Suomen Soodakattilayhdistys ry

YMPÄRISTÖTYÖRYHMÄN KOKOUS 4/2017

AIKA 17.10.2017 klo 13.00 – 14:30

PAIKKA Skype

LÄSNÄ

Markus Nieminen	Pöyry Finland Oy, Vantaa, siht.
Timo-Pekka Veijonen	Stora Enso, Pulp Competence Center, Imatra, PJ
Sanna Hämäläinen	Metsä Fibre Oy, Joutsenon tehdas, Lappeenranta
Jukka Röppänen	Andritz Oy, Helsinki
Kurt Sirén	Oy Sirra Ab, Kirkkonummi
Jorma Torniainen	Labtium Oy, Espoo

LIITE 1	Åforsk, Techniques for reducing intake of ammonia-nitrogen in strong gases and methanol to kraft recovery boilers – raportti 2.12.2014
LIITE 2	Oy Sirra Ab, Rikkitaseen hallinta ja soodasakkamäärän vähentäminen – tarjous 15.1.2017
LIITE 3	Oy Sirra Ab, Rikkitaseen hallinta ja soodasakkamäärän vähentäminen – esitys 15.2.2017

JAKELU:
Julkaisu: Soodakattilayhdistyksen kotisivulla
Tiedote: Hallitus, Yhdyshenkilöt, Ympäristötyöryhmä
Sihteeristö

1 POISSAOLOILMOITUKSET

Päivi Hyvärinen	UPM-Kymmene, Kymin tehdas, Kouvola
Jarmo Mansikkasalo	Valmet Technologies Oy, Tampere
Olli Dahl	Aalto-yliopisto, Espoo
Antti Tikkanen	Pöyry Finland Oy, Vantaa
Jarmo Mansikkasalo	Valmet Technologies Oy, Tampere
Oskari Frösén	Pöyry Finland Oy, Vantaa

2 ASIALISTA

Ei muutoksia.

3 EDELLISEN KOKOUKSEN PÖYTÄKIRJA

Edellisen kokouksen pöytäkirjan hyväksyminen siirrettiin seuraavaan kokoukseen

4 PROJEKTIEHDOTUKSET

Kokouksen tarkoituksena oli keskustella, mitä projekteja ehdotetaan hallitukselle vuoden 2018 projekteiksi.

Soodakattilayhdistyksen hallitus on linjannut, että työryhmien on esitettävä tulevaisuudessa uusien projektien hyväksyminen viimeistään vuoden viimeisessä hallituksen kokouksessa joulukuussa, jolloin seuraavan vuoden budjettia laaditaan. Lisäksi projektit pystytään aloittamaan jo vuodenvaihteen jälkeen, kun nykyisessä mallissa vuoden ensimmäinen neljännes vielä odotetaan toteutuspäätöstä.

Käytännössä työryhmien on valmisteltava uudet projektiehdotukset hallitukselle kesän tai viimeistään alkusyksyn aikana.

4.1 Soodakattilan NOx-päästön riippuvuus puuraaka-aineen typpipitoisuudesta – osa 2

Tavoite:
Tällä hetkellä keskeneräisen projektin jatkohanke jossa saataisiin lisätietoa puun typpipitoisuuksista:

- Kotimaisten puiden (mänty/koivu) sisältämästä typestä on olemassa niukasti tietoa. Paljon tietoa löytyy typpipitoisuuden vaihtelusta puun eri osissa ja lannoituksesta yksikössä kg/ha.
- Ei tietoa typpipitoisuuden vaihtelusta vuodenaikojen mukaan, esimerkiksi vaikuttaako puun kaato ajankohta typpipitoisuuteen. Jossain kattiloissa on huomattu NOx-päästön olevan pienempi talvella. Tähän voi vaikuttaa vahvasti kuorinta (vaikeutuu) ja puuhäviöiden kasvu.
- Jatkotutkimuksessa tulisi hankkia systemaattista tietoa puun typpipitoisuuksista.

Toimenpiteet:
Odotetaan ensimmäisen osan valmistumista ja tarkempia jatkoprojektiehdotuksia
VTT:llä on olemassa valmiudet analyyseihin.

4.2 Hajukaasujen polttosuosituksen päivitys

Tavoite:
Kirsi Hovikorven selvitystyön (valmistuu alustavasti helmikuussa 2018) jälkeen työryhmän tulisi käynnistää hajukaasujen polttosuosituksen päivitys ja sen laajentaminen hajukaasujen keräilyyn

Toimenpiteet:
Oman työryhmän perustaminen

4.3 Kustannustehokkain tapa poistaa ammoniakkia talteenottokierrosta

Tausta:
Aiemmassa Projektissa "Ammonia Formation and Recovery in a Kraft Pulp Mill and Fate of Biosludge Nitrogen" todettiin että suurin osa talteenotettavasta ammoniakista on likaislauhteessa. The ammonia found in the dirty condensates would represent 75% of this ammonia while the other 25% of this would be found in the vent gases from recausticizing. Since the ammonia in white liquor is ultimately found in the dirty condensates from pulping and evaporation, its flow from recausticizing is not included in the potential nitrogen recoverable from recausticizing. One challenge of recovering the NH3 from the dirty condensates would be to separate it apart from the MeOH. YTR:n kokouksessa 1/2013 listattiin kaksi menetelmää ammoniakin poistamiseksi talteenottokierrosta:

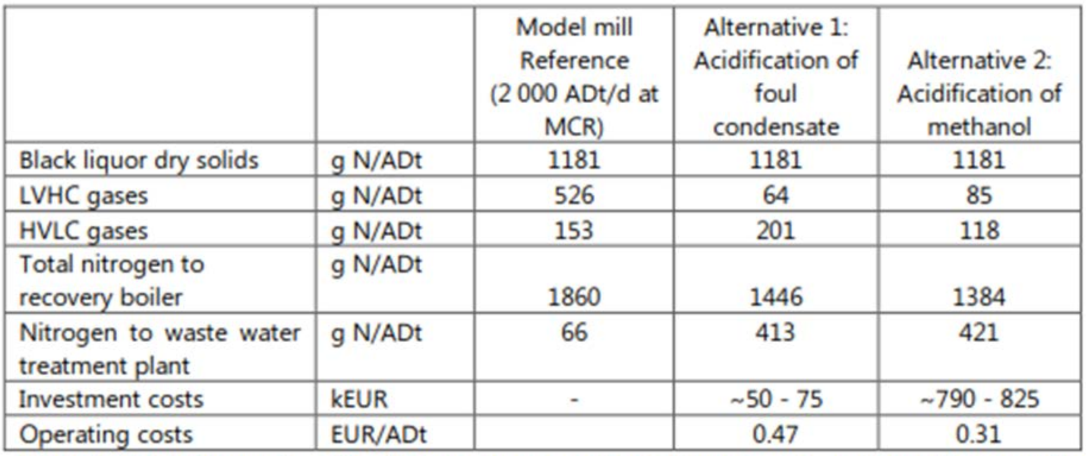
1. Stripperin pH-säätö happamaksi, jolloin ammoniumtyppi ei pääse höyrystymään stripperin kaasuihin
2. Stripperin kaasujen pesu happamalla liuoksella, jolloin ammoniakki saadaan pesuliuokseen ammoniummuodossa ja ei-haihtuvaksi

Tavoite:
Projektin tavoitteena on löytää kustannustehokkain tapa ammoniakin talteenottamiseksi lipeäkierrosta, tällä olisi mahdollisesti vaikutusta sellutehtaan NOx-päästöihin. Talteenotettu ammoniakki voidaan käyttää jätevesilaitoksella.

Tilanne:
Ruotsalainen Åforks-säätiö on teettänyt aiheesta teknis-taloudellisen tutkimuksen, LIITE 1.

Raportin yhteenveto:

- For the reference model mill case, approximately 30% of the nitrogen fed to the recovery boiler via black liquor and gases is due to intake of ammonia in low volume, high consistency (LVHC) gases, including the methanol fraction. Both studied alternatives were shown to efficiently reduce the intake of ammoniumnitrogen in LVHC gases by 85-90 %.
- Both processes are considered feasible from a process technology point of view.
- Alternative 1, comprising acidification of foul condensate prior to steam stripping, indicate much lower investment costs than Alternative 2, which comprises acidification of methanol from the methanol recovery system and further acidification and separation of the volatile methanol phase from the ammonium-containing water phase prior to firing in recovery boiler (or dedicated incinerator).



		Model mill Reference (2 000 ADt/d at MCR)	Alternative 1: Acidification of foul condensate	Alternative 2: Acidification of methanol
Black liquor dry solids	g N/ADt	1181	1181	1181
LVHC gases	g N/ADt	526	64	85
HVLC gases	g N/ADt	153	201	118
Total nitrogen to recovery boiler	g N/ADt	1860	1446	1384
Nitrogen to waste water treatment plant	g N/ADt	66	413	421
Investment costs	kEUR	-	~50 - 75	~790 - 825
Operating costs	EUR/ADt		0.47	0.31

Table 1. Related key values for nitrogen streams, estimated investment- and operation costs for the two alternative processes.

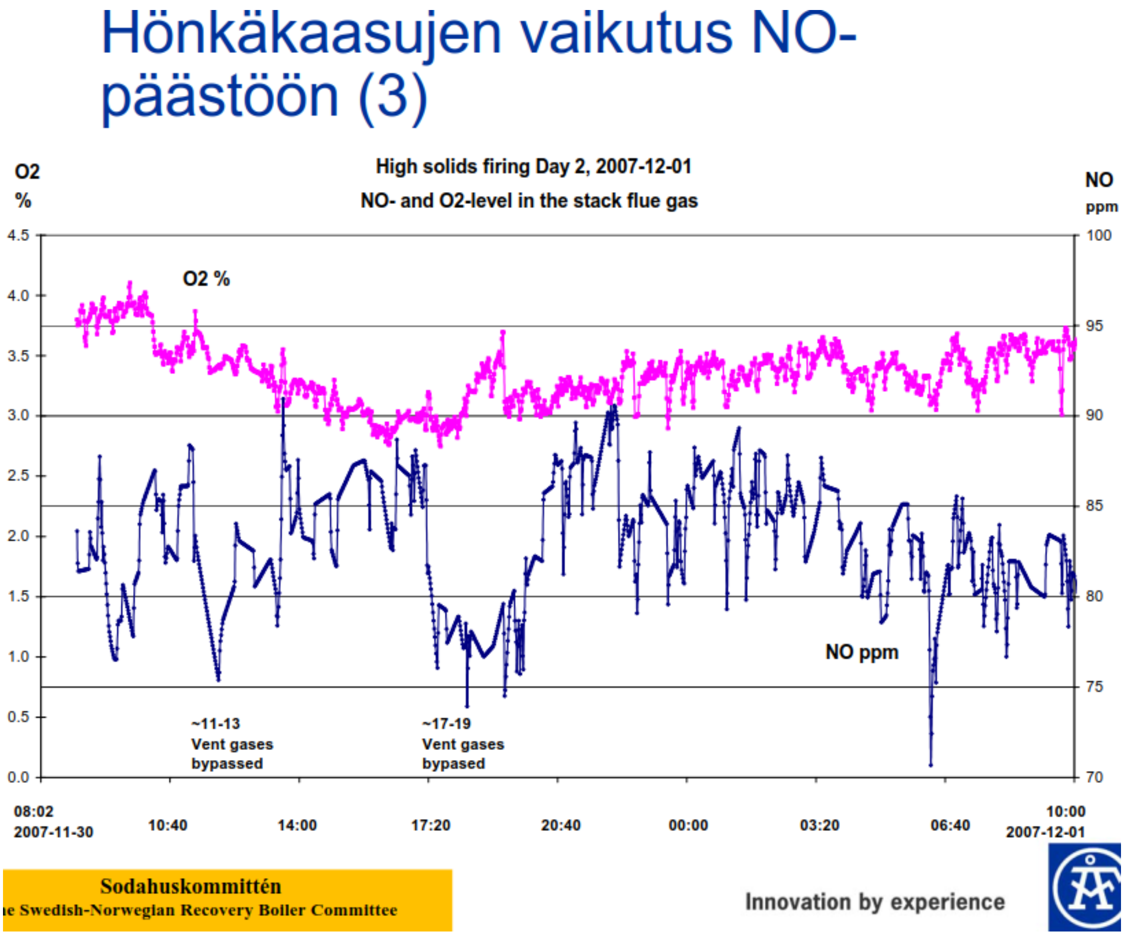
The main reason for the higher investment for Alternative 2 is due to additional required equipment such as mixing tank and stripping column as well as required piping, pumps, valves etc.
The new equipment for Alternative 1 is minor and does only comprise a pump for sulfuric acid, pH-control, distributor, piping and valves.

The effect from decreased nitrogen intake to the recovery boiler (or to a dedicated incinerator) on NOX emissions was not part of this study. A continuation of this study could be to perform practical field studies on the effect of decreased ammonium nitrogen intake in relation to the NOX-generation.

Molemmat menetelmät todettiin toimiviksi prosessiteknologian osalta. Tutkimuksessa ei kuitenkaan selvitetty ammoniakin (typen) vähennyksen vaikutusta soodakattilan NOx-päästöön. Työryhmän mielestä tämä olisi tutkimisen arvoinen aihe.

Yhdistys on vuosien varrella teettänyt useita projekteja liittyen soodakattilan typenoksidipäästöihin (NOx):
- Typpikemia mustalipeän poltossa (Hupa, ÅA 1995)
- NOx Soodakattiloissa (Vakkilainen, Pöyry 2002)
- Sellutehtaan typpioksidipäästöt ja niihin vaikuttavat tekijät – yhteenveto tämän päivän tietämyksestä (Hupa, ÅA 2005)
- Final Summary Report on Nitrogen Oxide Emissions from Finnish Pulp Mills (DeMartini, ÅA 2010)
- NOx-päästöt soodakattilasta (Lindberg, Aalto-yliopisto 2010)
- NOx emissions from recovery boilers – why discrepancy between Finnish and Swedish values (Vakkilainen, LUT 2010)
- Ammonia formation and recovery in a kraft pulp mill and fate of biosludge nitrogen (DeMartini, ÅA 2012)

Sodahuskommittén teettämässä tutkimuksessa tehtiin koeajoja Skoghallin soodakattilalla. Yhdessä kokeessa liuottajan hönkien kääntö ohiajopiippuun vähensi soodakattilan NOx-päästöä. Työryhmän mielestä tässä olisi myös tutkimuksen aihetta.



Hönkäkaasujen vaikutus NO-päästöön (3)

Sodahuskommittén
he Swedish-Norwegian Recovery Boiler Committee

Innovation by experience

Kuva 1. Koeajotuloksia NO-päästöstä Skoghallin soodakattilalta kun liuotinhöngät käännettiin ohiajopiippuun hetkellisesti. Liuotinhöngät syötetään tertiääri-ilmatasolle.

Toimenpiteet:
Sihteeri selvittää monessako tehtaassa liuotinhöngät poltetaan soodakattilassa.

Tämän jälkeen työryhmä miettiin ammoniakkimittausten teettämistä esimerkiksi liuottajan höngistä. Karkea arvio päivän kestävästä ammoniakkimittauksesta on 4000-6000 € (riippuu tehtaan sijainnista, monestako kohteesta mitataan jne.).

4.4 Rikkitaseen hallinta ja soodasakkamäärän vähentäminen

Tausta:
Sellutehtaan ylijäämäisen rikkitaseen hallitsemiseksi on tapana liuottaa lentotuhkaa ja viemäröidä se jäteveden mukana. Ympäristölupien uusinnan yhteydessä tehtaille voi tulla rajoituksia tähän käytäntöön, varsinkin kun Talvivaaran kaivoksen tapaus on nostanut sulfaatin liuotuksen julkisuuteen.

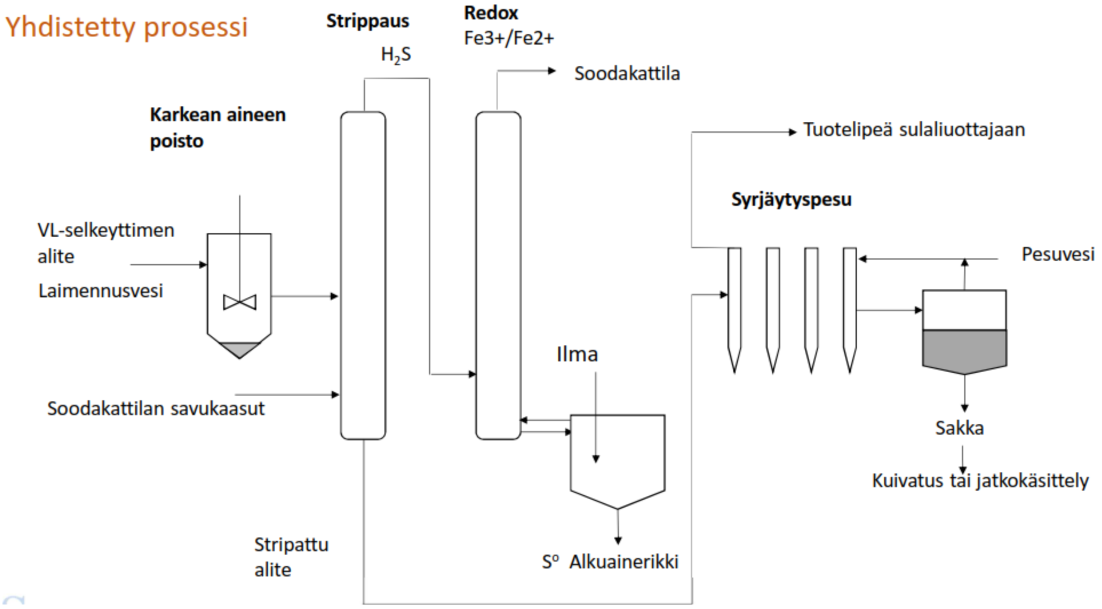
Yhdistyksen edellisissä projekteissa vuosina 2003-2009, KCL/Sirra tutkittiin sähkösuodintuhkan puhdistusta ja käsittelyä natriumsulfaatin hyötykäyttöä ajatellen. Lisäksi selvitettiin mahdollisia natriumsulfaatin käyttökohteita sekä tuotteen kuljetusta. Linkki Soodakattilapäivillä 2009 pidettyyn yhteenvetoraporttiin: Sahkosuodintuhkan_puhdistus_esitys osat_I-IV.pdf

Toinen yhdistyksen hanke selvitti kaatopaikalle menevän viherlipeäsakan vähentämistä, jonka osuus selluteollisuuden kaatopaikalle päätyvästä kiintojätteestä on noin 44 %. Viherlipeäsakka on tällä hetkellä vapautettu jäteverosta, koska hyötykäytölle ei ole löytynyt toimivaa kustannustehokasta ratkaisua. Liite raporttiin Viherlipeäsakan syrjäytyspesu

Tavoite:
Viherlipeäsakan syrjäytyspesun ja GLSS-prosessin yhdistäminen, sillä molemmissa proessesseissa on yhteneviä käytäntöjä, mikä tarjoaa mahdollisuuden molempien prosessien hallintaan. Molemmissa prosesseissa lipeä on nimittäin laimennettava.
Projektin tavoitteena on yhdistetyn prosessin käyttökelpoisuuden selvittäminen koeajamalla se pilot-laitoksessa. Lisäksi kokeillaan sakan happokäsittelyä raskasmetallien ja erityisesti kadmiumin hallitsemiseksi.

Hyöty:
Rikkitaseen hallinta (lentotuhkan liuotuksen lopettaminen) ja samanaikainen kaatopaikalle menevän viherlipeäsakan määrän vähentäminen, sakan hyötykäyttöedellytyksien parantaminen ja kemikaalisäästöt. GLSS-prosessista rikki saadaan ulos sellutehtaan kemikaalikierrosta ilman samanaikaisia natriumhäviöitä. Taloudellinen hyöty tulee ensisijaisesti ostettavan natriumhydroksidin säästöistä. Lisäksi ympäristövaikutukset ovat merkittävät, sillä happaman jätesuolan liuottaminen on mahdollista jopa lopettaa kokonaan.

Toteutus:
Projektissa yhdistetään GLSS-prosessin laitteisto viherlipeäsakan pesulaitteistoon, tarjous LIITE 2 ja esitys LIITE 3. Projektin toteutuksesta ja laitteiston kasaamisesta vastaa Oy Sirra Ab. Projektia varten tulee hankkia mahdollisesti lisää viherlipeäselkeyttimen alitetta eli sakkaa. Laboratorioanalyysit lopputuotteille eivät sisälly kyseiseen hankkeeseen ja ne tulee tilata ulkopuoliselta laboratoriolta.



Kuva 2. GLSS + syrjäytyspesulaitteiston yhdistäminen

Toimenpiteet:
Hallitus ei hyväksynyt projektia vuodelle 2017, hallituksen mielestä projekti on laitekehitystä.

Sirenin mukaan projektissa uutta on laitekokonaisuuksien yhdistäminen, mitä ei ole tehty aikaisemmin. Siren lisää laitekuvaan karkean massataseen, mitä virtoja menee ulos/mitä sisään.

Työryhmä jatkaa keskustelua seuraavassa kokouksessa.

4.5 Meesauunin päästöt eri polttoaineilla

Tavoite:
Selvittää meesauunissa käytettävien polttoaineiden vaikutusta savukaasuvirtaan/ päästöihin. Keskustelu biopolttoaineiden käytöstä ja päästöistä alkaa, kun BREF-dokumenttia päivitetään. Tutkittaisiin seuraavia polttoaineita:
- Kaasutuskaasu esim. kuoren kaasutus
- Biomassa esim. sahanpuru
- Ligniini
- Vety
- Verrokit: maakaasu ja polttoöljy

Toteutus:
Ympäristöraporttien ja/tai kyselyjen perusteella tehtävä tutkimus ja vertailu. Pitäisi saada dataa ennen ja jälkeen polttoainemuutoksen. Myös polttoaineen vaikutus kalkkikiertoon kiinnostaa, mutta se voi olla hankalaa toteuttaa käytännössä.

Mahdollinen yhteisprojekti Metsäteollisuus ry:n kanssa.

Toimenpiteet:
Sihteeri ottaa yhteyttä Metsäteollisuus ry:n ympäristötutkimustoimikuntaan, olisiko heillä kiinnostusta projektin toteuttamiseen.

5 SEURAAVA KOKOUS

Seuraava kokous sovittiin pidettäväksi 28.11.2017 klo 14-15 Skypen välityksellä.

Vakuudeksi

Markus Nieminen

LIITE 1

Åforsk, Techniques for reducing intake of ammonia-nitrogen in strong gases and methanol to kraft recovery boilers – raportti 2.12.2014

REPORT

Please refer to
Anders Norberg

Phone +46 10 505 87 00
Mobile +46 70 384 96 76
Fax +46 10 505 00 10
anders.norberg@afconsult.com

Date
2014-02-12

Order no
403190

Ångpanneföreningens Forskningsstiftelse

Techniques for reducing intake of ammonia-nitrogen in strong gases and methanol to kraft recovery boilers

ÅFORSK Ref N° 13-426

ÅF Industry AB

Anders Norberg
Janice Törmälä
Fredrik Lundqvist

Preface

This study is sponsored by Ångpanneföreningens Forskningsstiftelse (ÅForsk), a Swedish foundation that promotes research and development primarily within the field of energy, environment, safety, sustainability, materials, processes and products from renewable resources.

The objectives of this study are to identify and evaluate methods for reducing the amount of ammonia-nitrogen entering the kraft recovery boiler. Two methods for reducing the ammonia-nitrogen content of non-condensable gases and/or methanol which are often incinerated in the recovery boiler were identified, evaluated and compared with a reference case. The refernce case was based on the bleached softwood market kraft pulp model mill as defined in the FRAM (STFI-Packforsk, 2005) research programs (2 000 ADt bleached SW pulp/d). The study was performed as a desk-top study utilizing data from public articles and in ÅF files data archives.

Special thanks to Hans Norrström and Lars E Andersson for suggestions and constructive input during the work and their final review of the report.

Table of contents

Enclosures

Reference nitrogen mass balance block diagram
Alt 1 nitrogen mass balance block diagram
Alt 2 nitrogen mass balance block diagram

1 Executive Summary

The aim of this study was to identify and evaluate efficient ways to reduce the ammonium-nitrogen content in gases and methanol fed to kraft recovery boilers or dedicated incinerators within the kraft pulp mill. The effect-goal if a feasible process is implemented could be a reduction in NO_X-formation but was not within the scope of present the study. The study was performed as a desk-top study utilizing data from public articles and in ÅF files data archives.

A reference mill wide nitrogen mass balance was developed for the bleached softwood market kraft pulp model mill as defined in the FRAM (STFI-Packforsk, 2005) research programs (2 000 ADt bleached SW pulp/d). Identification and configuration of mill areas, process systems and production rate was thereby identical to the FRAM model mill. Regarding foul condensate, strong gases and methanol the model mill includes steam stripping of foul condensates followed by condensation of stripper gases and further distillation in a methanol column. Basic input data for the reference balance was mainly nitrogen content in Scandinavian softwood and concentration of nitrogen in foul condensate. Concentration of total nitrogen in other process streams was based on mass balance and data on nitrogen-split between process streams, e.g. strong black liquor to recovery boiler and smelt to dissolving tank etc.

Softwood pulping generally implies less nitrogen intake to the process than compared to hardwood pulping but is also well correlated to the amount of bark residues that is a very important factor. Most nitrogen is released in the cooking process as organic- and reduced nitrogen compounds. More than 90% of the reduced nitrogen (mainly as ammonia) is found in the foul condensate and the stripped clean condensate is virtually ammonia-free. Consequently, the majority of nitrogen is in volatile form and ends up in the stripper off-gas stream. In order to decrease ammonia-nitrogen in the Stripper Off Gases (SOG), the two processes identified and evaluated were 1) Acidification of the foul condensate prior to steam stripping and 2) Acidification of methanol and separation of the volatile and ammonia-free methanol phase.

Key results from the study are summarized in table 1 below. For the reference model mill case, approximately 30% of the nitrogen fed to the recovery boiler via black liquor and gases is due to intake of ammonia in low volume, high consistency (LVHC) gases, including the methanol fraction. Both studied alternatives were shown to efficiently reduce the intake of ammonium-nitrogen in LVHC gases by 85-90 %.

		Model mill Reference (2 000 ADt/d at MCR)	Alternative 1: Acidification of foul condensate	Alternative 2: Acidification of methanol
Black liquor dry solids	g N/ADt	1181	1181	1181
LVHC gases	g N/ADt	526	64	85
HVLC gases	g N/ADt	153	201	118
Total nitrogen to recovery boiler	g N/ADt	1860	1446	1384
Nitrogen to waste water treatment plant	g N/ADt	66	413	421
Investment costs	kEUR	-	~50 - 75	~790 - 825
Operating costs	EUR/ADt		0.47	0.31

Table 1. Related key values for nitrogen streams, estimated investment- and operation costs for the two alternative processes.

Both processes are considered feasible from a process technology point of view. Alternative 1, comprising acidification of foul condensate prior to steam stripping, indicate much lower investment costs than Alternative 2, which comprises acidification of methanol from the methanol recovery system and further acidification and separation of the volatile methanol phase from the ammonium-containing water phase prior to firing in recovery boiler (or dedicated incinerator). The main reason for the higher investment for Alternative 2 is due to additional required equipment such as mixing tank and stripping column as well as required piping, pumps, valves etc. The new equipment for Alternative 1 is minor and does only comprise a pump for sulfuric acid, pH-control, distributor, piping and valves.

Both processes produce ammonium-enriched clean condensate streams that are assumed to be used for pulp washing in the bleach plant. The bleach plant wash filtrates thereby contain higher concentration of aqueous reduced nitrogen (i.e ammonia) which we have assumed to partially replace N-containing chemicals added as nutrients to the effluent treatment. A minor amount of ammonia will however be recovered to the HVLC vent.

It is assumed that acidification in both Alternative 1 and Alternative 2 is made by using fresh sulfuric acid. We have assumed that all freshly added sulfur must be compensated for by addition of sulfur-free sodium as NaOH. In table 1 below some central nitrogen key values as well as alternative costs are listed for the alternate processes.

2 Background and objectives

2.1 Background

NO_X emissions to air have a negative impact on the environment. Therefore all kraft pulp mills must monitor and report NO_X emissions in order to ensure compliance with environmental license limits. Since the recovery boiler is the main source of NO_X emissions from a pulp mill, the reduction of NO_X from recovery boilers is a high priority for pulp mills and for environmental authorities.

The EU IPPC BAT recommendations for the pulp and paper industry (2001) are 0.6-1.8 kg NO_X /ADt, or 50-80 mg NO_X /MJ of energy input to the recovery boiler (as NO_2). The variation in the BAT recommendations is relatively large, because recovery boiler NO_X emissions depend on a number of factors such as the nitrogen content of the black liquor to the recovery boiler, the recovery boiler design, and how the recovery boiler is operated. The design and operation of auxiliary systems in the mill, such as the non-condensable gas (NCG) and condensate systems also impact NO_X emissions from the recovery boiler. NCG can be incinerated in the recovery boiler, power boiler, lime kiln, or a separate incinerator. The incineration point and the nitrogen content of the NCG impact the overall nitrogen balance in the mill, including the nitrogen content of the black liquor to the recovery boiler. Determination of the most appropriate incineration point is mill specific, and depends on factors such as the sulphur balance in the mill, and sulphur emission limits for the alternatives. In some mills NCG incineration in the kiln is suspected to cause ring formation, so the kiln is not always an option. A separate incinerator has relatively high investment- and operating costs which must be considered. In this study it assumed that NCG is incinerated in the recovery boiler.

Mill experiences and studies have shown that NO_X emissions can increase when the total amount of nitrogen from black liquor and NCG, (excluding air nitrogen) entering the recovery boiler increases (Clement & Barna, 1993). Of this reason cost effective techniques which can reduce the amount of nitrogen to the recovery boiler (Andersson & Norrström, 2010) without having a negative impact on other important environmental parameters are of interest to most kraft pulp mills.

The main problem by intake of fuel-nitrogen to a boiler is the risk for NO_X-formation and emissions. Present practices for handling NO_X-emissions comprise e.g. optimized configuration of air system and SNCR - selective non-catalytic reduction with urea or ammonia. Selective catalytic reduction is a technology employed in coal fired boilers but is due to safety reasons not recommended for kraft recovery boilers and is additionally also virtually impossible to install in existing recovery boilers, *ibidem*. In addition to firing in the recovery boiler, strong gases/liquefied methanol can also be fired in dedicated incinerators which can be of conventional type or specially designed for low-NO_X emissions.

The main suppliers to the pulp industry, as well as some of the pulp producers themselves have developed a number of alternatives for nitrogen capture from the foul condensate and methanol systems in kraft pulp mills. Some processes target foul condensate treatment before or in the foul condensate stripper system while other processes focus on either the resulting SOG or the liquefied methanol, if a methanol recovery plant is available.

2.2 Project objectives

The objectives of this study are to identify and evaluate methods for reducing the amount of nitrogen entering the recovery boiler (excluding air nitrogen as N_2). In particular, cost effective methods for reducing the nitrogen content, mainly as ammonia (NH_3), of non-condensable gases and/or methanol which are often incinerated in the recovery boiler are identified and evaluated.

The main activities in this project are:

1. Define a base case nitrogen balance for a model mill, including the non-condensable gas system. This balance is mainly based on reference material and ÅF data from various studies. Note that quantification of NO_X emissions from the recovery boiler is not included in the scope of this project.

2. Define and evaluate alternatives for reducing nitrogen into the recovery boiler for the model mill, based on research articles, patents, and ÅF experience.

Two main alternatives are considered:

Alt 1: Acidification of foul condensate before stripping, or in the stripper column, to convert volatile ammonia compounds to non-volatile ammonia ions which remain in the stripped condensate.

Alt 2: Acidification and separation of ammonia from SOG, or the mill's methanol by product.

Evaluation of each of the two process alternatives covers the following:

- Process description, including a general equipment specification
- Nitrogen balance to estimate the reduction of nitrogen to the recovery boiler
- Potential process consequences in other mill areas and operating experiences
- Equipment and operating cost estimates

3 Base case

3.1 Mill Description

The model mill considered is a Nordic softwood bleached kraft pulp mill. The design of the mill is based on best available and commercially proven technology. A detailed description of the mill is given in the 2005 FRAM project (STFI-Packforsk, 2005) and the update in 2010 "Energy consumption in the pulp and paper industry - Model mills 2010; Bleached kraft market pulp mill" (ÅForsk, 2010). Key design factors which are relevant to this study are summarized below.

- Production: 2000 ADt/d bleached softwood market kraft pulp, maximum continuous rate (MCR)
- Wood supply: 50% pine / 50% spruce
- Deknotted digester yield 47%, final bleached yield 44%
- The evaporation plant produces 80% dry solids liquor, and operates at 771 t H_2O/h. All of the intermediate condensate is used in the recausticizing plant for dregs washing, lime mud dilution, and as shower water on the lime mud filter. The clean condensate is used as wash liquor in the brown stock and bleach plant, and any excess is discharged as effluent.
- There is a stripping system for foul condensate from the digester and evaporation plant and a methanol rectification column with turpentine decanter and foul methanol liquor storage. Liquid methanol is incinerated in the recovery boiler.
- Non condensable gases are collected throughout the mill. Both low volume high concentration (LVHC) and high volume low concentration (HVLC) gases are burned in the recovery boiler.
- The smelt dissolving tank vent is returned to the recovery boiler.
- Primary effluent treatment consists of a clarifier to remove fiber sludge, cooling, and neutralization. Effluent flow after primary treatment is approx. 22 m^3/ADt and COD is approximately 26 kg/ADt.
- Biological effluent treatment consists of a bio-film reactor with suspended carriers and an activated sludge system (aeration basin and secondary clarifier). The system is designed for low bio-sludge production and low nutrient discharges. COD reduction is approximately 65-70%.
- The biological sludge from the secondary clarifier is dewatered to about 10% in a centrifuge and mixed with intermediate black liquor in the evaporation plant, before firing in the recovery boiler. Primary sludge is fired in the power boiler.

3.2 Nitrogen balance

The nitrogen balance for the base case is presented in Appendix 1.

Several studies have been done regarding the nitrogen chemistry in the kraft pulping process including nitrogen balances. There are some differences from study to study, for example, quantification of HVLC gases, however the general fate of nitrogen is similar. Following is a description of the nitrogen balance for the model mill.

3.2.1 Fiber line

The main source of nitrogen to the kraft pulping process is the wood chips to the digester. The nitrogen content of wood chips depends on, for example, whether the wood is hardwood or softwood, wood species, and bark content of the chips. Hardwoods generally have higher nitrogen content than softwood, and bark contains about ten times more nitrogen than wood, on a dry weight basis. The nitrogen content in wood can vary from 0.4 - 2.0 kg N/ t wood. In this study, softwood containing 693 g N / kg dry wood corresponding to 1 300 g N / ADt has been taken into account. The nitrogen in the wood is mainly in the form of peptides in the wood proteins and enzymes.

In addition to the nitrogen entering the digester with the wood chips, there is also nitrogen which enters the digester with white liquor. Since the chemical recovery system in the kraft pulping process is basically a closed cycle, the nitrogen in the white liquor originates from the wood chips. Nitrogen in the white liquor is mainly in the form of ammonia.

Approximately 90-95% of the nitrogen in the wood chips is released during the cooking process and exits the digester with the blow gases and the black liquor. Some nitrogen leaves the digester with the pulp to brownstock washing, but the majority of that nitrogen returns to the digester with the brownstock wash liquor.

A portion of the wood nitrogen which is released during the cooking process is converted to ammonia, and the remaining wood nitrogen is contained in organic nitrogen compounds. According to DeMartini et al. (2004) approximately 10-15% of the wood nitrogen is converted to ammonia. About half of the ammonia in the digester is released with the digester blow gases, while the organic nitrogen compounds and the remaining ammonia exit the digester with the weak black liquor to the evaporation plant.

3.2.2 Liquor cycle

Studies have also found that some additional ammonia is formed in the early effects of evaporation. According to Demartini et al. (2004) the amount of ammonia generated during evaporation is equivalent to approximately 12 - 13% of the wood nitrogen. Essentially all of the ammonia in the black liquor from the digester plus the additional ammonia formed during evaporation is released to the evaporation plant condensates.

The evaporated black liquor is fired in the recovery boiler. Approximately one third of the nitrogen in the black liquor leaves the recovery boiler as smelt to the smelt dissolving tank (Kymälainen et al. (1999)).

The nitrogen in the smelt is mainly in the form of cyanates which are mostly converted to ammonia during the smelt dissolving / recausticizing processes. According to Kymälainen et al.

(2004), green liquor nitrogen corresponds to approximately 40% of the black liquor nitrogen. Approximately 60% of the green liquor nitrogen remains in the white liquor to the digester, approximately 20% of the green liquor nitrogen is returned to the smelt dissolving tank as weak wash, and approximately 20% of the green liquor nitrogen exits the process as gaseous NH_3 around the slaker and causticizer vessels.

3.2.3 Condensate and Gas Handling systems

In the model mill, the evaporation plant condensates are divided into clean, intermediate, and foul condensates, depending on the level of contamination. Clean condensates typically have a COD of approximately 200 mg/L, and intermediate condensates can range from 500 - 1000 mg/L. Foul condensate from the digester and the evaporation plant contain methanol, malodorous sulphur compounds, turpentine, and potentially minor quantities of tall oil resins, thus the foul condensate COD is far higher. The foul condensate is stripped in a steam stripper where most volatile contaminants are recovered to the SOG. The stripped foul condensate is clean enough to be mixed with the clean condensate.

Evaporation condensate segregation varies from mill to mill, depending on how condensates are reused and on the quality requirements for condensate released as effluent. In general, new evaporation plants have condensate segregation designed so that all of the intermediate condensate which is generated can be consumed in recausticizing, since it is not acceptable to release intermediate condensate as effluent. In some mills there may be an excess of intermediate condensate which is stripped with the foul condensate, or even in a separate stripper, to produce clean condensate.

In the model mill all intermediate condensate is used in the recausticizing plant for dreg washing, lime mud dilution, and shower water on the lime mud filter. The clean condensate including the stripped condensate is used for post oxygen washing and bleach plant washing. Only a minor amount of the condensate used for washing is returned to the liquor cycle via the digester. Any excess clean condensate is released as effluent from the mill.

Digester blow gases contain about half of the ammonia that is in the digester. Essentially all of this ammonia remains with the digester foul condensate. The evaporation plant condensates contain the remaining half of the ammonia from the digester plus ammonia formed during evaporation of the black liquor. Studies made show (Gautreaux et al. (2004)) that all ammonia is released to the SOG during foul condensate stripping and that the stripped condensate is essentially nitrogen free. Based on Kymäläinen et al. (1999), it has been assumed that the foul condensate contains approximately 75% of the total condensate nitrogen while remaining nitrogen is found in the clean and intermediate condensates.

In the base case it has been assumed that half of the intermediate and clean condensates are used in the recausticizing plant while the remaining intermediate and clean condensates together with stripped condensate are used in the fiber line for washing in brownstock and bleaching. Fiber line wash filtrates that are not recycled are sent to the waste water treatment plant. A minor amount of the nitrogen in the fiber line wash filtrates is released to the HVLC collection system. It is assumed that the washing and bleaching operations do not absorb any nitrogen to the pulp.

There are some references, such as Kymäläinen et al. (1999), which describe nitrogen losses to the HVLC collection system in the recausticizing plant area. Unfortunately, no information regarding nitrogen HVLC losses in other mill areas has been found, thus the amount of nitrogen released from both the fiber line and evaporation plant is scaled proportionally to the recausticizing area HVLC nitrogen.

In most mills the HVLC gases are collected and in most modern pulp mills the HVLC gases from both the fiber line and evaporation plant are well covered as well as the vent gas from the dissolving tank. Unfortunately not all pulp mills cover the recausticizing plant area to the same extent. This is due to several reasons such as installation cost and primary focus on collecting the most extensive odor sources. In general the installation of a HVLC gas collection system implies a lot of piping and ducting that must be carefully designed in order to avoid high material cost etc. The cost for piping, ducting and the design thereof can be more expensive than the investment cost for the main equipment. For this reason, HVLC gas collection systems are often expanded gradually.

There are few specific technologies for reduction of LVHC nitrogen (Blomström & Lundahl, 2006). Most of these technologies are based on absorption of ammonia by simple water spraying since ammonia is readily soluble in water. This absorption process is somewhat similar to a HVLC cooling scrubber. Measurements and studies made on HVLC nitrogen are however extremely rare since most are focused on TRS and other parameters of interest. Resulting HVLC condensates, depending on the moisture content, are normally low volume and if not too odorous these condensates can be taken either to the waste water treatment plant or to the mill foul condensate collection system.

The SOG is treated in a methanol recovery system where the methanol is recovered as liquid methanol. Liquefied methanol is a more concentrated fuel than compared to SOG and the liquefied form facilitates both temporary storage and implies stable incineration in terms of stable heat input and reduced flame fluctuations. The recovered methanol is burned in the recovery boiler, alternatively the lime kiln or in a dedicated incinerator.

3.2.4 Effluent treatment

The amount of nitrogen required for the biological effluent treatment to function properly depends on the COD of the incoming effluent. A normal nitrogen requirement in a bleached kraft mill bio treatment is approximately 0.5 kg N/ADt. The incoming effluent contains some nitrogen and is added either as urea, Nutriol™ or a similar commercial nitrogen mixture.

The bio sludge from effluent treatment is taken back to the evaporation plant, dewatered, hydrolyzed and mixed with black liquor that is sent to the recovery boiler. Approximately half of the effluent nitrogen, 0.25 kg/ADt, is bound to the bio sludge according to ÅF file data. The bio sludge contains about 10 % as reduced ammonia nitrogen (Kymäläinen et al. (2000)), and the remaining 90 % of the bio sludge nitrogen is considered organically bound nitrogen with somewhat similar behavior and properties as the organic nitrogen found in black liquor.

For mills that do not recover bio sludge, it is estimated that the nitrogen content in most streams would be about 20% lower than the base case presented in this report. This observation seems indirectly to correlate with other studies made in this field where for example the flue gas NO concentration has been observed to increase by 21 % after bio sludge intake to the recovery cycle (Vähä et al. (2012).

4 Alternative 1 - Acidification of foul condensates and SOG

4.1 Process Description

In this alternative, the foul condensate is acidified to pH less than or equal to 6.5 prior to steam stripping. At this pH, most of the ammonia is captured as NH_4^+ in the liquid clean condensate from the stripper. The clean condensate is used in the bleach plant, and then sent to the waste water treatment plant. The added acid neutralizes the ammonia and in some cases, minor amounts of other alkaline compounds. There is some neutralizing heat formed however the temperature increase is relatively insignificant, mainly due to the large volume of foul condensate. In the M-Real process (Alfthan & Sjölander, 1999) the acid is added directly to the foul condensate tank, whereas the acid is added to the upper part of the stripper column in the Södra Cell process (Olsson & Zacchi, 2004). The chemical principle is however the same even if there may be some minor differences when it comes to equipment details etc. In general these processes do not require any special equipment except for acid preparation and dosing equipment.

The quality of the acid and the purity demand seems to vary somewhat in these methods. The M-Real process used sulfuric acid but the Södra Cell process seems open to a wide range of different types of acids. Theoretically any acid would work, but due to corrosion problems some acids such as hydrochloric acid are less suitable. A dilute sulfuric acid seems to be the most commonly used acid for these types of applications. A standard material such as ASTM 316 or similar material seems to be the preferred material and should be suitable as long as the acid control operates as expected.

There are some other potential problems which may occur in these processes. In softwood mills the foul condensate may contain extractives. These extractive compounds as well as TRS compounds present in the foul condensate may partly polymerize when acid is added and cause clogging problems or unwanted scaling from where the acid is added and downstream. If clogging occurs in the stripper the cleaning procedure may be complicated and time consuming. These types of problems are however not fully documented but recorded in ÅF file data. Neutralization of ammonia by sulfuric acid may also cause precipitation of ammonium sulfate that may cause local problems, especially in the acid mixing zone, thus proper mixing seems important. For this reason, even if the ammonium sulfate is very soluble, there is a small but not negligible risk that the stripper trays, especially in the inlet region, may be exposed to deposit formations that may clog valves, downcomers or else disturb the stripper operation.

4.2 Nitrogen Balance

The nitrogen balance for this alternative is illustrated in enclosure 2. The balance is mainly based on the M-Real patent, but similar results are expected with the Södra Cell process. The nitrogen content for some of the key streams compared to the base case is shown in table 2 below.

	Base case g N/Adt	M-Real process g N/ADt	change, %
Wood	1300	1300	-
White liquor	368	294	-20
Weak black liquor	1362	1346	-1
Biosludge intake	250	250	-
Digester foul condensate	236	220	-7
Evaporation foul condensate	247	237	-4
SOG	480	13	-97
Stripped condensate	10	446	4360
Clean/intermediate condensates	155	586	278
MeOH to recovery boiler	451	12	-97
LVHC to recovery boiler	75	52	-31
Black liquor to recovery boiler	1181	1181	-
Total nitrogen to recovery boiler	1860	1446	-22
Green liquor	614	490	-20
Lime mud	31	26	-16
Purchased N to effluent treatment	434	87	-80

Table 2. Nitrogen amounts for some key process streams for the M-Real process compared to the base case.

According to the balance the total nitrogen fed to the recovery boiler (excl. nitrogen as N_2) can be reduced by about 22 % or about 400 g N/ADt by the acidification of the foul condensates and the SOG. The amount of ammonia is markedly increased in the stripped and intermediate condensates. The method is simple and requires a minimum of additional process equipment. The nitrogen as ammonia in foul condensate is captured to the stripped clean condensate for further use in the fiber line operations. Some nitrogen will be recovered to the fiber line HVLC collection system but most nitrogen will finally be found in the effluents taken to the waste water treatment plant.

4.3 Potential consequences in other mill areas

According to the balances the HVLC nitrogen increases by about 30 % due to the use of the nitrogen enriched condensate in the fiber line. Unpublished Swedish mill experience indicates that the process decreases the clean condensate COD. Even if this is expected due to improved removal of acidic TRS compounds it should be a welcomed side effect.

In terms of nitrogen, the optimal scenario would be if the nitrogen enriched clean condensate from the stripper can be taken directly to the waste water treatment. In this case however, the clean condensate used in the fiber line washing and bleaching processes would have to be replaced with fresh water, and the mill’s total fresh water consumption would increase.
If acidulation is made with fresh sulfuric acid, additional NaOH will be required as make-up in order to maintain the Na/S balance.

5 Alternative 2 - Nitrogen condensate recovery from Kraft methanol

Metso (Brucher & Norberg, 2009) has developed a process for capture of nitrogen from liquid methanol. A.H. Lundberg (Der & Jensen, 2010) has developed a process similar to Metso's but it is however not considered in this study. Andritz (Saviharju & Eneberg, 2003) has developed a process for nitrogen capture which is based on acid scrubbing of the SOG. The Metso and Andritz processes differ from each other but both result in a more nitrogen concentrated condensate compared to Alternative 1. The lower volumetric flows and higher nitrogen concentration implies in new possibilities, such as sending the nitrogen enriched condensate directly to the waste water treatment plant without first passing the bleach plant.

5.1 Process Description

5.1.1 The Metso "PuriMeth™" process

In the Metso process liquid methanol is processed, and a methanol recovery plant is a first requisite for the process. The purpose of the Metso "PuriMeth™" process is to remove the nitrogen in a first stage and oxidation of odorous TRS compounds in a second stage. In this study only the nitrogen removal stage is considered. The resulting nitrogen and odor -free methanol can then be further processed or incinerated without causing increased NO_X.

The process is relatively simple; initially the methanol from the methanol storage tank is mixed with sulphuric acid, and then transferred to a column where the volatile methanol and TRS phase is separated from the ammonium containing water phase. The gas phase is condensed for further use whereas the ammonium containing condensate can be used for nitrogen replacement in the waste water treatment plant or further refined and sold as a fertilizer if sufficiently free from TRS compounds and other impurities.

5.1.2 The Andritz process

In the Andritz process the SOG is scrubbed with acid, resulting in an enriched nitrogen condensate. The amount of condensate from the ammonia scrubber is higher compared to the Metso process, but still much lower compared to the M-Real and the Södra Cell methods. According to ÅF file data the nitrogen capture efficiency seems to correlate to the gas- liquid contact arrangement inside the scrubber system. Similar to the Metso process the resulting condensate can be taken to the waste water treatment plant to replace purchased nitrogen.

5.2 Nitrogen Balance

A nitrogen balance, mainly based on the Metso "PuriMeth™" process, is shown in enclosure 3. Depending on the scrubbing efficiency the Andritz process balance should in general appear somewhat similar. According to ÅF file data the resulting methanol is more or less totally free from nitrogen and depending on the amount of water present in the system and steam used in the column the condensate nitrogen concentration is approximately. 30 - 45 g/l. There is a minor increase in both nitrogen and other volatile TRS compounds to the LVHC collection system due to the vent from the condenser. The condensate is sent to the water treatment plant.

Table 3 below summarizes the nitrogen content for some of the key streams in relation to the base case.

	Base case	**Metso Power process**	
	g N/Adt	**g N/ADt**	**change, %**
Wood	1300	1300	-
White liquor	368	280	-24
Weak black liquor	1362	1317	-3
Biosludge intake	250	250	-
Digester foul condensate	236	191	-19
Evaporation foul condensate	247	219	-11
SOG	480	408	-15
Stripped condensate	10	8	-20
Clean/intermediate condensates	155	136	-12
MeOH to recovery boiler	451	0	-100
LVHC to recovery boiler	75	85	13
Black liquor to recovery boiler	1181	1181	-
Total nitrogen to recovery boiler	1860	1384	-26
Green liquor	614	467	-24
Lime mud	31	25	-19
Purchased N to effluent treatment	434	85	-82

Table 3. Nitrogen amounts for some key steams for the Metso "PuriMeth™" process compared to the base case. The total amount of nitrogen to the recovery boiler is decreased by about one fourth.

In the Metso "PuriMeth™" process, the total nitrogen to the recovery boiler is reduced by approximately 26 % or about 475 g N/ADt compared to the base case and about 4 % more than compared to Alternative 1. The installation does however require more equipment to be installed and the higher investment cost has to be evaluated relatively the small increase in efficiency. The Metso "PuriMeth™" process may however be justified if the nitrogen free methanol shall be further purified with respect to sulfur but this case has not been examined in this study.

As in Alternative 1, most process streams contain lower nitrogen amounts and the nitrogen enriched condensate from the Metso "PuriMeth™" process can be sent directly to the waste water treatment plant since this relatively concentrated nitrogen stream will not affect the water balance significantly.

5.3 Potential consequences in other mill areas

According to ÅF file data there are no known Metso "PuriMeth™" installations. There is however one Swedish mill that has been operating an Andritz installation for a couple of years. The mill operating the Andritz installation has had extensive clogging problems and because of this the system is presently not in operation but by-passed. The Metso "PuriMeth™" only processes the methanol after the methanol recovery process, not the total SOG, so there are reasons to believe that such clogging issues may be less serious, or possibly not an issue at all.

The mill that was operating the Andritz installation started to recover bio sludge to the evaporation plant in 2004 and it was observed that the overall nitrogen level in the mill increased. After installation of the Andritz process the resulting nitrogen condensate was taken to the waste water treatment and no related serious consequences has been reported in this matter.

Ordinary “Low-NO_X” incinerators are generally expensive but the Metso “PuriMeth™” process enable relatively cheap “low-NO_X” incineration of the kraft methanol since treated methanol can be taken to almost any ordinary mill incineration system such as the lime kiln. Sulfur capture is however required in order to keep the SO_2 emissions at a fairly low level.

Similar to Alternative 1, if fresh sulfuric acid is used for acidulation a corresponding amount of NaOH is required for maintaining the Na/S balance.

6 Economic evaluation

The investment- and operating costs for both Alternative 1 and 2 has been estimated. The investment cost covers all estimated costs for a "turnkey" delivery designed for the mill capacity as presented in section 3.1.

The reduced NO_X in the recovery boiler flue gas may in some countries, such as Sweden, also affect the operating costs. The Swedish NO emission fee in relation to both Alternative 1 and 2 is discussed in section 6.2.

6.1 Alternative 1

6.1.1 Investment cost

Even if the M-Real process has not been specified in detail it is assumed that the process comprises the following equipment:

- Centrifugal pump
- pH controlling equipment incl. control valve
- Liquid distributor
- Piping, incl. manual valves

It is assumed that sulfuric acid, mixed to approximately 30 w% is available within a reasonable distance from the installation. The assumed base material is ASTM 316. The turnkey cost is estimated to between 50 - 75 kEUR. The piping cost is the biggest uncertainty since it depends on the existing layout.

6.1.2 Operating cost

The operating cost has been estimated in table 4 below. It has been calculated that about 413 g N/ADt of the nitrogen enriched condensate sent to the fiber line is finally sent to the waste water treatment plant, thus savings due to replacement of urea or similar chemicals can be made. This process requires somewhat more acid than compared to the Alternative 2. Due to the use of clean condensate in the bleach plant area this process implies increased nitrogen losses to the HVLC collection system, thus slightly less amounts of nitrogen for use in the waste water treatment plant than compared to Alternative 2.

		EUR/ADt
Sulfuric acid (as 100-w %)	0.14 EUR/kg	0.27
NaOH (as 100-w %)	0.39 EUR/kg	0.61
Electricity	0.07 EUR/kWh	0.01
Nitrogen replacement	-1.0 EUR/kg	-0.41
TOTAL		0.47

Table 4. Estimated costs for consumables based on typical figures.

The operating cost is estimated to about 0.5 EUR/ADt, corresponding to an annual operating cost of about 620 kEUR but reduced to about 330 kEUR if the waste water treatment plant and the nitrogen saving is taken into account. Typical figures have however been used and may vary. The NaOH consumption for neutralization is conservatively estimated. It is assumed that neutralization of the condensate flow is required irrespective if recycled to the black liquor or

discharged with bleach plant wash filtrates to the effluent treatment and as seem from table 4 the NaOH cost is the biggest.
In the study there has not been any attempt to quantify the recovery boiler NO_X-formation effect with aspect to decreased ammonium-nitrogen intake. Accordingly, any costs associated with recovery boiler NO_X-formation are disregarded.

6.2 Alternative 2

6.2.1 Investment cost

It is assumed that the Metso “PuriMeth™” process comprises the following equipment:

- Mix tank
- Column with internals
- Condenser
- Centrifugal pumps
- Field instrumentation incl. control valves (8 loops assumed)
- Piping incl. manual valves
- Steel structure

It is assumed that diluted acid is available relatively close to the installation site and only additional piping and control valve is needed. The assumed base material is Duplex or LDX type of steel for the Mix tank, upper part of the column and the condenser. The turnkey cost for this system is estimated to about 790 - 825 kEUR. As for Alternative 1 there are uncertainties in not only the piping cost but also in required steel structures etc.

6.2.2 Operating cost

The Metso “PuriMeth™” process operation cost has been estimated in table 5 below. Similar to Alternative 1 typical values for consumables has been assumed and may vary between different mills. A cost for NaOH for neutralization of freshly added sulfuric acid is also included. The first stage of the Metso “PuriMeth™” process, results in an increased annual operation cost estimated to about 512 kEUR/a but taking the waste water treatment nitrogen savings into account the annual operating cost is reduced to about 217kEUR/a. Perhaps the operation cost looks more attractive if the second stage of this process, where TRS-free methanol is produced, is taken into account. The second stage is however beyond the scope for this study and has not been considered. Due to the minor amount of acid used in this process less neutralizing NaOH is required than compared to Alternative 1. Since it is assumed that the recovered nitrogen condensate is sent directly to the waste water treatment this process also implies less nitrogen losses to the HVLC collection system. Similar to Alternative 1 the NaOH cost is the biggest.

		EUR/ADt
Sulfuric acid (as 100-w %)	0.14 EUR/kg	0.18
NaOH (as 100-w %)	0.39 EUR/kg	0.41
Electricity	0.07 EUR/kWh	0.004
Low pressure steam	0.01 EUR/kg	0.13
Nitrogen replacement	1.0 EUR/kg	-0.42
(Warm water production	0.5 m^3/ADt	-)
TOTAL		0.31

Table 5. The estimated operation cost related to the first stage of the Metso “PuriMeth™” process.

There have not been any attempts to quantify effects on NO_X-formation in the recovery boiler resulting from lower intake of ammonium-nitrogen to the recovery boiler. Accordingly, any costs associated with recovery boiler NO_X-formation are disregarded.

7 Conclusions

Over the years several processes and technologies to reduce the nitrogen intake (excl. air N_2) to kraft pulp mill recovery boilers have been developed. Such reduction is expected to result in a decreased recovery boiler NO_X emission.

Most processes apply acidification of foul condensates, gases or methanol and produce nitrogen (ammonium) enriched condensate. In cases where there is a waste water treatment plant using reduced nitrogen it seems possible to make savings if the recovered nitrogen can be replace a purchased nitrogen source. Most of the main suppliers have developed technologies for nitrogen capture as a part of a bigger scope where TRS free methanol is recovered. Some of these technologies are however still under development, especially when it comes to the refining of the methanol. There seems however to be a negative operating cost when considering the nitrogen removal stage only and A.H. Lundberg is the only known supplier where such a concept has been commercialized.

The processes evaluated in this study demonstrate that it theoretically seems possible to reduce the recovery boiler nitrogen load by 20-25 % at relatively low capital and operating costs. There are however several factors that affect the total result. The potential use of the recovered nitrogen streams is of great importance since reuse in internal mill processes tends to suppress the benefit due to losses either to HVLC or other condensates that are recirculated back to the evaporation plant. For this reason, the waste water treatment plant, where reduced nitrogen is consumed, is perhaps the most obvious consumer. Acidification of foul condensates, SOG or kraft methanol may however not be problem free. According to ÅF file data some mills suffer from clogging due to polymerization of TRS compounds and extractives. In one mill, where the SOG is scrubbed with diluted sulfuric acid, these problems have caused serious disturbances and today the nitrogen capture system is bypassed.

If a NO_X regulation with an emission fee is effective, there can be significant operating cost savings when the nitrogen to the recovery boiler is reduced. Therefore further work to overcome the practical problems with the technologies reviewed in this study is highly recommended.

8 Further studies

The effect from decreased nitrogen intake to the recovery boiler (or to a dedicated incinerator) on NO_X emissions was not part of this study. A continuation of this study could be to perform practical field studies on the effect of decreased ammonium nitrogen intake in relation to the NO_X-generation.

In Sweden bigger incinerator systems with an annual capacity of more than 25 GWh are covered by an additional emission fee for flue gas NO. Depending on several factors such as the recovery boiler reduction efficiency, type of processed wood etc. the emission fee may be high or low. The NO emission and the resulting NO emission fee is generally higher for older recovery boilers in mills where hardwood pulp is produced. Further studies are however required to clarify the relation between the results from the present study and the NO_X generation. Such study would be of great importance to verify both environmental aspects and potential economical savings.

9 References

09-163, Å. R. (u.d.). *Energy Consumption in the Pulp and Paper Industry - Model mills 2010, Bleached Kraft Market Pulp Mill.*

Alfthan, C. J., & Sjölander, C. (1999). *Patentnr 9800190-2.* Sweden.

Andersson, L., & Norrström, H. (2010). Metoder för NOx reduktion på sodapannor. *Sodahuskonferensen 2010* (ss. 23 - 35). Stockholm: ÅF Industry AB.

Blomström, S., & Lundahl, R. (2006). *Patentnr WO/2010/016786.* US.

Brucher, J., & Norberg, A. (2009). *Patentnr SE531478.* Sweden.

Clement, J. L., & Barna, J. L. (1993). The effect of black liquor fuel-bounding nitrogen on NOx emissions. (ss. 653 - 660). TAPPI Proc Int Environ Conf Exhib, Book 2.

Demartini, N., Forssen, M., Hupa, M., Niemela, K., & Ulmgren, P. (u.d.). Distribution and Release of Nitrogen Compounds at Kraft Pulp Mills - A Survey of Three European Mills.

Der, B., & Jensen, A. (2010). *Patentnr WO2010091492.*

Gautreaux, W. T., Matthews, J. L., Hardee, J. L., & Bunting, K. P. (2004). *Ammonia Scrubber for Condensate Stripper Off-Gases.* North Charleston, South Carolina: MeadWestaco Corporation, Kraft Division.

Kristoffer Svedin, C. I. (2009). *LIME KILN MODELING CFD & One-dimensional simulations.* Stockholm: Värmeforsk.

Kymäläinen, M., Forssén, M., & Hupa, M. (1999). The fate of Nitrogen in the Chemical Recovery process in a Kraft pulp mill: Part 1: A general view. *Journal of Pulp and Paper Science 25 (12)*, 410-417.

Kymäläinen, M., Forssén, M., Demartini, N., & Hupa, M. (2000). *Effects of differences in the Kraft recovery process on harmful nitrogen.* Process Chemistry Group. Turku, FINLAND: Åbo Akademi University.

Olsson, J., & Zacchi, G. (2004). *Patentnr 9903676-6.* Sweden.

Saviharju, K., & Eneberg, H. (2003). *Patentnr EP001424435.*

Vähä-Savo, N., Demartini, N., & Hupa, M. (2012). Fate of biosludge nitrogen in black liquor evaporation and combustion. *TAPPI JOURNAL; 11, 9*, p 53-59.

ÅForsk. (2010). *Energy Consumption in the Pulp and Paper Industry - Model mills 2010, Bleach Kraft Market Pulp Mill.* Reference 09-163.

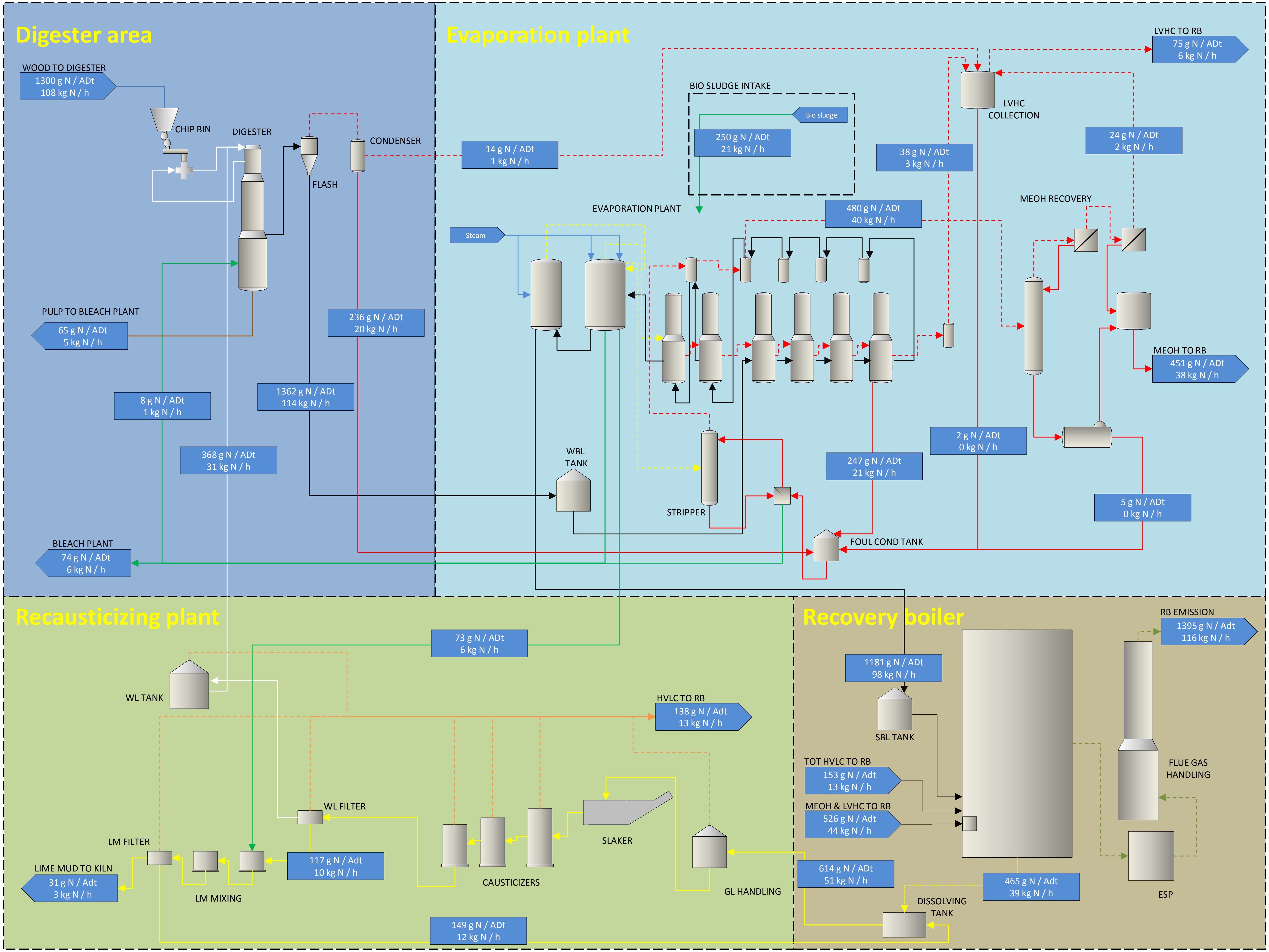
10 Enclosures

No 1 - Reference nitrogen mass balance block diagram

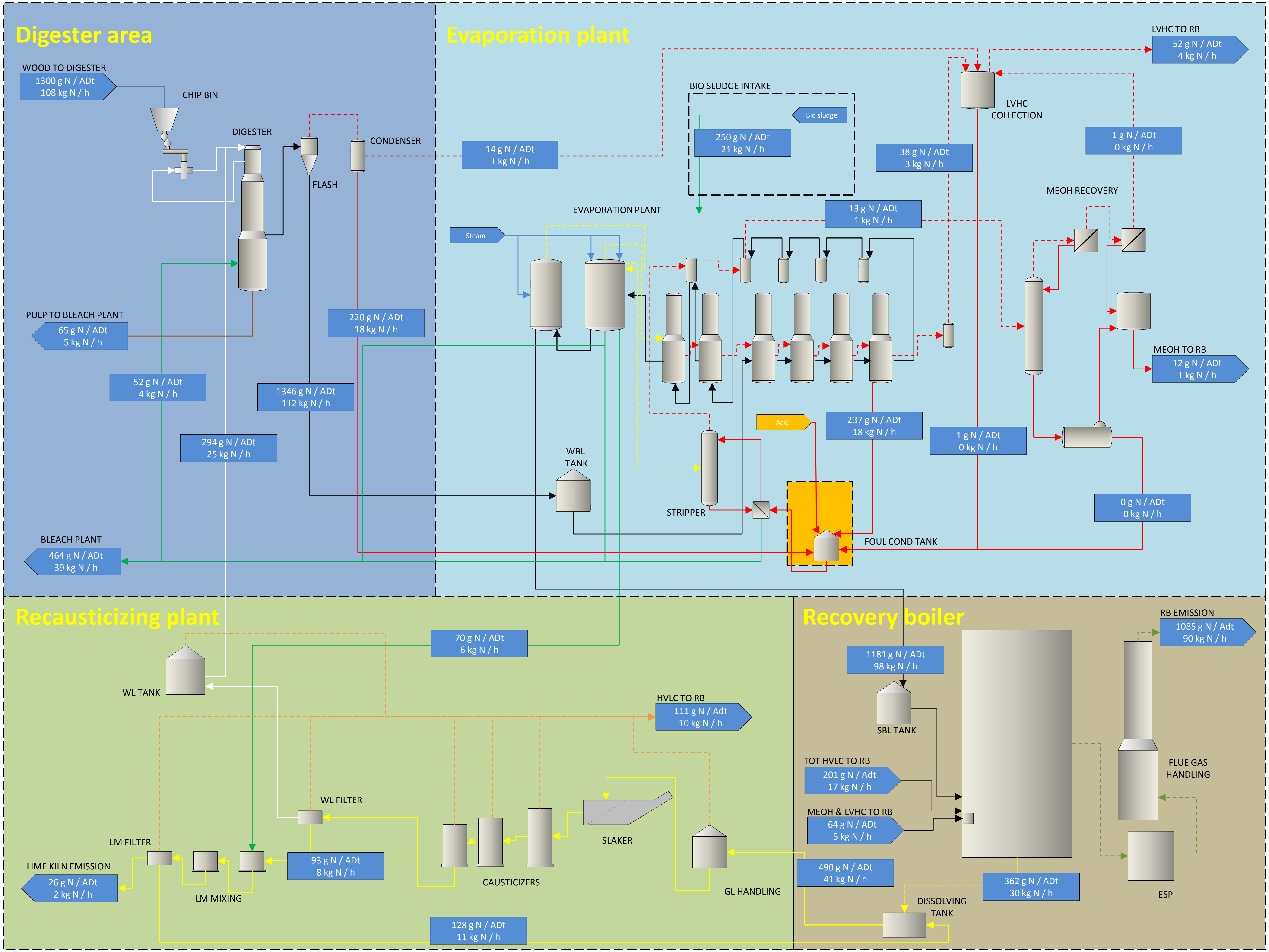
No 2 - Alternative 1 nitrogen mass balance block diagram

No 3 - Alternative 2 nitrogen mass balance block diagram

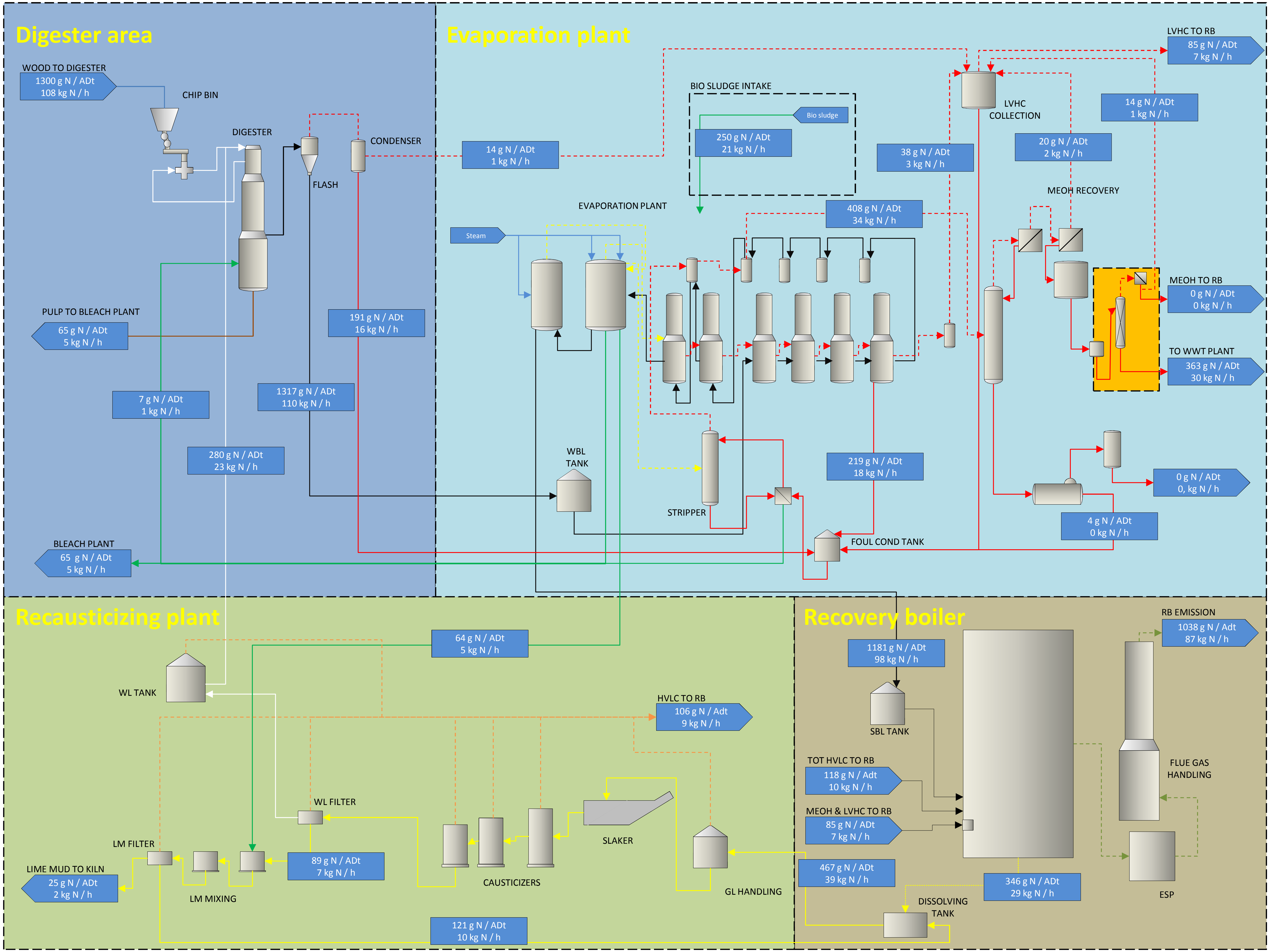
Enclosure 1: Reference nitrogen mass balance block diagram



Enclosure 2: Alternative 1 nitrogen mass balance block diagram



Enclosure 3: Alternative 2 nitrogen mass balance block diagram



LIITE 2

Oy Sirra Ab, Rikkitaseen hallinta ja soodasakkamäärän vähentäminen – tarjous 15.1.2017

PROJEKTIEHDOTUS 15.1.2017/KS/Oy Sirra Ab

SKY/YTR

Rikkitaseen hallinta ja soodasakkamäärän vähentäminen

Idea: Viherlipeäsakan syrjäytyspesun ja GLSS-prosessin yhdistäminen. Molemmat prosessit vaativat viherlipeän laimentamista. Jos voidaan yhdistää ne, saadaan samalla laimennuksella molempien hyödyt.

Hyöty sellutehtaalle: Rikkitaseen hallinta ja samanaikainen kaatopaikalle menevän viherlipeäsakan määrän vähentäminen, sakan hyötökäyttöedellytyksien parantaminen. Klooridioksidilaitoksen jätesuolan nykyistä parempi hyödyntäminen.

Tavoite: Yhdistetyn prosessin käyttökelpoisuuden selvittäminen koeajamalla se pilot-laitoksessa. Datan hankkiminen täyden mittakaavan laitoksen suunnittelun pohjaksi.

Tausta: aikaisemmissa hankkeissa ”Viherlipeäsakan syrjäytyspesu” ja ”Viherlipeäsakan syrjäytyspesu, Osa 2: alkuaineet” kehitettiin prosessia, jolla viherlipeäsakka voidaan pestä alkalisuoloista ilman meesaa apuaineena. Tällä tavalla voidaan vähentää kaatopaikalle menevää sakkamäärää 50 – 60 %. Samalla saadaan helpompi lähtökohta jatkoprosessille, jolla pyritään tekemään sakka hyötykäyttökelpoiseksi, ja siten eliminoimaan kaatopaikkajäte mahdollisimman täydellisesti.

Pohjoisissa tehtaissa, joissa keitetään mäntyöljyä, rikkitase on yleensä ongelma. Rikkitase rajoittaa klooridioksidilaitoksen jätesuolan hyödyntämistä, pakottaa lentotuhkan liuottamiseen ja vaikeuttaa kaliumin- ja kloorinpoistoprosessin käyttöönottoa. KCL-projektissa ”Management of sulfur balance” kehitettiin GLSS-prosessikonsepti (Green Liquor Simplified Stripping). Prosessissa stripataan viherlipeästä rikkivetyä, H_2S, joka hapetetaan redox-reaktiolla alkuainerikiksi. Rikki saadaan siten ulos sellutehtaan kemikaalikierrosta ilman samanaikaisia natriumhäviöitä. Klooridioksidilaitoksen jätesuola voidaan silloin ottaa sisään kemikaalikiertoon, ja saada sekä sen natrium että sen happamuus hyötykäyttöön. Taloudellinen hyöty tulee ensisijaisesti ostonatriumhydroksidin säästöistä. Kemikaalisäästöt ovat arvioiden mukaan noin 2,7 milj. euroa vuodessa. Ympäristövaikutukset ovat merkittävät, sillä happaman jätesuolan liuottaminen on mahdollista jopa lopettaa kokonaan.

Molemmissa prosesseissa lipeä on laimennettava, mistä syntyy ajatus että ne voitaisiin yhdistää, ja saada sekä rikkitaseen hallinta että kaatopaikkajätteen määrän vähentäminen samalla prosessilla. Käytännössä tämä tarkoittaa sitä, että puhtaan viherlipeän sijaan käytetään GLSS-prosessissa sakkaselkeyttimen alitetta. Alitteesta stripataan rikkivety, minkä jälkeen sulfidivapaa alite viedään syrjäytyspesuun. Aikaisemmassa hankkeessa todettiin, että sakan jatkokäyttöä ajatellen on turvallisuuden vuoksi tärkeätä poistaa sulfidi, jotta rikkivetyvaaraa ei voi missään käyttökohteessa syntyä. Yhdistämällä prosessit saadaan sulfidi pois, ja saadaan siten kaksinkertainen hyöty.

Syrjäytyspesun jälkeen sakka viedään jatkokäsittelyyn, jossa sen hyötykäyttömahdollisuuksia parannetaan. Jatkoprosessin kehittäminen on suurehko projekti, eikä sitä ole mahdollista viedä loppuun tämän hankkeen puitteissa, mutta voidaan kuitenkin ottaa askeleita eteenpäin. Vaihtoehtoina ovat ensisijaisesti olleet vaahdotus ja happokäsittely, joiden ensisijaisena tarkoituksena on alentaa kadmium- ja myös muiden raskasmetallien pitoisuuksia. Vaahdotusta on tutkittu aikaisemmin, ja tässä työssä voidaan keskittyä happoliuotukseen. Selvitetään ainakin haponkulutus ja mahdollisuutta saostaa kadmium, lyijy ym. metalleja liuoksesta, ja siten erottaa ne pääaineksesta. Vahvana hyötykäyttövaihtoehtona on metsälannoite, jossa erityisesti kadmiumpitoisuus vaatii huomiota.

GLSS–prosessi ja syrjäytyspesu

GLSS-prosessissa rikkivety stripataan viherlipeästä laskemalla tämän pH:ta hiilidioksidilla. Hiilidioksidi otetaan soodakattilan savukaasuista. Periaatteessa on myös mahdollista käyttää puhdasta hiilidioksidia. Muodostunut rikkivety hapetetaan alkuainerikiksi kolmiarvoisella raudalla erillisessä tornissa. Rauta pelkistyy reaktiossa kaksiarvoiseksi, mutta se regeneroidaan kolmiarvoiseksi hapettamalla se ilmalla erillisessä astiassa. Rauta toimii siten katalysaattorina. Tämä osa prosessista on olemassa kaupallisena nimellä Lo-Cat.

Lipeän sulfidi ja hydroksidi vaihtuvat vetykarbonaatiksi ja karbonaatiksi. Vetykarbonaatin liukoisuus on hieman pienempi kuin muiden komponenttien, minkä vuoksi on edullista laimentaa lipeä hieman saostumien välttämiseksi.

Sakan syrjäytyspesuprosessissa lipeäkomponentit pestään pois pystysuorissa putkissa vastavirtaperiaatteella. Prosessi on tarkemmin kuvattu hankkeen raportissa. Kokeissa todettiin, että alite on laimennettava, jotta laskeutumisnopeus olisi riittävä. Koska molemmat prosessit vaativat laimentamista, on tarkoituksenmukaista yhdistää ne.

Toteutus:

Ajetaan sakkaselkeyttimen alitetta GLSS-prosessissa, ja siitä edelleen syrjäytyspesulaitteiston läpi. Käytetään olemassa olevaa strippaus- ja talteenottolaitosta, joka on käytettävissä tekijän tiloissa. Syrjäytyspesulaitteisto on myös olemassa ensimmäisen tutkimushankkeen jälkeen. Voidaan myös käyttää aikaisempaa projektia varten hankittua selkeyttimen alitetta, josta on olemassa analyysituloksia, mikäli se ei ole muuttuneet liikaa säilytyksen aikana. Prosessin jälkeen tehdään happokäsittely, jossa pyritään liuottamaan ensisijaisesti kadmium. Suodoksesta saostetaan raskasmetalleja esim. sulfideina, ja pyritään saamaan kadmium ja lyijy erotetuksi hyötyaineista mahdollisimman pieneen fraktioon.

Työvaiheet:

1. Tarvittaessa hankitaan lisää sakkaselkeyttimen alitetta tehtaalta. Kunnostetaan ja pystytetään GLSS-laitteisto ja viherlipeän syrjäytyspesulaitteisto käyttökuntoon. Lisätään tarvittavia osia, kuten alitteen esikäsittely ym.

2. Alite esikäsitellään erottamalla karkea aines. Karkeat hiukkaset voivat tarttua stripperin täytekappaleisiin ja tukkia ne. Erotus voidaan tehdä sekoittimella varustetulla säiliöllä, josta syötetään eteenpäin ainoastaan se osa, joka ei laskeudu nopeasti pohjalle. Laimennetaan samalla alite esim. suhteessa 2:1.

3. Ajetaan strippaus ja redoxtorni alitteella. Koska soodakattilan savukaasua ei ole käytettävissä työskentelypaikalla, käytetään pullokaasua (typpi + hiilidioksidi). Seurataan ajon aikana sulfidipitoisuutta, jotta tiedetään milloin sulfidi on riittävästi poistettu. Vaihdellaan ja mitataan myös kaasu- ja nestevirtauksia, ja kerätään dataa prosessin koon kasvattamista varten.

4. Kun strippaus on valmis, syötetään sulfidivapaa alite syrjäytyspesulaitteistoon. Seurataan pesuvaikutusta määrittämällä jäännösalkali. Voidaan kierrättää tuotelipeä muutama kerta sen väkevöittämiseksi.

5. Jatkokäsittelyprosessi raskasmetallien ja erityisesti kadmiumin hallitsemiseksi: käsitellään pesty sakka hapolla. Testataan 1) rikkihappo 2) suolahappo. Selvitetään minkä verran sakka kuluttaa happoa. Hapon kulutus on olennainen seikka happokäsittelyn taloudellisten edellytysten arvioinnissa.

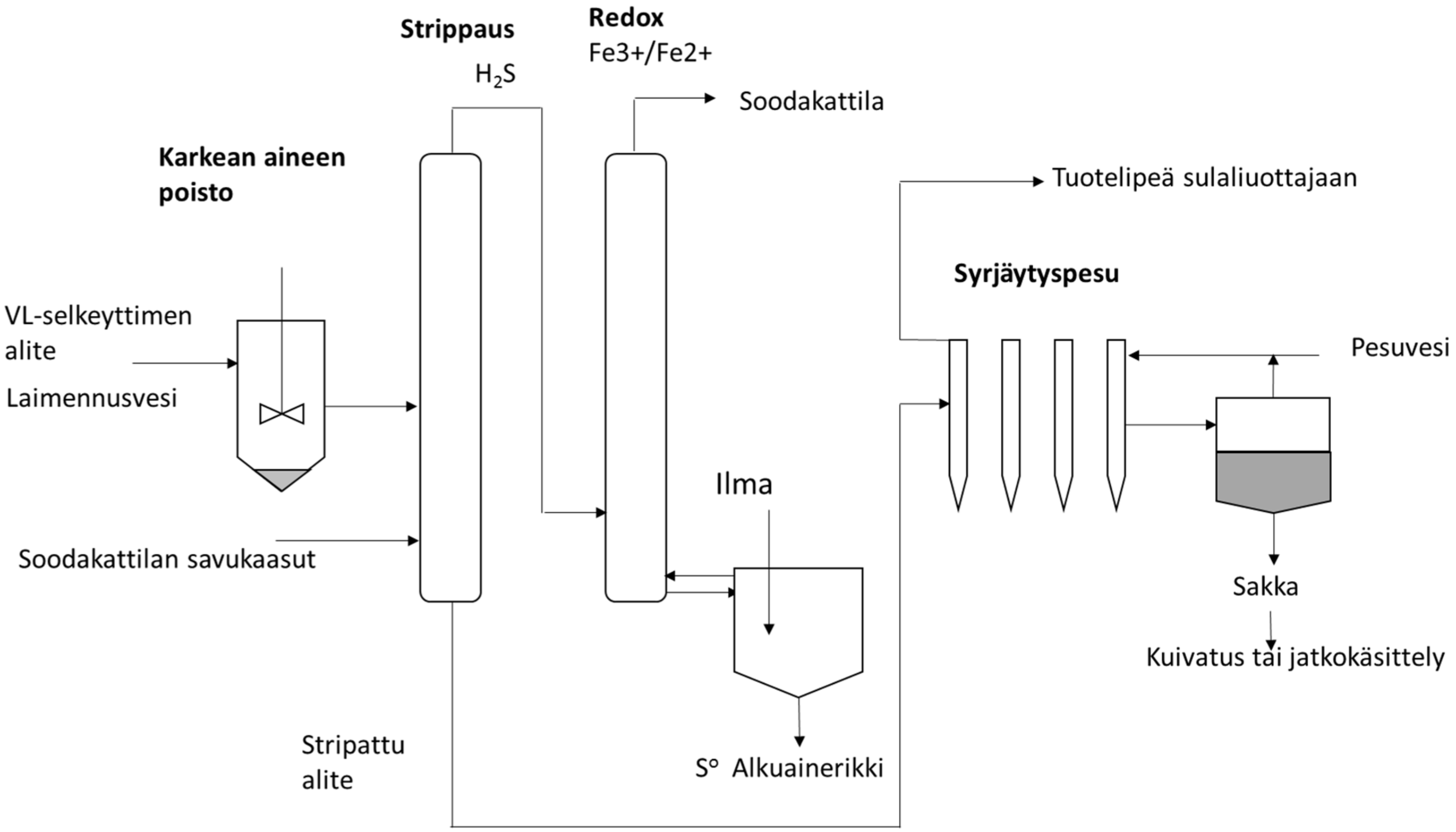
6. Kiintoaineen erotuksen jälkeen voidaan saostaa metalleja suodoksesta niiden konsentroimiseksi pieneen jakeeseen. Oikeissa oloissa pitäisi olla mahdollista saada kadmium saostumaan yhdessä kuparin, lyijyn ja vismutin kanssa sulfideina, ilman että muut metallit saostuvat samanaikaisesti. Jos tämä onnistuu, saadaan kadmium ja lyijy pieneen fraktioon.

7. Analyysit: keskeisimmät määritykset ovat kadmium ja lyijy. Analyysien laajuudesta, tekijästä ja rahoituksesta on keskusteltava YTR:ssä. Saadaan joka tapauksessa näytteitä, joista voidaan jälkeenpäin tehdä tarvittavia määrityksiä tarpeen mukaan.

8. Raportointi

Hinta: prosessikoeajot olemassa olevalla laitteistolla (ilman raskasmetallianalyyseja)	17000 € + alv

Raskasmetallianalyyseistä sovittava erikseen
jonkin laboratorion kanssa.


Strippaus
Redox
Fe3+/Fe2+
H_2S
Soodakattila
Karkean aineen poisto
Tuotelipeä sulaliuottajaan
Syrjäytyspesu
VL-selkeyttimen alite
Laimennusvesi
Pesuvesi
Ilma
Soodakattilan savukaasut
Sakka
Kuivatus tai jatkokäsittely
Stripattu alite
S° Alkuainerikki

LIITE 3

Oy Sirra Ab, Rikkitaseen hallinta ja soodasakkamäärän vähentäminen – esitys 15.2.2017

Projektiehdotus: Rikkitaseen hallinta ja soodasakkamäärän vähentäminen

SKY/YTR 15.2.2017

Ajatus: viherlipeäsakan syrjäytyspesun ja GLSS-prosessin yhdistäminen

Hyöty sellutehtaalle: rikkitaseen hallinta ja samanaikainen kaatopaikalle menevän viherlipeäsakkamäärän vähentäminen. ClO_2-laitoksen jätesuolan nykyistä parempi hyödyntäminen, K & Cl –poistomahdollisuuksien parantaminen

Tavoite:

- Yhdistetyn prosessin käyttökelpoisuuden selvittäminen koeajamalla se pilot-laitoksessa.
- Datan hankkiminen täyden mittakaavan laitoksen suunnittelun pohjaksi

Tausta:

Viherlipeäsakan syrjäytyspesu edellyttää VL-sakkaselkeyttimen laimentamista toimiakseen.

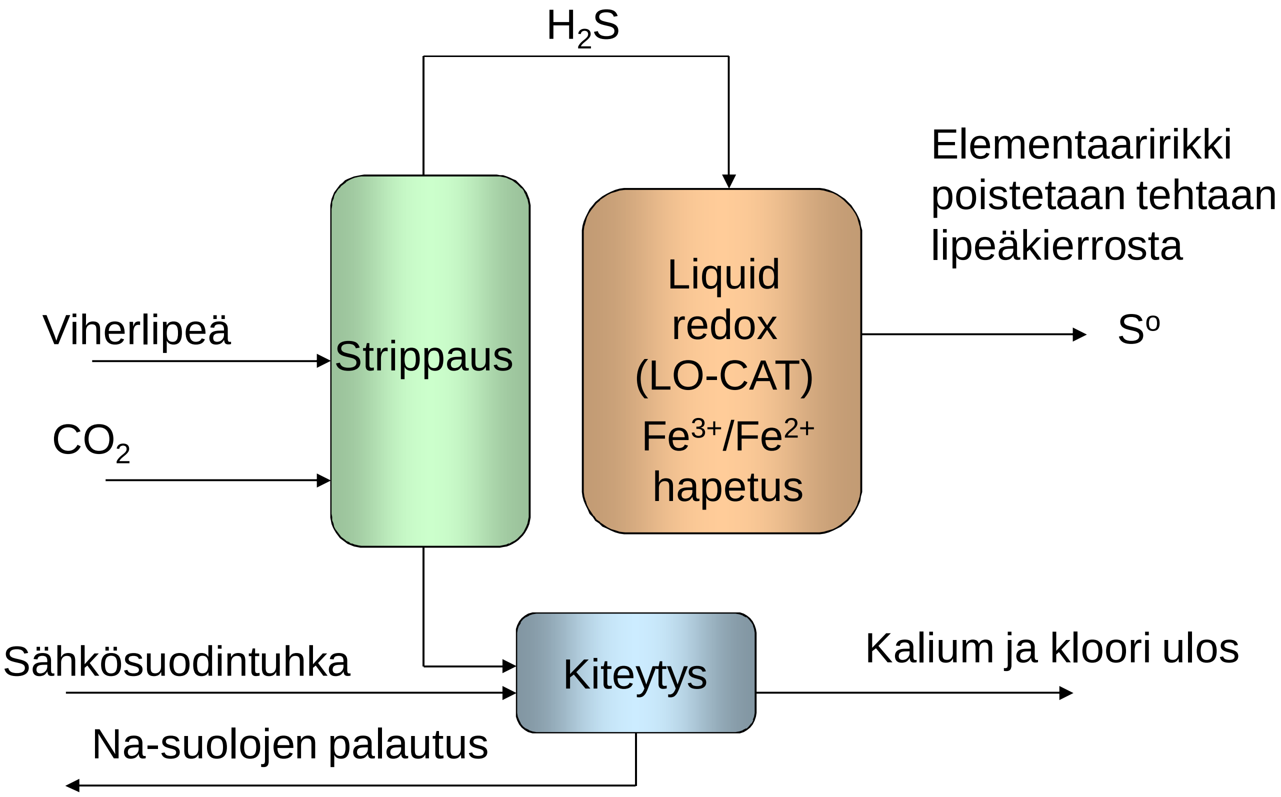
GLSS-prosessi (Green Liquor Simplified Stripping) käyttää lähtöaineena viherlipeää. Se vaatii myös laimentamista suolojen liukoisuuksien takia ($NaHCO_3$, Na_2CO_3).

Prosesseja lienee mahdollista yhdistää ajamalla laimennettua viherlipeäselkeyttimen alitetta GLSS-prosessiin.

VL-sakan syrjäytyspesuhankkeessa todettiin että sakan turvallinen hyötykäyttö edellyttää sulfidin poistamista. GLSS –prosessi tarjoaa mahdollisuuden tähän, ja samalla saadaan tehtaan rikkitaseen hallinta.

GLSS

Tutkittu prosessikokonaisuus:



E. Välimäki, esitys Soodakattilapäivänä 2012

Strippaus ja rikinpoisto

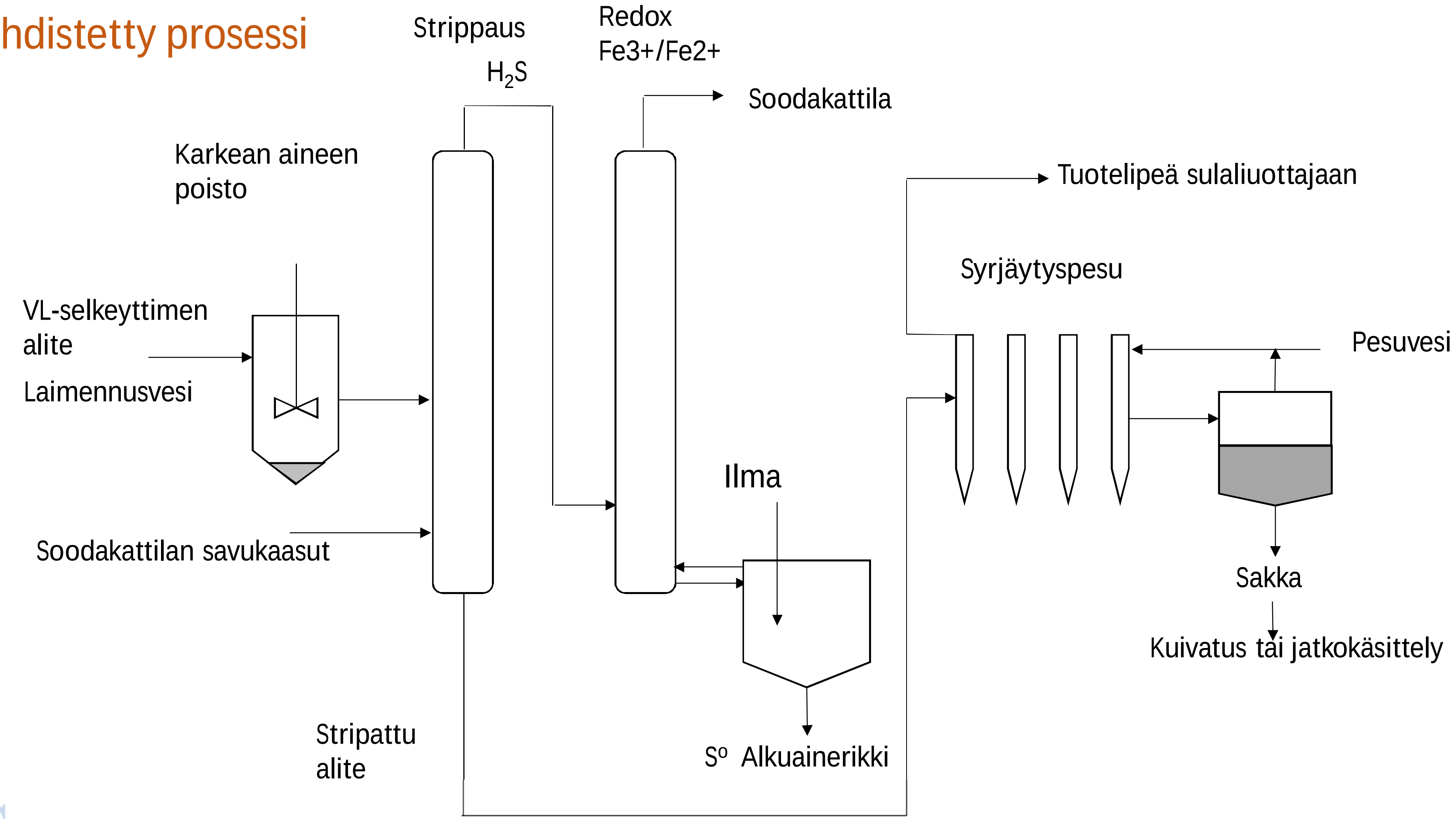
Sirra

GLSS -prosessi ja sen hyödyt

Taustalla Metson vanha SCP prosessi
- hyvä mutta monimutkainen
- liian kallis rikkitaseen hallintaan

- GLSS-prosessi halpa ja yksinkertainen
- Mahdollistaa rikkitaseen hallinnan ilman Na-häviöitä
- Na, S, K & Cl voidaan tasapainottaa toisistaan riippumattomasti
- Helpottaa K & Cl -prosessin käyttöönottoa (rikkitaseen kautta)
- Merkittävät kemikaalisäästöt, laskelmat 2,7 milj. €/vuosi (750 000 ADt tehdas)
- Merkittävä ympäristövaikutus: voidaan ottaa sisään kemikaalikiertoon ClO_2 – jätesuola osittain tai kokonaan, Na saadaan hyötykäyttöön

Yhdistetty prosessi



Työt

1. Tarvittaessa hankitaan lisää VL-alitetta
2. Pystytetään GLSS-pilot, järjestetään karkeiden hiukkasten erotus
3. Ajetaan strippaus + redox (GLSS)
4. Ajetaan stripattu sulfidivapaa alite syrjäytyspesulaitteistoon
5. Tehdään happokäsittely (vaihtoehtona Cd- ym. raskasmetallihallintaan)
6. Kokeillaan Cd, Pb, Cu ja Bi –saostusta näiden eristämiseksi
7. Analysointi: ei voida sisällyttää tähän osan, on oltava eri osahanke
8. Raportointi

Kustannukset ja aikataulu

Prosessikoeajot (ilman raskasmetallianalyyseja)	17000 € + alv

Raskasmetallianalyyseistä on sovittaja erikseen tekevän laboratorion kanssa

Hanke toteutettaisiin vuoden 2017 aikana