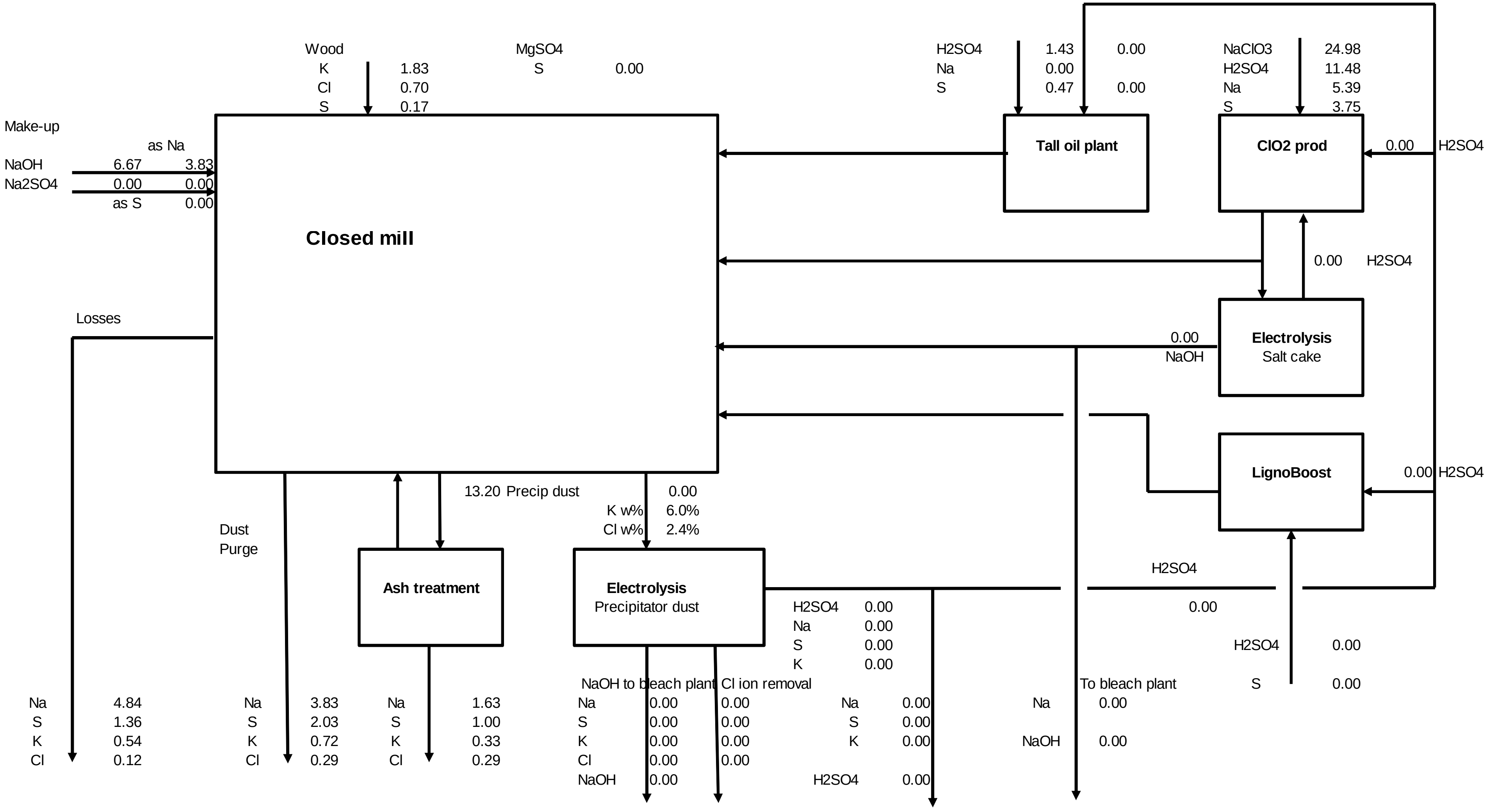
Case 1c

Euca
CRP
kg/ADt



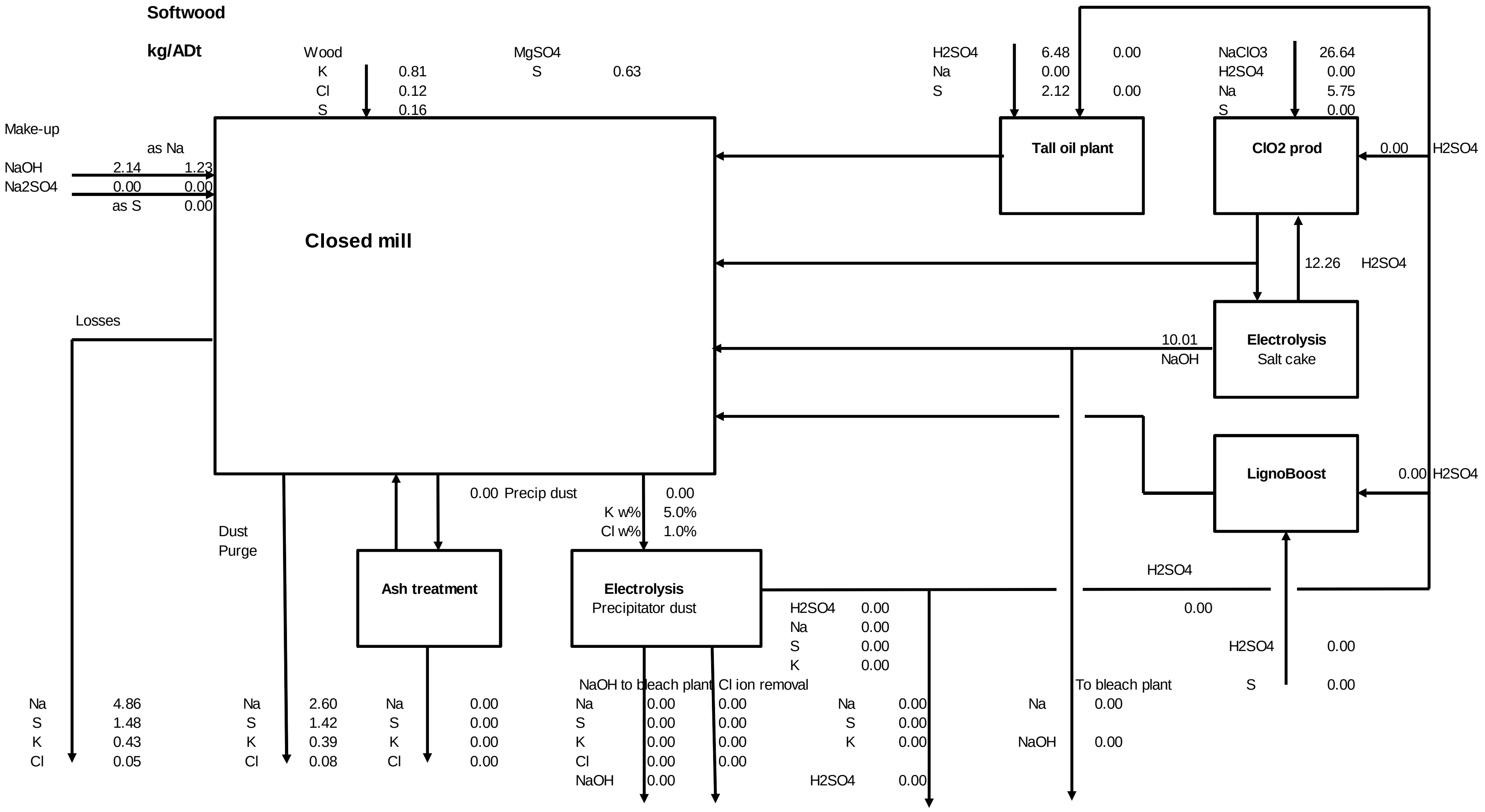
Case 1d

Euca
CRP H2SO4
kg/ADt



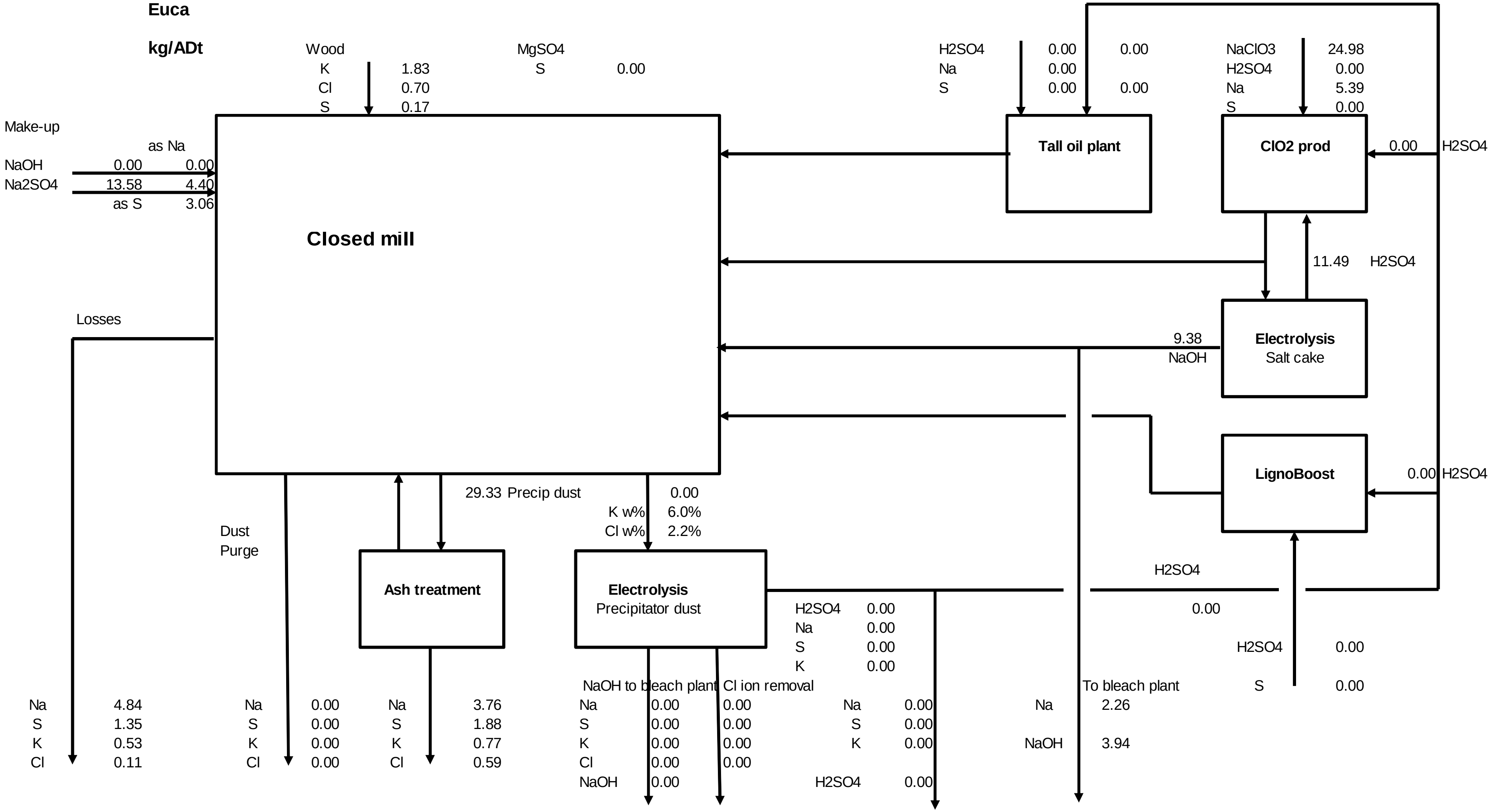
Case 2a
Electrolysis
Salt cake from ClO2
Softwood

kg/ADt



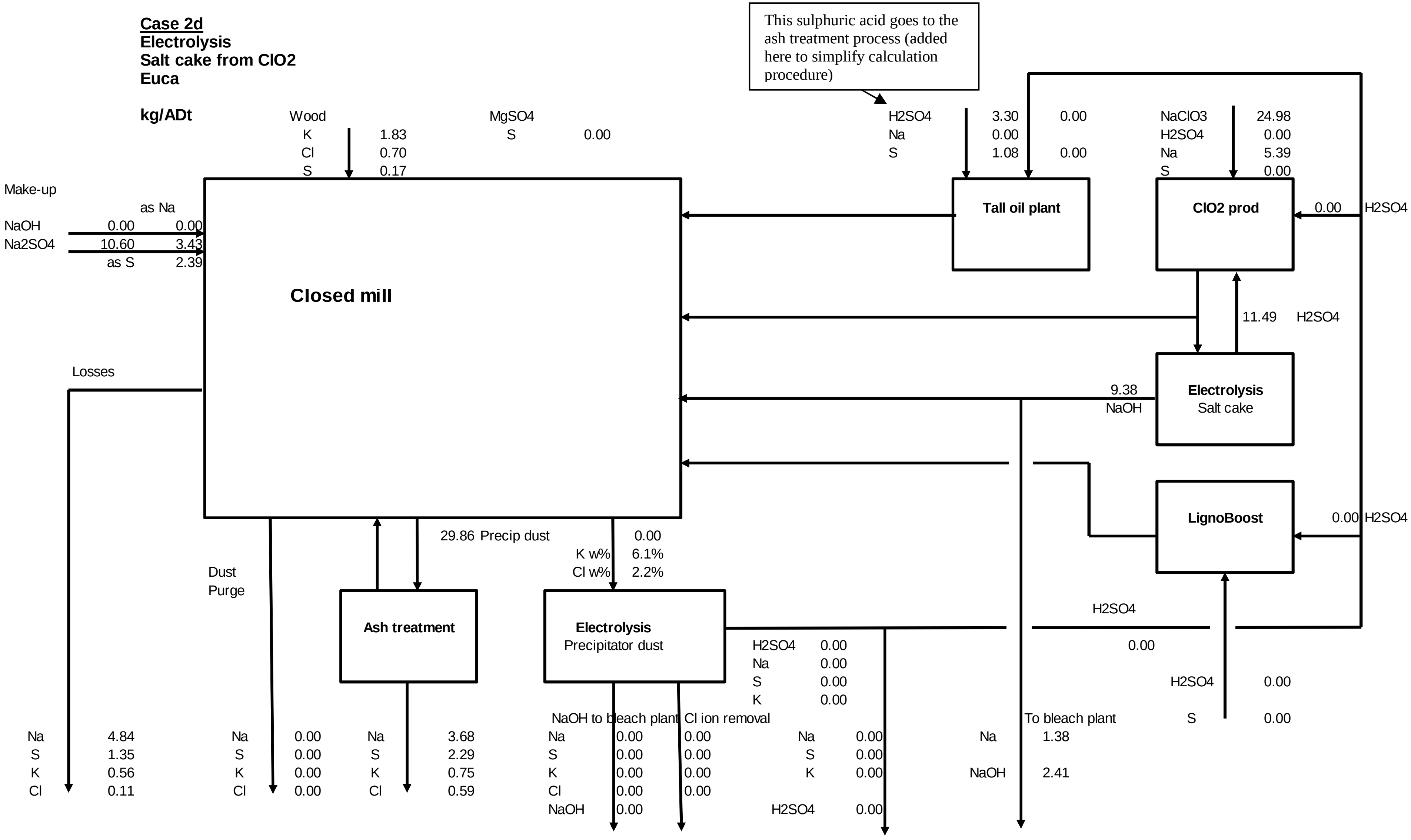
<u>Case 2c</u>
Electrolysis
Salt cake from ClO2
Euca

kg/ADt



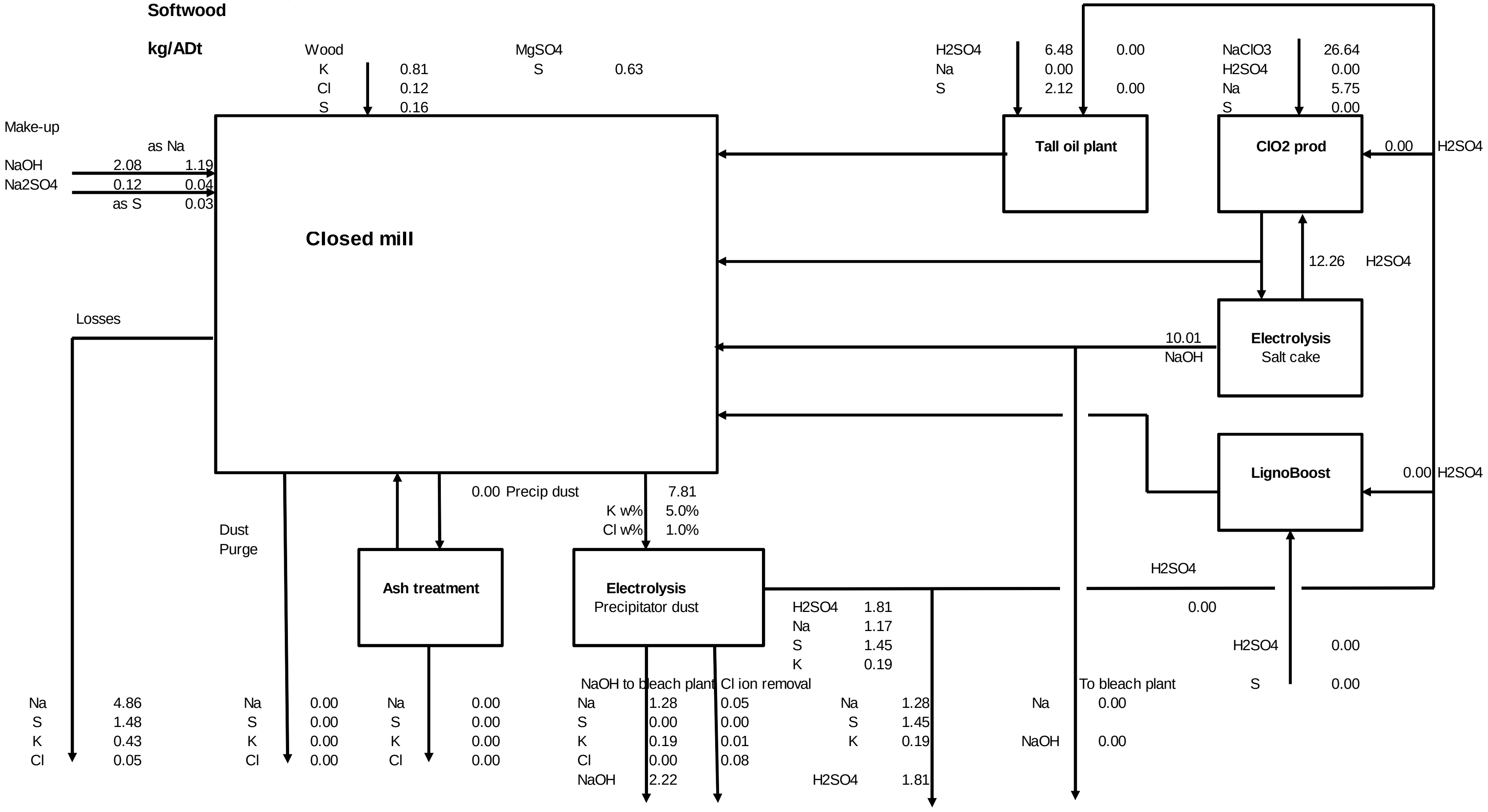
Case 2d
Electrolysis
Salt cake from ClO2
Euca

kg/ADt



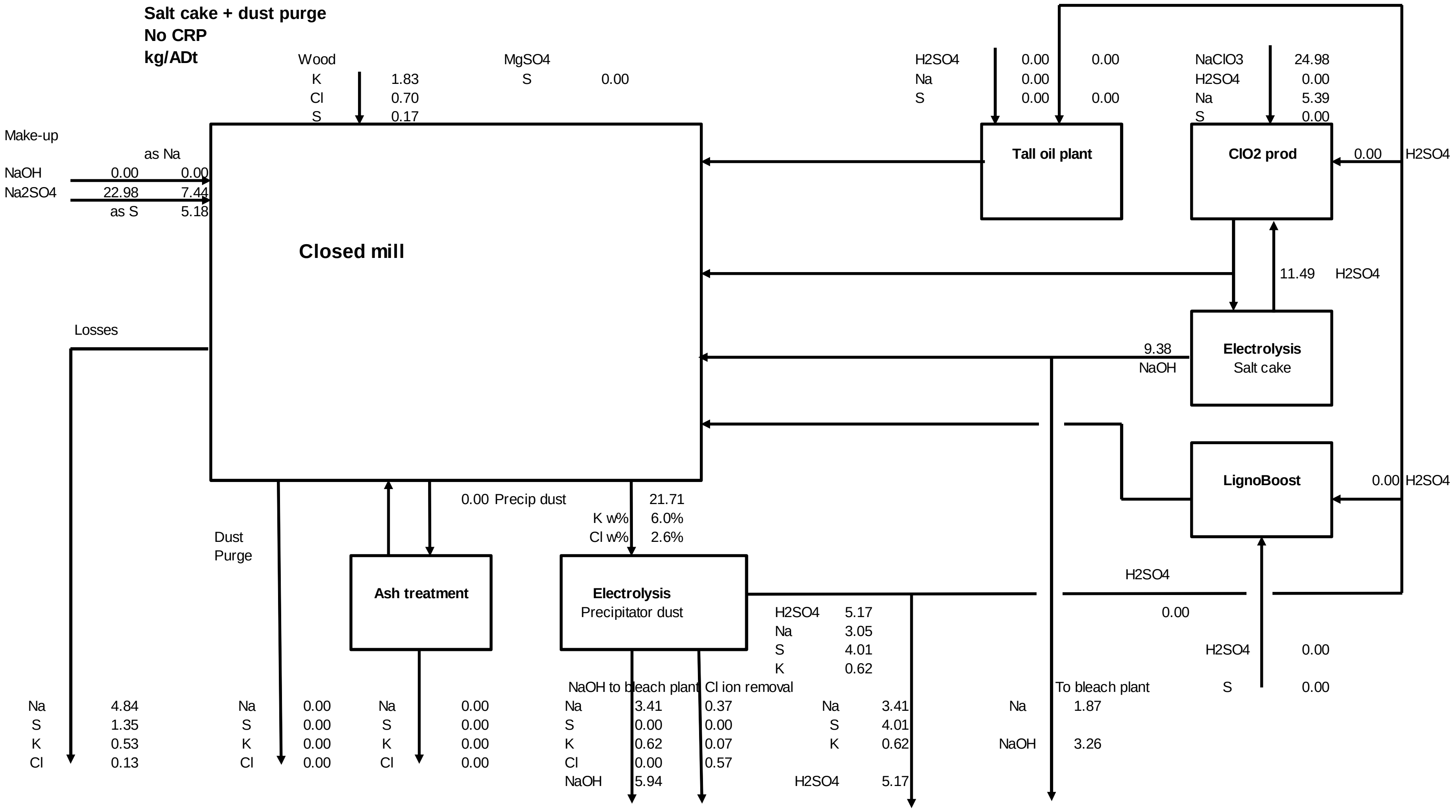
Case 3a
Electrolysis
Salt cake + dust purge
Softwood

kg/ADt



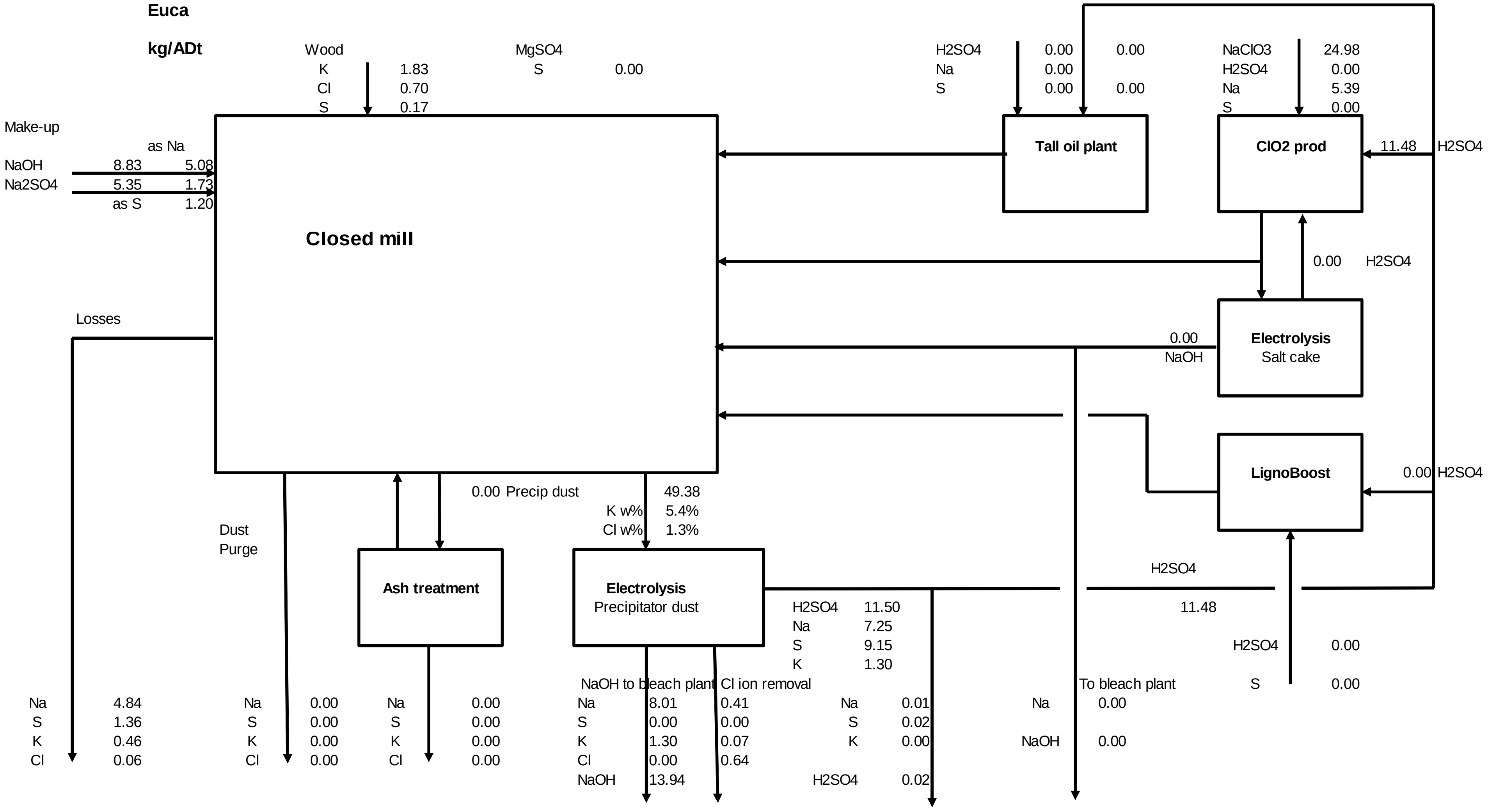
Case 3b **Softwood**

Electrolysis
Salt cake + dust purge
No CRP
kg/ADt



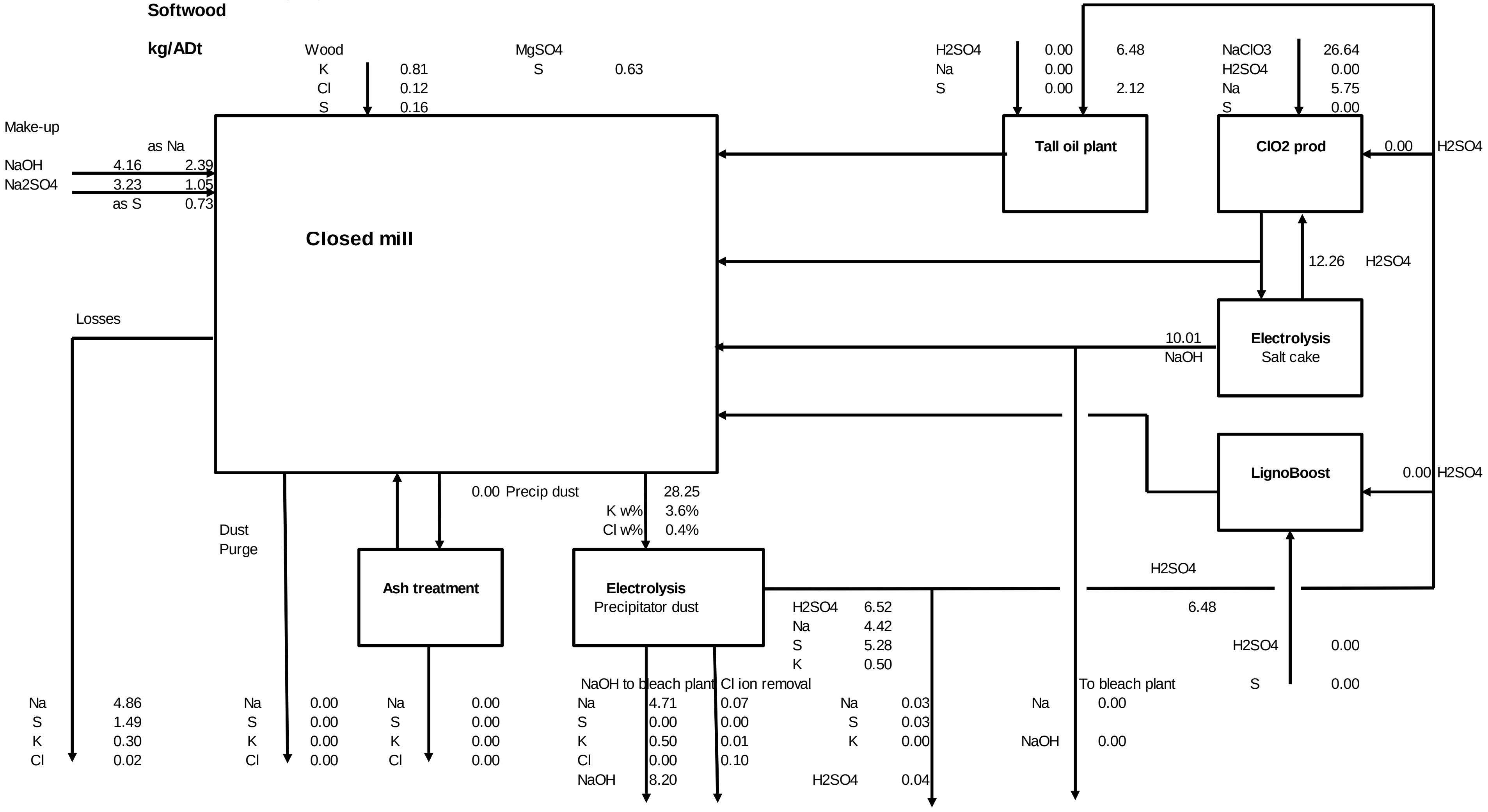
Case 4b
Electrolysis
Only precipitator dust
Euca

kg/ADt



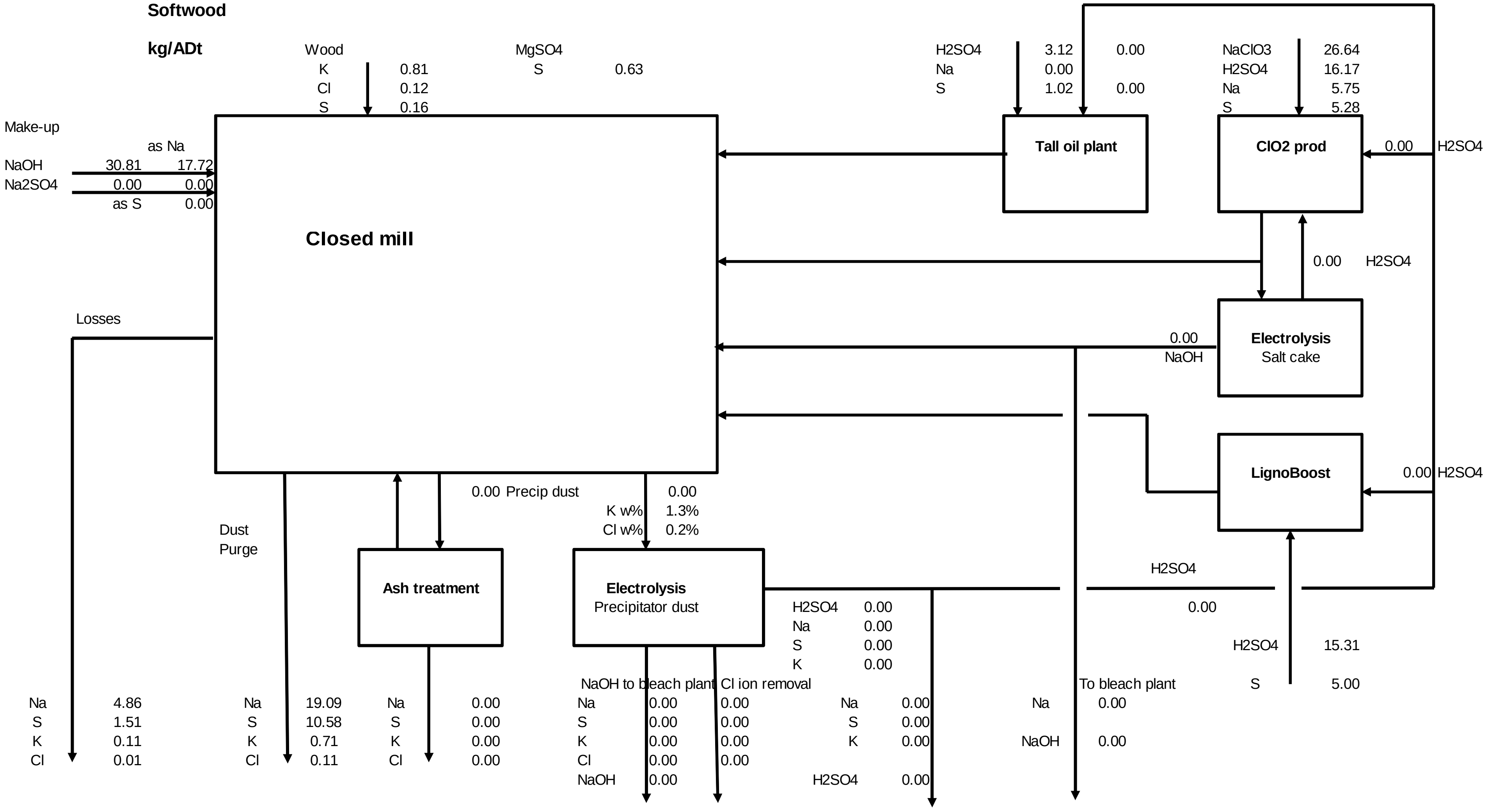
Case 5a
Electrolysis for all H2SO4
Salt cake + dust purge
Softwood

kg/ADt



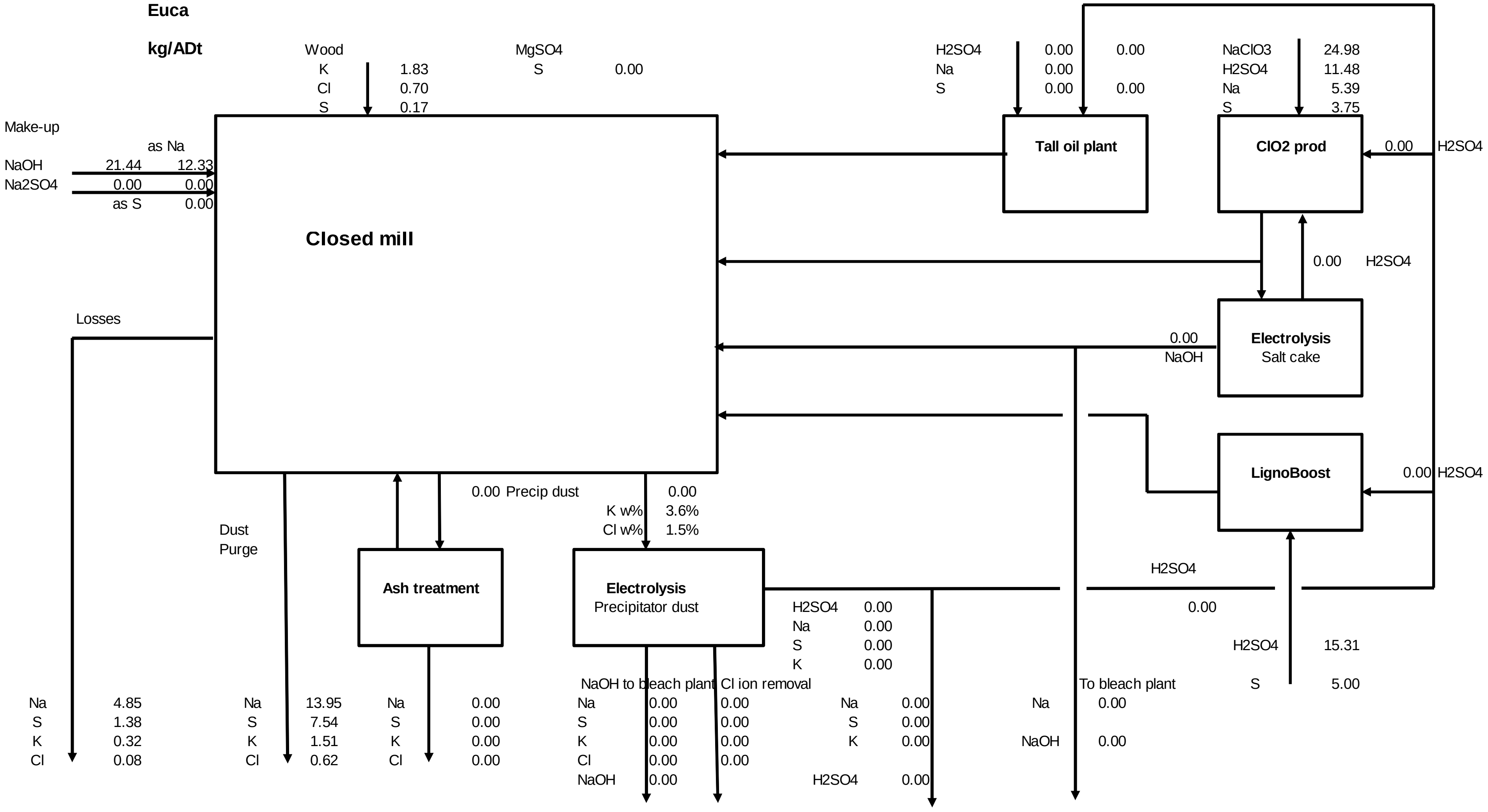
Case 6a
Base case
LignoBoost
Softwood

kg/ADt



Case 6b
Base case
LignoBoost
Euca

kg/ADt



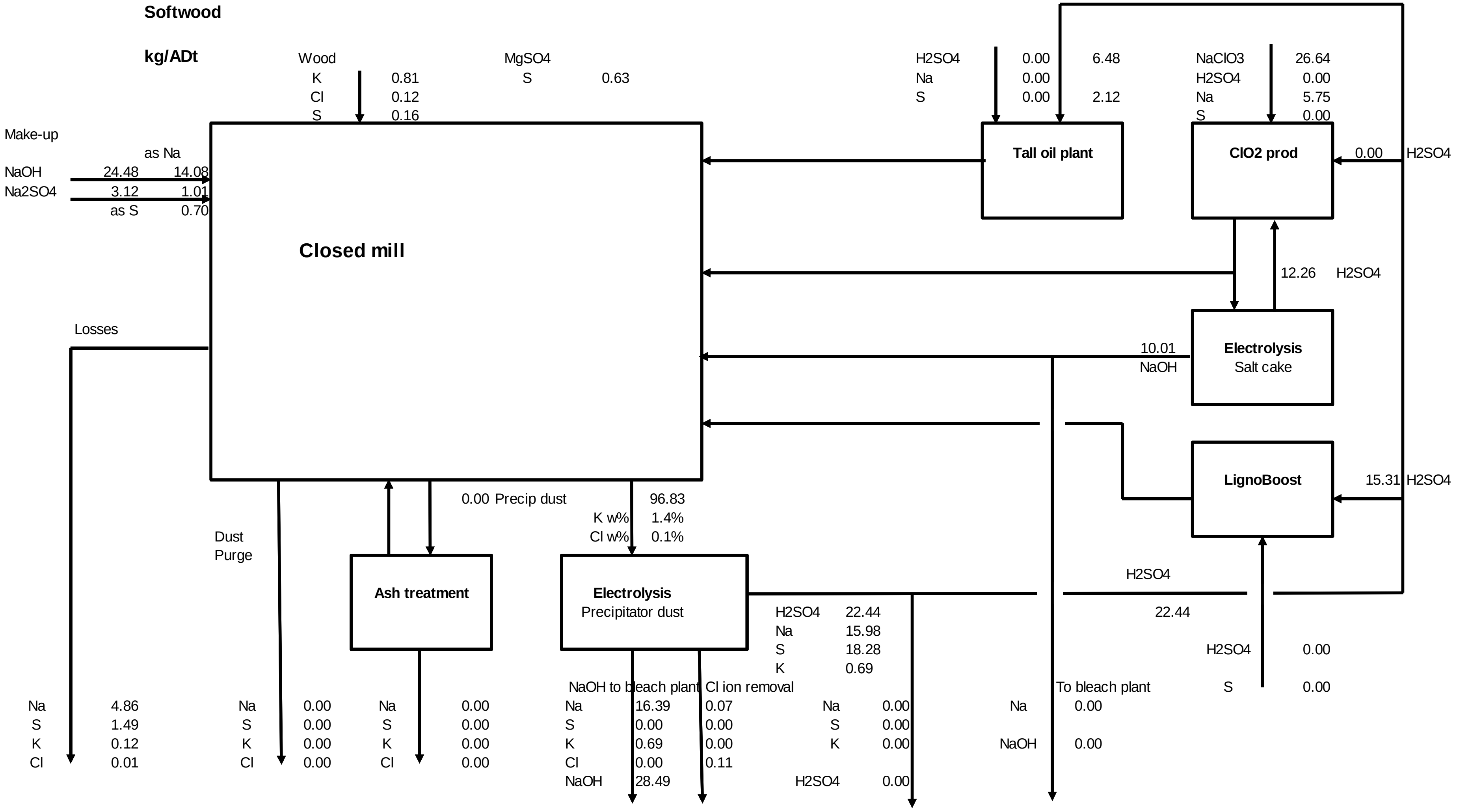
Case 7a

LignoBoost. Electrolysis for all H2SO4

Salt cake + precip dust

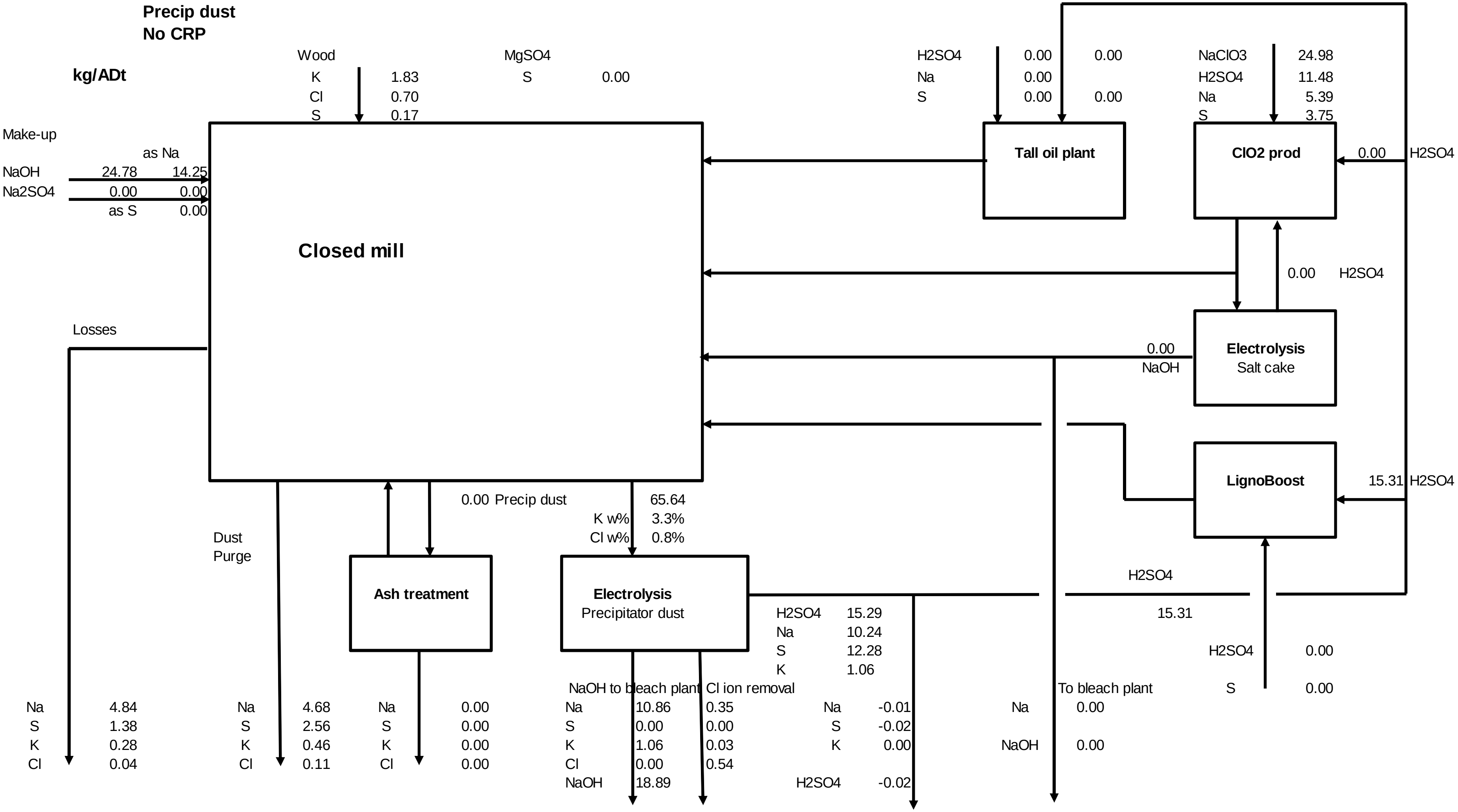
Softwood

kg/ADt



Case 7b

Euca
LignoBoost
Electrolysis for LignoBoost only
Precip dust
No CRP



APPENDIX 2. Na/S- and K/Cl-balances. All units in kg/adt.

CASE 1a

In			**Na + K**	**S**	**K**	**Cl**
Wood			0.48	0.16	0.81	0.12
Make up						
NaOH			8.75			
Na2SO4			0.00	0.00		
MgSO4				0.63		
Tall oil plant				1.02		
ClO2			5.75	5.28		
LignoBoost				0.00		
Sum in			14.98	7.09	0.81	0.12
Out						
General losses			4.86	1.50	0.18	0.02
Dust purge			10.12	5.59	0.63	0.10
CRP purge			0.00	0.00	0.00	0.00
Electrolysis SC purge			0.00			
Cl ion removal			0.00		0.00	0.00
Acid out from PD el			0.00	0.00	0.00	
NaOH from PD el.			0.00		0.00	0.00
Sum out			14.98	7.09	0.81	0.12

CASE 1b

In				**Na + K**	**S**	**K**	**Cl**
Wood				1.08	0.17	1.83	0.70
Make up							
NaOH				3.80			
Na2SO4				1.85	1.28		
MgSO4					0.00		
Tall oil plant					0.00		
ClO2				5.39	3.75		
LignoBoost					0.00		
Sum in				12.12	5.21	1.83	0.70
Out							
General losses				4.84	1.36	0.52	0.13
Dust purge				7.28	3.84	1.31	0.57
CRP purge				0.00	0.00	0.00	0.00
Electrolysis SC purge				0.00			
Cl ion removal				0.00		0.00	0.00
Acid out from PD el				0.00	0.00	0.00	
NaOH from PD el.				0.00		0.00	0.00
Sum out				12.12	5.21	1.83	0.70

CASE 1c

In				**Na + K**	**S**	**K**	**Cl**
Wood				1.08	0.17	1.83	0.70
Make up							
NaOH				3.35			
Na2SO4				0.00	0.00		
MgSO4					0.00		
Tall oil plant					0.00		
ClO2				5.39	3.75		
LignoBoost					0.00		
Sum in				9.83	3.92	1.83	0.70
Out							
General losses				4.84	1.36	0.52	0.11
Dust purge				2.57	1.36	0.47	0.18
CRP purge				2.42	1.20	0.49	0.40
Electrolysis SC purge				0.00			
Cl ion removal				0.00		0.00	0.00
Acid out from PD el				0.00	0.00	0.00	
NaOH from PD el.				0.00		0.00	0.00
Sum out				9.83	3.92	1.48	0.70

CASE 1d

In				**Na + K**	**S**	**K**	**Cl**
Wood				1.08	0.17	1.83	0.70
Make up							
NaOH				3.35			
Na2SO4				0.00	0.00		
MgSO4					0.00		
Tall oil plant					0.00		
ClO2				5.39	3.75		
LignoBoost					0.00		
Sum in				9.83	3.92	1.83	0.70
Out							
General losses				4.84	1.36	0.52	0.11
Dust purge				2.57	1.36	0.47	0.18
CRP purge				2.42	1.20	0.49	0.40
Electrolysis SC purge				0.00			
Cl ion removal				0.00		0.00	0.00
Acid out from PD el				0.00	0.00	0.00	
NaOH from PD el.				0.00		0.00	0.00
Sum out				9.83	3.92	1.48	0.70

CASE 2a

In				**Na + K**	**S**	**K**	**Cl**
Wood				0.48	0.16	0.81	0.12
Make up							
NaOH				1.23			
Na2SO4				0.00	0.00		
MgSO4					0.63		
Tall oil plant					2.12		
ClO2				5.75	0.00		
LignoBoost					0.00		
Sum in				7.46	2.91	0.81	0.12
Out							
General losses				4.86	1.48	0.43	0.05
Dust purge				2.60	1.42	0.39	0.08
CRP purge				0.00	0.00	0.00	0.00
Electrolysis SC purge				0.00			
Cl ion removal				0.00		0.00	0.00
Acid out from PD el				0.00	0.00	0.00	
NaOH from PD el.				0.00		0.00	0.00
Sum out				7.46	2.91	0.81	0.12

CASE 2c

In				**Na + K**	**S**	**K**	**Cl**
Wood				1.08	0.17	1.83	0.70
Make up							
NaOH				0.00			
Na2SO4				4.40	3.06		
MgSO4					0.00		
Tall oil plant					0.00		
ClO2				5.39	0.00		
LignoBoost					0.00		
Sum in				10.87	3.23	1.83	0.70
Out							
General losses				4.84	1.35	0.53	0.11
Dust purge				0.00	0.00	0.00	0.00
CRP purge				3.76	1.88	0.77	0.59
Electrolysis SC purge				2.26			
Cl ion removal				0.00		0.00	0.00
Acid out from PD el				0.00	0.00	0.00	
NaOH from PD el.				0.00		0.00	0.00
Sum out				10.87	3.23	1.29	0.70

CASE 2d

In				**Na + K**	**S**	**K**	**Cl**
Wood				1.08	0.17	1.83	0.70
Make up							
NaOH				0.00			
Na2SO4				3.43	2.39		
MgSO4					0.00		
Tall oil plant					1.08		
ClO2				5.39	0.00		
LignoBoost					0.00		
Sum in				9.91	3.64	1.83	0.70
Out							
General losses				4.84	1.35	0.56	0.11
Dust purge				0.00	0.00	0.00	0.00
CRP purge				3.68	2.29	0.75	0.59
Electrolysis SC purge				1.38			
Cl ion removal				0.00		0.00	0.00
Acid out from PD el				0.00	0.00	0.00	
NaOH from PD el.				0.00		0.00	0.00
Sum out				9.91	3.64	1.31	0.70

CASE 3a

In				**Na + K**	**S**	**K**	**Cl**
Wood				0.48	0.16	0.81	0.12
Make up							
NaOH				1.19			
Na2SO4				0.04	0.03		
MgSO4					0.63		
Tall oil plant					2.12		
ClO2				5.75	0.00		
LignoBoost					0.00		
Sum in				7.47	2.93	0.81	0.12
Out							
General losses				4.86	1.48	0.43	0.05
Dust purge				0.00	0.00	0.00	0.00
CRP purge				0.00	0.00	0.00	0.00
Electrolysis SC purge				0.00			
Cl ion removal				0.05		0.01	0.08
Acid out from PD el				1.28	1.45	0.19	
NaOH from PD el.				1.28		0.19	0.00
Sum out				7.47	2.93	0.81	0.12

CASE 3b

In				**Na + K**	**S**	**K**	**Cl**
Wood				1.08	0.17	1.83	0.70
Make up							
NaOH				0.00			
Na2SO4				7.44	5.18		
MgSO4					0.00		
Tall oil plant					0.00		
ClO2				5.39	0.00		
LignoBoost					0.00		
Sum in				13.92	5.35	1.83	0.70
Out							
General losses				4.84	1.35	0.53	0.13
Dust purge				0.00	0.00	0.00	0.00
CRP purge				0.00	0.00	0.00	0.00
Electrolysis SC purge				1.87			
Cl ion removal				0.37		0.07	0.57
Acid out from PD el				3.41	4.01	0.62	
NaOH from PD el.				3.41		0.62	0.00
Sum out				13.92	5.35	1.83	0.70

CASE 4b

In				**Na + K**	**S**	**K**	**Cl**
Wood				1.08	0.17	1.83	0.70
Make up							
NaOH				5.08			
Na2SO4				1.73	1.20		
MgSO4					0.00		
Tall oil plant					0.00		
ClO2				5.39	0.00		
LignoBoost					0.00		
Sum in				13.28	1.38	1.83	0.70
Out							
General losses				4.84	1.36	0.46	0.06
Dust purge				0.00	0.00	0.00	0.00
CRP purge				0.00	0.00	0.00	0.00
Electrolysis SC purge				0.00			
Cl ion removal				0.41		0.07	0.64
Acid out from PD el				0.01	0.02	0.00	
NaOH from PD el.				8.01		1.30	0.00
Sum out				13.29	1.38	1.83	0.70

CASE 5a

In	**Na + K**	**S**	**K**	**Cl**
Wood	0.48	0.16	0.81	0.12
Make up				
NaOH	2.39			
Na2SO4	1.05	0.73		
MgSO4		0.63		
Tall oil plant		0.00		
ClO2	5.75	0.00		
LignoBoost		0.00		
Sum in	9.67	1.52	0.81	0.12
Out				
General losses	4.86	1.49	0.30	0.02
Dust purge	0.00	0.00	0.00	0.00
CRP purge	0.00	0.00	0.00	0.00
Electrolysis SC purge	0.00			
Cl ion removal	0.07		0.01	0.10
Acid out from PD el	0.03	0.03	0.00	
NaOH from PD el.	4.71		0.50	0.00
Sum out	9.67	1.52	0.81	0.12

CASE 6a

In	**Na + K**	**S**	**K**	**Cl**
Wood	0.48	0.16	0.81	0.12
Make up				
NaOH	17.72			
Na2SO4	0.00	0.00		
MgSO4		0.63		
Tall oil plant		1.02		
ClO2	5.75	5.28		
LignoBoost		5.00		
Sum in	23.95	12.09	0.81	0.12
Out				
General losses	4.86	1.51	0.11	0.01
Dust purge	19.09	10.58	0.71	0.11
CRP purge	0.00	0.00	0.00	0.00
Electrolysis SC purge	0.00			
Cl ion removal	0.00		0.00	0.00
Acid out from PD el	0.00	0.00	0.00	
NaOH from PD el.	0.00		0.00	0.00
Sum out	23.95	12.09	0.81	0.12

CASE 6b

In				**Na + K**	**S**	**K**	**Cl**
Wood				1.08	0.17	1.83	0.70
Make up							
NaOH				12.33			
Na2SO4				0.00	0.00		
MgSO4					0.00		
Tall oil plant					0.00		
ClO2				5.39	3.75		
LignoBoost					5.00		
Sum in				18.80	8.92	1.83	0.70
Out							
General losses				4.85	1.38	0.32	0.08
Dust purge				13.95	7.54	1.51	0.62
CRP purge				0.00	0.00	0.00	0.00
Electrolysis SC purge				0.00			
Cl ion removal				0.00		0.00	0.00
Acid out from PD el				0.00	0.00	0.00	
NaOH from PD el.				0.00		0.00	0.00
Sum out				18.80	8.92	1.83	0.70

CASE 7a

In				**Na + K**	**S**	**K**	**Cl**
Wood				0.48	0.16	0.81	0.12
Make up							
NaOH				14.08			
Na2SO4				1.01	0.70		
MgSO4					0.63		
Tall oil plant					0.00		
ClO2				5.75	0.00		
LignoBoost					0.00		
Sum in				21.32	1.49	0.81	0.12
Out							
General losses				4.86	1.49	0.12	0.01
Dust purge				0.00	0.00	0.00	0.00
CRP purge				0.00	0.00	0.00	0.00
Electrolysis SC purge				0.00			
Cl ion removal				0.07		0.00	0.11
Acid out from PD el				0.00	0.00	0.00	
NaOH from PD el.				16.39		0.69	0.00
Sum out				21.32	1.49	0.81	0.12

CASE 7b

In				**Na + K**	**S**	**K**	**Cl**
Wood				1.08	0.17	1.83	0.70
Make up							
NaOH				14.25			
Na2SO4				0.00	0.00		
MgSO4					0.00		
Tall oil plant					0.00		
ClO2				5.39	3.75		
LignoBoost					0.00		
Sum in				20.72	3.92	1.83	0.70
Out							
General losses				4.84	1.38	0.28	0.04
Dust purge				4.68	2.56	0.46	0.11
CRP purge				0.00	0.00	0.00	0.00
Electrolysis SC purge				0.00			
Cl ion removal				0.35		0.03	0.54
Acid out from PD el				-0.01	-0.02	0.00	
NaOH from PD el.				10.86		1.06	0.00
Sum out				20.72	3.92	1.83	0.70

APPENDIX 3. SENSITIVITY ANALYSES OF IMPORTANT ECONOMIC PARAMETERS.

fraction of base	**NaOH price** **Scandinavia** (kSEK/ton)	**South America** (kSEK/ton)	**2a** (y)	**2c** (y)	**2d** (y)	**3a** (y)	**3b** (y)	**4b** (y)	**5a** (y)	**7a** (y)	**7b** (y)
0.50	1.6	2.8	25.71	62.31	47.54	30.37	21.52	7.27	neg	neg.	6.63
0.75	2.3	4.2	10.66	11.08	11.12	11.47	7.55	4.77	19.75	19.26	4.30
1.00	3.1	5.6	6.72	6.08	6.30	7.07	4.58	3.55	9.43	8.00	3.19
1.25	3.9	7.0	4.91	4.19	4.39	5.11	3.28	2.83	6.19	5.04	2.53
1.50	4.7	8.3	3.87	3.20	3.37	4.00	2.56	2.35	4.61	3.69	2.10

fraction of base	**H2SO4 price** **Scandinavia** (kSEK/ton)	**South America** (kSEK/ton)	**2a** (y)	**2c** (y)	**2d** (y)	**3a** (y)	**3b** (y)	**4b** (y)	**5a** (y)	**7a** (y)	**7b** (y)
0.50	0.4	0.8	8.24	8.89	8.67	8.68	6.08	4.17	12.85	11.35	3.76
0.75	0.6	1.2	7.41	7.22	7.29	7.80	5.22	3.84	10.88	9.38	3.45
1.00	0.8	1.7	6.72	6.08	6.30	7.07	4.58	3.55	9.43	8.00	3.19
1.25	1.0	2.1	6.16	5.25	5.54	6.47	4.07	3.30	8.32	6.97	2.96
1.50	1.2	2.5	5.68	4.62	4.94	5.96	3.67	3.09	7.44	6.17	2.76

fraction of base	**Na2SO4 price** **Scandinavia** (kSEK/ton)	**South America** (kSEK/ton)	**2a** (y)	**2c** (y)	**2d** (y)	**3a** (y)	**3b** (y)	**4b** (y)	**5a** (y)	**7a** (y)	**7b** (y)
0.50	0.9	1.0	6.7	4.2	4.6	7.0	3.5	3.6	8.6	7.5	3.2
0.75	1.4	1.5	6.7	5.0	5.3	7.1	4.0	3.6	9.0	7.8	3.2
1.00	1.8	2.0	6.7	6.1	6.3	7.1	4.6	3.6	9.4	8.0	3.2
1.25	2.3	2.5	6.7	7.9	7.7	7.1	5.4	3.5	9.9	8.2	3.2
1.50	2.7	3.0	6.7	11.1	9.9	7.1	6.6	3.5	10.5	8.5	3.2

	Electricity price **Scandinavia** (SEK/MWh)	**South America** (SEK/MWh)	**2a** (y)	**2c** (y)	**2d** (y)	**3a** (y)	**3b** (y)	**4b** (y)	**5a** (y)	**7a** (y)	**7b** (y)
0.50	206	154	4.7	4.7	4.9	4.8	3.7	3.0	5.3	4.0	2.6
0.75	309	231	5.5	5.3	5.5	5.7	4.1	3.2	6.8	5.3	2.9
1.00	412	308	6.7	6.1	6.3	7.1	4.6	3.6	9.4	8.0	3.2
1.25	515	385	8.6	7.1	7.4	9.3	5.2	3.9	15.3	16.1	3.6
1.50	618	462	12.0	8.5	8.9	13.5	6.1	4.4	40.8	neg	4.0

	CAPEX (case specific, see Table 9.3)		**2a**	**2c**	**2d**	**3a**	**3b**	**4b**	**5a**	**7a**	**7b**
0.50			3.4	3.0	3.1	3.5	2.3	1.8	4.7	4.0	1.6
0.75			5.0	4.6	4.7	5.3	3.4	2.7	7.1	6.0	2.4
1.00			6.7	6.1	6.3	7.1	4.6	3.6	9.4	8.0	3.2
1.25			8.4	7.6	7.9	8.8	5.7	4.4	11.8	10.0	4.0
1.50			10.1	9.1	9.4	10.6	6.9	5.3	14.1	12.0	4.8

Deposit cost/fees (SEK/ton)	**Cases** **2a**	**2c**	**2d**	**3a**	**3b**	**4b**	**5a**	**7a**	**7b**
0	6.7	6.1	6.3	7.1	4.6	3.6	9.4	8.0	3.2
500	4.7	4.8	4.9	4.7	4.1	3.0	6.1	4.9	2.6
1 000	3.7	4.0	4.0	3.5	3.8	2.6	4.5	3.5	2.2
1 500	3.0	3.4	3.4	2.8	3.5	2.3	3.6	2.8	1.9