# LIITE I

## Kustannusseuranta

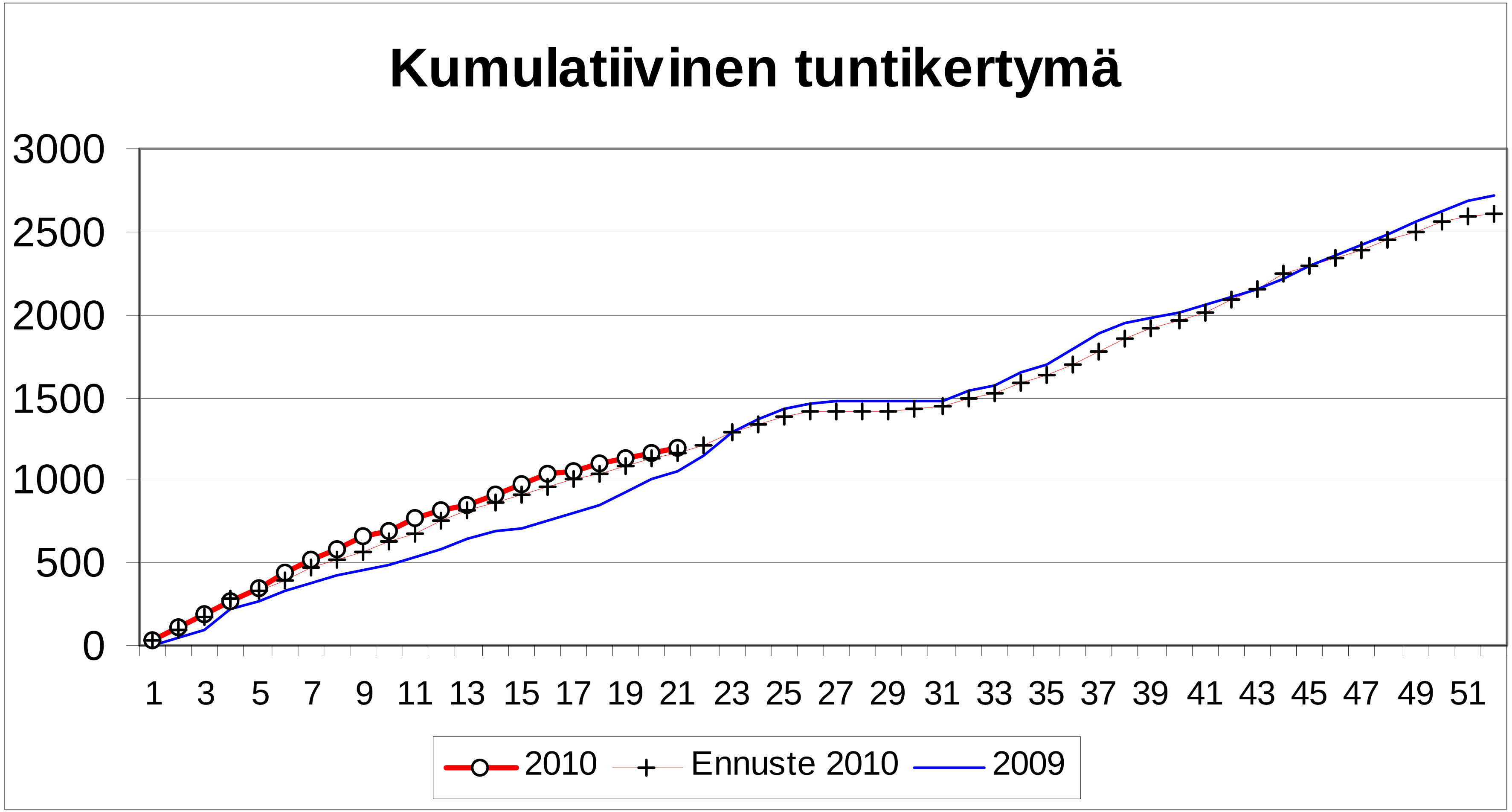
| | budjetti vuodelle 2011 | Toteuma vuonna 2010 | budjetti vuodelle 2010 | Toteuman osuus budjetista |
|---|---|---|---|---|
| TULOT | | | | |
| Jäsenmaksut ja muu säännöllinen tuki | | | | |
| Kattilan käyttäjät | 130 000 | 64 000 | 130 000 | 49 % |
| Kattilan valmistajat | 29 000 | 14 500 | 29 000 | 50 % |
| If Vahinkovakuutus | 7 000 | 3 500 | 7 000 | 50 % |
| Pohjola | 4 500 | 2 250 | 4 500 | 50 % |
| YIT Teollisuus- ja verkkopalvelut | 9 000 | 4 500 | 9 000 | 50 % |
| Pöyry Industry Oy | 9 000 | 4 500 | 9 000 | 50 % |
| VTT Expert Services | 4 500 | 2 250 | 4 500 | 50 % |
| Inspecta | 9 000 | 4 500 | 9 000 | 50 % |
| Ulkojäsenet | 4 500 | 4 500 | 4 500 | 100 % |
| Yhteensä | 206 500 | 104 500 | 206 500 | 51 % |
| | | | | |
| Ennakkojäsenmaksut | 0 | 0 | 55 116 | 0 % |
| | | | | |
| Kokousten osallistumismaksut | | | | |
| Konemestaripäivä | 25 000 | 25 005 | 25 000 | 100 % |
| Vuosikokous | 0 | 0 | 0 | |
| Soodakattilapäivä | 35 000 | 0 | 35 000 | 0 % |
| 45 v. juhla | 0 | 0 | 0 | 0 % |
| Yhteensä | 60 000 | 25 005 | 60 000 | 42 % |
| | | | | |
| Ulkopuolinen rahoitus | | | | |
| Julkinen rahoitus | | | | |
| TEKES-projekti SKYREC | 100 220 | 0 | 180 000 | 0 % |
| Julkinen rahoitus yhteensä | 100 220 | 0 | 180 000 | 0 % |
| | | | | |
| Muu ulkopuolinen rahoitus | | | | |
| Andritz | 0 | 10 000 | 10 000 | 100 % |
| Metso Power | 0 | 10 000 | 10 000 | 100 % |
| Metsä-Botnia | 0 | 10 000 | 10 000 | 100 % |
| Muut | 0 | 10 000 | 10 000 | 100 % |
| Stora Enso | 0 | 10 000 | 10 000 | 100 % |
| UPM-Kymmene | 0 | 10 000 | 10 000 | 100 % |
| Sumitomo | 0 | 35 000 | 35 000 | 100 % |
| Muu ulkopuolinen rahoitus yhteensä | 0 | 95 000 | 95 000 | 100 % |
| | | | | |
| SKYREC projektin ennakkorahoitus | 87 058 | 0 | 115 000 | 0 % |
| | | | | |
| Ulkopuolinen rahoitus yhteensä | 187 278 | 210 000 | 390 000 | 54 % |
| | | | | |
| Muu rahoitus | 0 | 0 | 0 | |
| | | | | |
| Korkotuotot | 1 000 | 0 | 1 500 | 0 % |
| | | | | |
| TULOT YHTEENSÄ | 454 778 | 224 505 | 713 116 | 31 % |
| | | | | |
| MENOT | | | | |
| Jatkuvaluonteiset tehtävät | | | | |
| Sihteeristötyö | | | | |
| Toiminnan ohjaus ja tilinpito | | | | |
| Sihteeristön työ | 25 000 | 12 054 | 25 000 | 48 % |
| Taloushallinnon työ | 8 000 | 4 282 | 8 000 | 54 % |
| Kirjanpito | 6 000 | 3 467 | 8 000 | 43 % |
| Muut ostokulut | 2 000 | 167 | 2 000 | |
| Kansainvälinen toiminta | 10 000 | 3 145 | 10 000 | 31 % |
| Kotisivun ylläpito | 6 000 | 3 238 | 6 000 | 54 % |
| Sihteeristötyö yhteensä | 57 000 | 26 353 | 59 000 | 45 % |

| | | | | |
|---|---|---|---|---|
| Hallitus | 8 000 | 3 386 | **8 000** | **42 %** |
| Kestoisuustyöryhmä | 6 000 | 1 731 | **6 000** | **29 %** |
| Vaurioraportointi | 1 000 | 676 | **1 000** | **68 %** |
| Lipeätyöryhmä | 6 000 | 2 757 | **6 000** | **46 %** |
| Ympäristötyöryhmä | 6 000 | 2 254 | **6 000** | **38 %** |
| Automaatiotyöryhmä | 6 000 | 3 303 | **6 000** | **55 %** |
| Ohjelmatyöryhmä | 4 000 | 2 287 | **4 000** | **57 %** |
| Konemestaripäivä | 25 000 | 24 117 | **25 000** | **96 %** |
| Vuosikokous | 13 000 | 18 385 | **11 000** | **167 %** |
| Soodakattilapäivä | 35 000 | 1 280 | **35 000** | **4 %** |
| Ohjelmatyöryhmä yhteensä | 77 000 | 46 069 | **75 000** | **61 %** |
| | | | | |
| Jatkuvaluonteiset tehtävät yhteensä | 167 000 | 86 530 | **167 000** | **52 %** |
| | | | | |
| Projektit | | | | |
| SKYREC | 187 278 | 96 697 | **400 000** | **24 %** |
| | | | | |
| Kestoisuustyöryhmän tehtäväalue | 0 | | | |
| VARO-tietokanta | 1 500 | 0 | **2 000** | **0 %** |
| Kestoisuustyöryhmän tehtäväalue yhteensä | 1 500 | 0 | **2 000** | **0 %** |
| | | | | |
| Lipeätyöryhmän tehtäväalue | | | | |
| | | 0 | **0** | **#DIV/0!** |
| Lipeätyöryhmän tehtäväalue yhteensä | 0 | 0 | **0** | **#DIV/0!** |
| | | | | |
| Ympäristötyöryhmän tehtäväalue | | | | |
| Pienhiukkaset | 0 | 10 000 | **10 000** | **100 %** |
| Lipeäkierron ammoniakkitase | 0 | 0 | **15 000** | **0 %** |
| Päästöjakauma | 0 | 0 | **15 000** | **0 %** |
| Ympäristötyöryhmän tehtäväalue yhteensä | 0 | 0 | **40 000** | **0 %** |
| | | | | |
| Automaatiotyöryhmän tehtäväalue | | | | |
| Turva-automaatiosuosituksen painatus | 0 | 1 175 | **1 500** | **78 %** |
| Määräaikaistestaus-projektin jatko | 0 | 0 | **15 000** | |
| Automaatiotyöryhmän tehtäväalue yhteensä | 0 | 1 175 | **16 500** | **7 %** |
| | | | | |
| Ohjelmatyöryhmän tehtäväalue | | | | |
| Opinnäytetyöstipendi | 2000 | 0 | **2 000** | **0 %** |
| Ohjelmatyöryhmän tehtäväalue yhteensä | 2 000 | 0 | **2 000** | **0 %** |
| | | | | |
| Työryhmien muut uudet projektit | | | | |
| | | 0 | **0** | **0 %** |
| Työryhmien muut uudet projektit yhteensä | 83 300 | 0 | **32 300** | **0 %** |
| | | | | |
| Projektit yhteensä | 274 078 | 97 872 | **492 800** | **20 %** |
| | | | | |
| Pankin palvelumaksut ja muut rahoituskulut | 200 | 41 | **200** | **20 %** |
| | | | | |
| MENOT YHTEENSÄ | 441 278 | 184 443 | **660 000** | **28 %** |
| | | | | |
| TULOS | | | | |
| Tulot | 454 778 | 224 505 | **713 116** | **31 %** |
| Menot | 441 278 | 184 443 | **660 000** | **28 %** |
| Tilikauden tulos | 13 500 | 40 062 | **53 116** | |
| | | | | |
| Edellisen tilikauden ylijäämä | | | **-857** | |
| Välittömät verot | | | **0** | |
| | | | | |
| Tilikauden voitto / tappio | | **40 062** | | |

*Luvut ilman arvonlisäveroa

# LIITE II

## Tuntikertymä


Kumulatiivinen tuntikertymä
3000
2500
2000
1500
1000
500
0
1
3
5
7
9
11
13
15
17
19
21
23
25
27
29
31
33
35
37
39
41
43
45
47
49
51
2010
Ennuste 2010
2009

# LIITE III

# ATR:
# Safety instrumentation recommendation for recovery boilers – version for comments

3.6.2010

SUOMEN SOODAKATTILAYHDISTYS FINNISH
RECOVERY BOILER COMMITTEE

**Finnish Recovery Boiler Committee**
**Registered Association**

# SAFETY INSTRUMENTATION RECOMMENDATION FOR RECOVERY BOILERS

**Finnish Recovery Boiler Committee**
**Automation Work Group**

**15.1.2003**
**8th Sept. 2008 rev. A**

**Rec. 2**

# INTRODUCTION

The members of the Finnish Recovery Boiler Committee have desired a clear set of instructions about the implementation of the safety instrumentation for recovery boilers.  This is due to a concern about safety and the variety of implementations between different manufacturing plants.

The first version of the recommendation published in 2003 was revised in the autumn of 2008.In the revised recommendation, the information that had become available by the autumn of 2008 was made use of. The new revision introduces the calibration of a risk graph for a recovery boiler, clarifies model interlocks and documentation needed as well as presents some theory about the verification of integrity levels with the help of a computational analysis.

It is not the intention of this recommendation to force the manufacturers and users to employ similar equipment and control solutions. The recommendation aims, with the help of instructions and model documents, to present an example solution, which can be used as a help for planning, design, manufacturing and use.

Our intent is to develop the recommendation further, and for this reason we ask you to send any possible observations about faults, suggestions for improvements, and experiences to the secretariat of the Finnish Recovery Boiler Committee. Our contact details can be found on the web-pages of the committee.

The committee does not assume the responsibility for any errors in this recommendation or any possible problems due to these. The updated version can be obtained from the committee's web-pages or from the secretariat.

This recommendation is translated into English. If the original Finnish text and its English language translation differ from each other, the original Finnish recommendation applies.

Finnish Recovery Boiler Committee (Registered Association)

Keijo Salmenoja
Chairman of the Board

Mauri Loukiala

Chairman of the Automation Work Group

Mauri Heikkinen 8.9.2008

Finnish Recovery Boiler Committee (reg. assoc.)

# Safety instrumentation recommendation for recovery boilers

CONTENTS:

## APPENDICES

| | |
|---|---|
| Appendix 1 | Definition of the safety integrity level for a recovery boiler with the help of a risk graph |
| Appendix 2 | Verification of integrity levels |
| Appendix 3 | Examples of interlock diagrams |
| Appendix 4 | Models of basic diagrams |
| Appendix 5 | Example of a circuit-specific operation description |
| Appendix 6 | Examples of display images |
| Appendix 7 | Model circuit design and wiring diagrams |
| Appendix 8 | Models of testing documents |
| Appendix 9 | Guide for operation and maintenance |
| Appendix 10 | Marking recommendation for safety related systems |

members of the Finnish Recovery Boiler Committee

# SAFETY INSTRUMENTATION RECOMMENDATION FOR RECOVERY BOILERS

## 1 GENERAL

This recommendation applies to **S**afety **I**nstrumented **S**ystems (**SIS**) for recovery boilers.

The responsibility for this recommendation is assumed by the Automation Work Group of the Finnish Recovery Boiler Committee
The first version of the recommendation was completed in 2003.

The recommendation was revised in 2007 on the instructions of the Automation Work Group of the Finnish Recovery Boiler Committee. The credits for the revision belong to Chairman Mauri Heikkinen Pöyry Forest Industry Oy and the members Sami Forsström Andritz Oy, Reijo Hukkanen Stora-Enso, Mika Kaijanen Tukes, Raimo Koskinen Sunila Oy, Heikki Lappalainen Andritz Oy, Esa Palojärvi Metso Power Oy, Kauko Ylioinas BMS Kemi and Janne Peltonen Mipro Oy.

The recommendation aims, with the help of instructions and model documents, to present an example solution, which can be used as a help for planning, design, manufacturing and use. Any laws, decrees and the instructions and guidelines by competent authorities should be observed and abided to.

The recommendation has been carefully prepared, and, on drawing it up, the opinions of various interest groups (manufacturers and distributors) about the structure and activities of SIS have been listened to. Also, the starting point has been that the equipment to be used complies with the requirements of the laws and degrees in effect in Finland and of the authorities responsible. The responsibility for the implementation of SIS belongs to the manufacturers of the equipment and those who implement its control system. It is the responsibility of the users or operators to ensure that SIS is employed correctly and with care and maintained in a similar way.

The recommendation is aimed to comply with the EN-61508 and EN-61511 standards as far as applicable in respect to the definition of safety instrumentation, design, implementation, operation and maintenance. This applies to both the recommendations concerning implementation as well as to the model documents.

This recommendation is divided in two parts: Part 1 is the implementation recommendation, and Part 2 contains the model documents related to the implementation. KLTK's Safety instruction G10, for example, presents general information about how to carry through a SIS project and about SIS's lifecycle. These matters are not repeated in this recommendation. When the need has arises, there is a reference to the instruction in question.

## 1.1 Sources

EN 61508 Sähköisten/elektronisten/ohjelmoitavien elektronisten turvallisuuteen liittyvien järjestelmien toiminnallinen turvallisuus, osat 1-7. (The operational safety of electrical/electronic/programmable safety-related systems, Parts 1-7).

EN 61511 Functional safety: Safety Instrumented Systems for the process industry sector, parts 1-3.

IEC 62061 Safety of machinery – Functional safety – Electrical, electronic and programmable electronic control systems.

SFS-EN 50156 Polttolaitteistojen sekä niiden apulaitteiden sähkölaitteet, osat 1-3. (Electric devices for firing equipment and their auxiliary devices, Parts 1-3)

Decree on the Industrial Handling and Storage of Dangerous Chemicals, 29th January 1999/59

Kauppa- ja teollisuusministeriön päätös painelaiteturvallisuudesta 8.10.1999/953. (The decision of the Ministry of Trade and Industry concerning the safety of pressure equipment) 8th October 1999/953).
Pressure Equipment Directive

97/23/EC Machinery Directive

98/37/EC.

TUKES-julkaisu 4/2000, Opas kattilalaitoksen vaaran arvioinnin laatimiseksi. (TUKES publication 4/2000. Guide for boiler plant risk assessment)

Kattilalaitosten turvallisuuskomitea (KLTK) Suojeluohje G7 Soodakattilat 2000 (The Safety Committee for Boiler Plants (KLTK) Safety Instruction G7 Boiler plants 2000).

TUKES-opas 2007, Turva-automaatio prosessiteollisuudessa. (TUKES guide 2007. Safety automation in process industries.

## 1.2 Concepts and definitions

Diagnostics is an operation performed by a safety related system or by some external system or a group of operations by which it is possible to discover a failure suffered by some system related to safety.

Diagnostic coverage (DC) reveals, in percentage terms, the portion of the dangerous faults in the system detected with the help of the diagnostic operations.

Self-diagnostics refers to operations used to discover failures. Utility programs in programmable safety devices are used to test the components of a programmable control unit or one of its channels (e.g., ROM) or the operations of operable modules (e.g., I/O modules).

Residual risk is the risk that still remains after some risk related safety systems have been implemented, in accordance with the risk reduction principles, for the process under control.

Acceptance is used to show, with the help of inspections and testing, that SIS, after its installation, complies with all the safety requirements set for it.

Target is a device or operation that SIS guides to a safe state if necessary.

Usability is the probability by which a planned functionality operates when required.

Operating system is the basic software for SIS.

The closed current principle means that a safety function remains in operation readiness with the help of constant auxiliary energy input and can function when the energy supply is interrupted.

Source signifies a measurement or operation, which either alone or together with another source can trigger a safety function, i.e., to lead the sources into a safe state.

The period between scheduled tests is the time period after which the safety related system will be regularly tested to discover the hidden faults that may have accumulated in the system during that period.

Basic process control system (BPCS) is an automation system which does not include safety related systems and is meant for the normal regulation and control of a recovery boiler plant.

Process safety time is the time period between an appearance of a dangerous fault in the control system and the moment when an accident will happen due to this dangerous fault if the safety function is not performed.

Risk refers to the combination of the probability of a certain dangerous event and of its consequence.

Risk analysis aims to systematically make use of available information to recognize hazards and to estimate the magnitude of risks that people or a population, property, or an environment is subjected to.

Risk assessment is a process that combines risk analysis with the assessment of the risk’s significance.

E/E/PE is based on electric (E) and/or electronic (E) and/or programmable electronics (PE) technologies.

Protection means mechanical control by which the target to be controlled is lead to a safe state if the circumstances so demand. Protection functions regardless of possible interlocks or new controls. The functions of a safety related system are, typically, protections.

SIS means Safety Instrumented System and consists of sensors, logic solvers, final control elements (relays, valves, motors etc.) and the cabling between these.

SIS logic part (SIS$_l$) is that part of SIS that is connected to sensors and actuators.SRS is an acronym for Safety Related System and it consists of mechanical safety systems (e.g., safety valves) and of Safety Instrumented System (SIS).

Verification scrutinizes every work phase with practices of checking and acceptance that conform to a certified quality system.

Safe failure results, in a case of a failure of some device or system, in a safe state, or the failure does not affect the operation of safety functions.

Safety integrity describes the reliability of a safety function, i.e., that the safety function is realized when needed. Safety integrity combines the safety integrity of the equipment (equipment failure) as well as the systemic safety integrity (systematic errors in the system implementation).

Safety integrity level (SIL) is a discrete level to define the requirements of safety integrity of the safety functions for E/E/PE systems that are safety related. The safety integrity levels are graded from 1 to 4. Of these, 4 is the highest safety integrity.

Type acceptance is an inspection by a third party to ensure that a product, process or service that is appropriately identified complies with a certain standard or with detailed requirements.

Work flow principle ensures that a safety function is activated when the device receives an input of auxiliary energy.

Hazard is a possible source of damage or a situation enabling damage to occur.

Dangerous occurrence can give rise to damage.

Damage signifies a physical injury or health hazard or damage to property or environment.

Redundancy means performing the same function with two or more parallel devices or systems. In spite of their apparent independence, the different channels used to effect redundancy may run the risk of a common failure.

Fault or malfunction indicates an abnormal state, which might reduce the capability of a device or a system to perform a required safety function.

Failure means that a device or a system is no longer capable of performing a required safety function. Failures are either of a random nature (in devices) or systematic (in devices or programs).

Fault tolerance is the capability of a device or a system to continue performing the required safety function regardless of a failure. Fault tolerance in the implementation of safety functions is normally attained by employing redundancy or fail-safe structures.

Fault tolerance time is the period between the occurrence of a hazardous situation (caused by the process itself or by a device malfunction) and the point in time when the process behavior changes to a critical mode, the result of which is a dangerous event if there are no safety systems employed.

Common failure is a failure which causes a simultaneous failure in two or more channels that are performing a safety function in a multichannel system.

# 2 PART 1

## 2.1 GENERAL

The safety instrumentation of a recovery boiler is that part of the automation system that reduces risks by protecting the boiler from getting into a dangerous condition, or in a dangerous condition guides the boiler into a safe condition. The acronym SIS (Safety Instrumented System) is used for safety instrumentation. SIS includes the equipment and installations (for example, logic, cabling, and field and electric equipment) needed for the implementation of safety functions.

## 2.2 MANAGEMENT OF OPERATIONAL SAFETY

The management of the plant's operational safety is a part of the implementation of SIS. An essential part of SIS is documentation, which ensures that the assessment and maintenance of the safety level of safety systems is possible. During the duration of the entire undertaking, it must be kept in mind regarding the documentation, that one should be able to trace the systematic verification and acceptance of the integrity levels. Drawing up of an appropriate safety plan for the project guarantees that all the necessary actions to ensure safety will be done.

The lifecycle of SIS is divided into a definition phase, design and building phase, installation and verification phase, and operation and maintenance phase. The recommendation based on IEC61508 presents, generally applied, the phases, responsibilities and documentation of the life cycle.

Verification must be applied at each work stage during the project, and the overall acceptance should take place at the final installation location before deployment.

## 2.3 RISK ASSESSMENT

Recovery boilers must be subjected to risk assessment, which includes a hazard and risk analysis and an evaluation of the significance of the risk. In evaluating the significance of the risk, one should consider different danger situations and their consequences, and then decide about the degree of tolerability that is acceptable. Risk reduction which is deemed necessary may consist of different SRSs and of external means to reduce risks (education, restricted movements, or other ways). SRS includes, in addition to SISs for E/E/PE, also SRSs for other technology such as safety valves, rupture disks etc.

It is useful to divide the hazard and risk analysis into two processes, so that the first process focuses on finding unrecognized hazards and the second on the evaluation of the risks discovered. By first concentrating solely on detecting hazards will ensure that the end results in charting those hazards will be as good as possible.

The safety integrity level (SIL) by safety functions is to be defined based on the hazard and risk analysis. The most widespread method in the definition of the safety integrity level is risk graph in accordance with EN 61508 and 61511. The method is based on risk consideration, where the consequences of, exposure to, avoidance of, and the possibility of a danger and its frequency of occurrence are observed when SIS is not being used. The risk graph and calibration suitable for recovery boilers are shown in Appendix 1 of Part 2. Calibration is shown separately for damage to persons, environment, materials, or property. The appendix also shows a model of a hazard and risk analysis form, in which hazards, the reasons for those hazards, their consequences, as well as the current preparation and extent (the required safety integrity level, SIS) are presented.

## 2.4 ORGANIZATION

The parties to the different phases in SIS project and their responsibilities must be defined in the beginning of the project. SIS's safety plan must present the tasks of the various parties, supply limitations (equipment, documents) and participation in tests and deployments.

It is necessary to contact a permission authority or inspection office in good time and find out about the required assessment, inspection and permission procedures.

### 2.4.1 Parties

#### 2.4.1.1 Operator

The end user (operator) is responsible for providing the chemical and process information and requirements specification that are essential for SIS. If the delivery of SIS is separate from the complete boiler system, the operator must assume the responsibility for the functionality and acceptance of the whole.

It is the operator's responsibility to ensure the maintenance, change management and regular inspections for the equipment in operation.

#### 2.4.1.2 SIS supplier

The supplier of SIS must supply a system that meets the requirements specifications of the operator and complies with those of the law.

### 2.4.1.3 Boiler supplier

The boiler supplier is responsible for the equipment it delivers. If SIS is also included in the total delivery of the boiler, the supplier also takes the responsibility for its documentation, appropriateness, suitability and for the necessary inspections and acceptance procedures.

### 2.4.1.4 Assessor of SIS

An inspection office or a party that has no self-interests in the manufacturing and is competent can act as an assessor of SIS depending on the skill and competency. The operator or the supplier of the boiler selects a suitable assessor, but it is recommendable that, for the selection, there is communication with the authorities responsible for assessing compliance to the requirements - generally this is the inspection office.

The assessor inspects and verifies the application's operational safety and its compliance with the requirements. The assessor inspects the actions of each phase (definition, planning, implementation, operation and maintenance) of the lifecycle and information obtained from each of the phases. It is the task of the assessor to decide whether the aims of the applied standards and the requirements and procedures decreed have been complied with.

### 2.4.1.5 Inspection office

The tasks of the inspection office include the evaluation of the safety instrumented systems for pressure equipment, especially for integrated machinery and in periodic inspections. It is also the task of the inspection office to ensure the technical safety and reliability of the equipment being built and implemented and, after that, when it is being used.

### 2.4.1.6 Authority

Tukes (Safety Technology Authority) is the controlling authority in Finland for technical safety and reliability in its field. Its area of activity includes, among others, industrial handling of dangerous chemicals and pressure equipment and pressurized systems.

Tukes grants permits for plants involved in extensive industrial handling and storing of dangerous chemicals. Modifications and extensions which can be considered equal with building a new plant need a Tukes's permission.

In connection with the permit application or notification about a modification, the operator must present the plans regarding the principles and sufficiency of the implementation of SIS for the planned purpose and the inspection methods to be used during the system use.

### 2.4.2 Competency requirements

All the persons who deal with the operations of the SIS as a whole or of the lifecycles of software safety, including managerial tasks, should have the appropriate education, technical know-how, experience and competence which are related to their specific tasks.

The competence of the persons responsible for the planning, testing and deployment of SIS must be indicated in the description of SIS. In addition, the documentation must contain information about the persons responsible. That information must show their education, competence and previous experience in SIS projects.

The following factors should be considered when considering the competence of these persons for their tasks.

- Appropriate technical knowledge suited to their application area
- Technical knowledge applicable to the technology in question (e.g., electrics, electronics, programmable electronics and software technology)
- Knowledge about the safety technology applicable to the technology in question
- Knowledge about legislation and safety regulations
- The consequences if the systems related to E/E/PE safety do not function
- The safety integrity levels of the systems related to the E/E/PE safety.
- The novelty of planning methods, structure or application
- Previous experience and its significance in relation to the particular tasks to be performed and the technology to be used
- The importance of competency in the particular tasks to be performed
- Courses taken that are related to the subject

## 2.5 DOCUMENTATION

Documentation must be made such that the matters are presented either in the same documentation or with clear references to other documents.
The table of contents could be made of, for example:

**Definition phase**

- Safety plan
- Hazard and risk analyses
    - Hazop analysis
    - Integrity level definitions
- SIS requirement definitions
- Evaluation report for the definition phase

**Planning and implementation phase**

- Operational specifications
- Safety locking diagrams
- SIS implementation description
- Field equipment guide and installation instructions
- Verification of integrity levels
    - Integrity level calculations and failure rate data
- I/O card and box layout for safety logic
- Plan for installation and deployment
- SIS logic diagrams
- SIS program diagrams
- SIS displays
- Circuit design and wiring diagrams
- Production tests
    - FAT plan
    - FAT instruction
    - FAT logsheet
    - FAT test report
- Assessment report for the planning and implementation phase

**Installation and acceptance phase**

- SAT plan
- SAT instruction
- SAT records
- SAT acceptance report
- Assessment report for the installation and acceptance phase

**Operation and maintenance phase**

- Plan for operation and maintenance
- Plan for periodic testing
- Instructions for periodic testing
- Records for periodic testing

- Reports for periodic testing
- Assessment report for the operation and maintenance phase

## 2.5.1 Definition phase

The documents of the definition phase are drawn up in collaboration with the operator, with the persons responsible for the electrical design and instrumentation design and with the main equipment supplier.

### 2.5.1.1 Safety plan

The safety plan presents an implementation plan related to safety. It describes the process of a SIS project by stages and the methods by which safety is ensured. The focus is on quality assurance and matters related to the assessment of the appropriateness of the implementation.

The contents of the safety plan are, briefly:

1. **Target**

A short description of the target (plant)

2. **Regulations, recommendations and standards to be applied**

A list of laws, regulations, recommendations and standards to be followed in the definition, planning and implementation of the plants' SRSs.

3. **Supply limitations**

A short clarification about the planning and implementation supply limitations regarding the client, equipment supplier and SIS supplier.

4. **Organization and responsibilities**

The persons who are responsible for the definition, planning and implementation of SIS, tasks, responsibilities, supply limitations and competency (see 2.4.1).

5. **Documentation**

A short description about the documentation to be produced during the definition, planning and implementation of SRS.

6. **Modification procedures**

A description about how the management of possible changes is to be realized during the planning, testing, deployment and maintenance phases.

## 7. Testing, inspection, survey, acceptance and auditing methods

A short description about the testing, inspection, survey, acceptance and auditing procedures to be used during the project.

## 8. Training plan

A short description about the training on safety functions and about SIS training for the operational personnel.

## 9. Schedule

The main issues, documents and different inspections for the definition, planning and implementation of SIS are defined in the schedule.

### 2.5.1.2 Hazard and risk analysis

Generally, it is the main equipment supplier who draws up the hazard and risk analysis, which is then examined together with the operator. The document should consider dangers associated with recovery boilers and assess the related risks and risk reduction methods.

There are two stages for the hazard and risk analysis:

**Stage 1 (HAZOP or similar)**

In stage 1, a hazard assessment is made for a plant/equipment/device by using, for example anomaly examination (HAZOP Hazard and Operability Study) or a similar analysis method.

In the assessment the actions to reduce risks are defined with SIS or by other risk reduction methods (e.g., rupture disks, safety mechanisms).

**Stage 2 (SIL definition)**

In stage 2, an assessment is made, based on the report of stage 1, about the risks associated with hazards and about risk reduction methods. Safety integrity levels (SIL) for the safety functions to be implemented in SIS are also defined.
Risk assessment focuses on personal risks, but also serious environmental harm, material damage and production losses may be assessed.

Appendix 1 in Part 2 shows in more detail the implementation and documentation of the hazard and risk analysis for a recovery boiler.

The necessary parts of hazard and risk analyses must be updated if in the planning and acceptance stages:

- decisions are made, which can change the grounds of the decisions made in stages 1 and 2
- new hazard situations come up

#### 2.5.1.3 SIS requirements definition (safety functions implemented by SIS)

The requirements definitions for SIS are normally provided by the main equipment supplier. The requirements definition is based on the hazard and risk analysis, and it must contain the functional requirements of total safety for the SIS equipment and for SIS safety functions (descriptions of safety functions) and their integrity level requirements. The level of safety must be defined for each recognized hazard.

The requirements definition discusses the requirements expected from the operations and reliability of safety functions, verification of compliance with the requirements, as well as preparation for hazardous situations, their prevention, limitation of consequences etc.

The requirements definition must be completed before the definition of SIS's logic part and its procurement.

#### 2.5.1.4 Safety interlock diagrams

Interlock diagrams are designed by the main supplier. In the safety interlock diagrams all the safety functions presented in the requirements definition are shown unambiguously. Correct device positions are used and the interlock values for process variables are shown as accurate number values. The interlock diagrams should be completed before programming starts.

#### 2.5.1.5 Field equipment guide and installation instructions

The field equipment guide and installation instructions show the field equipment solutions to be used in the project for the planning and design of instrumentation and electrification. The instructions must also give instructions about installations and markings.

### 2.5.2 Planning and implementation phase

The documentation for the planning and implementation phase presents the part of the SIS documentation that is created when a SIS is designed and completed in accordance with the definition phase.

### 2.5.2.1 Description of SIS implementation

The description of SIS implementation shows the part of the safety instrumented system and the part of the field equipment. The description of the logic solver is created by the supplier of the safety instrumented system. The description of the field equipment and installation is created by the designer of the electrical and instrumentation plan supplementing the part done by the supplier of the safety instrumented system, or a separate implementation description is drawn up by that designer.

A selection of the principles to be used in the implementation of SRS is made in the SIS's implementation plans. The description must indicate the equipment used and their behavior in possible equipment break-downs as well as the necessary program blockings to prevent outsiders from changing calibration or parameters.

When selecting the implementation principles, attention should be paid to the SIS’s periodic tests and testing interval. One should note that it should be possible to organize a considerable portion of the periodic tests to be conducted during the normal operation of the plant and in connection with its shutdown as well as with its startup.

### 2.5.2.2 Verification of integrity levels

Verification of integrity levels is part of the implementation description. In verification, the attainability of safety integrity for safety functions must be shown, in accordance with the hazard and risk analysis and the requirements definition. Verification must be performed by examining separately the sufficiency of the device architecture and the probability of an equipment failure due to a fault. This should be based either on the reliability data (failure rate, failure rates due to dangerous faults, and diagnostics) related to the field equipment and logic solver or, if these values are missing, on other estimations and experience. The verification of integrity levels is explained in more detail in Appendix 2 of Section2.

Integrity level calculations are the task for the supplier of the safety instrumented system. These calculations are based on the reliability data (failure rates, failure rates due to dangerous faults, and diagnostics itself) obtained from the designer of the field sections (electrification and instrumentation).

### 2.5.2.3 The safety instrumented system’s layout for cabinets, boards and I/O.

The safety instrumented system’s layout for cabinets, cards and I/O is designed by the system's supplier. The layouts must also show any possible spare cards.

#### 2.5.2.4 The plan for installation and deployment

The plan for installation and deployment consists of several documents from different areas. The complete document is produced by the end client, who collects documents from the different areas of interest to be used in the planning of deployment. The client also draws up a detailed schedule about the stages of deployment and the duties and responsibilities for each party.
The plan for the logic solver and electrification as well as for the installation and deployment of instrumentation is to be accomplished by the designers of the areas of interest in question.

#### 2.5.2.5 SIS program diagrams

The programming for the SIS's logic solver is the responsibility of the system’s supplier. The program must have such documentation that it can be understood without the presence of the program author.

#### 2.5.2.6 SIS displays

SIS displays are shown either on SIS's own terminals or in the normal process control system.

#### 2.5.2.7 Circuit design and wiring diagrams

The text ”RELATED TO INTERLOCKS” must be affixed to the circuit design and wiring diagrams of the field equipment that is to be connected to the safety instrumented system. The circuit design and wiring diagrams are made by the designer in that area.

### 2.5.3 Testing documentation

Testing (FAT factory acceptance testing, SAT site acceptance testing, and periodic testing) documentation includes a testing plan, testing instructions, testing records, and a testing report.

#### 2.5.3.1 Testing plan

The testing plan includes the target of testing, testing organization, conditions and reasons for testing, documentation needed in testing, testing equipment, testing methods, testing acceptance criteria, instructions for creating a testing report, as well as the report distribution.

### 2.5.3.2 Testing instructions

Accurate testing instructions based on tests are made. The instructions explain the preparations for each testing stage, and instruct on how to simulate the sources and how to realize possible temporary connections between the channels. They also explain the interlocks (targets) for each testing stage. Different equipment combinations (1/2, 2/3) must be tested separately and presented in the testing instructions.

The aim of the testing instructions is to guide the testing to such an accuracy that it is possible, afterwards, trace the testing process.

### 2.5.3.3 Testing records

The testing records must be prepared beforehand in line with the testing instructions and in such a way that the operations realized and the interlocks occurring can be witnessed and the locking limits can be written down.

### 2.5.3.4 Testing report

The testing report is prepared at the end of testing. The report states the testing target, date, and participants and includes a mention about the test acceptance and the signatures and their clarifications of all the participants. In addition, the modifications and additions made on the definition and testing material are recorded in the report. If the repair, modification and addition operations cannot be tested with the testing under way, it should be recorded when the deficiencies will be tested.

The end client or the supplier of the safety instrumented system is responsible for creating the testing plan, instructions and the testing records.

## 2.5.4 Operation and maintenance phase

### 2.5.4.1 The plan for operation and maintenance

A plan for the operation and maintenance of the safety instrumented system must be made. This plan should tell about the target of the plan and the persons responsible for it, and contain an explanation about SIS's documentation, an introduction of the operating and maintenance personnel to SIS, the plant's general safety instructions, guidance to periodic testing, and instructions for maintenance and modification procedures (permissions, acceptances, documentation etc.). The plan is drawn up by the end client together with the supplier of the safety instrumented system.

## 2.6 THE LOGIC SOLVER OF THE SAFETY INSTRUMENTED SYSTEM

The logic solver (SIS$_l$) of the safety instrumented system must be independent of the basic process control system. It can, nevertheless, be connected to the basic process control system through, for example, channel connections or hardwiring. A separate SIS unit means a separate logic or a (integrated) logic that has been built with separate control system components and contains only the operations meant for safety protections. It should be kept in mind that the logic solvers and the components must be certified for the purpose intended.

SIS$_l$ is implemented in accordance with the defined highest integrated safety level based on the hazard and risk analysis. Even though the above mentioned logic solvers, as single-channeled, had been accepted at the safety integrity level 3 (SIL3), SIS$_l$ when connected with a recovery boiler, for the sake of usability, must be built in such a way that the processors can be changed during the operation. Similarly, redundant I/O's for the input and output cards must be located in such a way that the failure of an individual card cannot result in the deterioration of the usability or safety of the plant.

The measurements of the circuits related to SIS are wired first to SIS$_l$, from where the measurement data for indications, reporting, adjustment and for similar needs is lead to the process control system either directly through a channel, through an I/I transformer or with additional outputs from SIS$_l$.

Connection of safety related regulation and control circuits to SIS is realized with a separate control from SIS$_l$, with which the final control element (valve, damper, fan, pump etc.) can be brought to a safe state at the so-called "hard side" independently of the basic process control system. Regulation and control operations which do not have safety requirements are implemented in the basic process control system.

Controlling motor valves and motors related to motor centers to a safe state is implemented with the help of safety relays which are connected to the safety logic.

When necessary, to attain the required integrity level, a separate additional control target is needed. This will further reduce the risk associated with the possible non-functioning of the control target in question. This means, in the case of the primary air blower for example, that in addition of the safety control for the blower's motor, the safety logic also guides the air flow regulation panels to a safe position.

### 2.6.1 The plan for a logic solver (hardware)

The logic in its equipment container is installed in the SIS cabinet. Also the incoming and outgoing cables from the field are placed there. The required isolators and relays are also located in the same cabinet or in a distribution frame to be positioned on the side of the cabinet. Redundant input and output signals are located on different boards in such a way that as high as possible degree of usability is achieved (for example, measurements with the selection principle 2 out of 3).

A separate marking is attached to the cabinets, frames, cards and channels that are connected with SIS, to indicate that the equipment belongs to the safety related circuits. The cross-connection to the signals related to SIS is done by red wiring to distinguish it from the signals going to the basic process control system.The markings of SIS and the circuits related to it must comply with the Report 9/2000, Rev A “Marking recommendation for safety related systems” issued by the Finnish Recovery Boiler Committee.

Voltage feed to the logic solver is arranged from a voltage source that is equipped with a screening transformer. In addition to this, a standby voltage feed must be arranged for the logic solver (and through it to the field equipment) in case of interruptions and faults in the main voltage feed. The standby voltage feed must connect automatically and without an interruption once the main supply has ceased functioning. The standby supply is accomplished with UPS equipment and a set of direct current batteries. The standby voltage supply must be able to feed the system at least 45 minutes (normal jettisoning and qualifying period). An alarm for the operator must be connected to the condition monitoring of both the main feed and the standby supply.

### 2.6.2 The plan for the logic solver (software)

The documentation must include own interlock diagrams for the SIS circuits’ operations and/or unambiguous verbal descriptions as well as the basic circuit arrangement which shows the whole circuit on a single document from the source to the target (trip limits, operation, I/Os, connections to other parts) (see Section 2, Appendices 3, 4 and 5).

Separate displays about the SIS safety functions are created for the interface to the safety logic or that to the basic process control system (see Section 2, Appendix 6). These give information about measurement data, binary state data, and, in addition to controls, also about the state of the measuring instruments and about controlled targets under final state monitoring.

Its own alarm pages, in which the SIS alarms can be put into their own category, must be made for SIS in the basic process control system. Apart from the SIS functions, information is needed also about sensor and signal faults in the field equipment. A notification or an alarm text with a time stamp attached (for example in 100 ms intervals) must be generated when

SIS is triggered. The system must be able to tell the basic reason for the triggering of SIS. Similarly, the alarms must be able to monitor the deviations of redundant measurement messages (for example, if the deviation is more than 10%).

SIS programs must be protected with a password or by other means in such a way that any modification of the programs by outsiders is prevented.

## 2.7 FIELD EQUIPMENT

### 2.7.1 General

The field equipment, in the case of a recovery boiler, does not need a separate SIS which would have its own field equipment and logic solver; for this it is sufficient to use equipment that is normally used in the basic process control. Nevertheless, it should be noted that the signal data from measuring instruments, control switches, limit switches or other sources is first brought to $\text{SIS}_l$, from where the signal can be further taken to the basic process control system to be utilized there.

Similarly, no separate valves are installed only for the SIS's controls. The necessary closing and opening operations are realized using the process control valves. This, however, presupposes that the required integrity level is achieved.

The higher the requirement for a safety function's integrity level, the more independent and reliable should the equipment for SIS be.

In addition, in the case of field equipment, it is necessary to pay attention to the redundancy and reliability requirements as demanded by the safety integrity levels (SIL) and usability.

When specifying the field equipment one must also pay attention to the possibility of periodic testing during operation.

The safety of SIS as a whole (sensors – logic solver – actuators) should be checked with the help of a computational analysis, to ensure that the integrity level defined with the help of the risk analysis is achieved with the selected structural solution for the safety instrumented system. To be able to conduct a computational analysis in order to ensure the adequacy of the operational safety for the entire SIS, one should demand, for all the field equipment selected, an approval for safety related systems and its failure possibility values in accordance with the EN-61508 standard. There is an example of the computational analysis in Appendix 2 of Section 2.

### 2.7.2 Measuring devices

The measuring devices should be analog 2-pin transmitters with high quality self-diagnostics. The transmitters should be, primarily, certified transmitters meant for safety use. When using normal transmitters, the measurements should be realized using the 2/3 comparison principle to achieve as high usability as possible.

When using the safety transmitters with a higher quality self-diagnostics (the best solution), a higher integrity level and usability is achieved using two transmitters and 1/2D principle. There are two separate signals, the measuring signal and the diagnostics signal, that can be obtained using safety transmitters. The diagnostics signal gives information about the state of the transmitter. It is not necessary to guide the plant into a safe state due to the failure of one transmitter. The responsibility for that is transferred to the other transmitter alone, and the operator is alerted to the failure condition. The failed transmitter must be replaced within a set time period.

In addition to the protective interlocking caused by the process interlock limit, the failure of the transmitter, as well as that of the cable, must trigger a safety interlocking function. All pressure and surface measurements related to the recovery boiler's SIS are to be realized by pressure and pressure difference transmitters. The transmitters must block programming and be adjusted with approved calibrated devices. Redundant measurements must be tuned in the same area.

The compensation of the measurement signals in safety related circuits must be realized in connection with air volume measurements. However, this is not necessary in cylinder surface measurements, where a raw signal should be used as the tripping signal primarily. The reason for this is that compensations increase SIS's circuits, different calculation methods and algorithms complicate the clarity of the whole and the significance of compensations in measurements is not that great. Compensation calculations in SIS must be done in such a way that the compensation signals are included in SIS. If the same compensation signal is used for compensating several measurement signals, the safety of that solution must be justified.

### 2.7.3 Push buttons and switches

Fast stop, jettison and emergency-stop push buttons must be of the mushroom shape, red in color and equipped with a sufficient number of heads. The buttons must lock when pressed in. The interlock caused by the emergency-stop buttons is acknowledged with a separate acknowledgement button located in the control room. The buttons on the field must be marked in such a way that it is clear what effect the use of the button will have and that the button can be seen clearly from a distance of at least 10 meters.

Limit switches must be of such type and connected in such a way that the so-called closed current principle is realized. The switches may be either inductive (2-pin) or mechanic with self-cleaning contacts.

### 2.7.4 Valves

The valves connected with the controls of SIS must be equipped with spring actuated devices. The driving direction of the actuator must be selected in such a way that the spring force guides the valve to a safe state while the pressure air leaves the actuator.

The guidance to a safe state is realized with a solenoid valve, which is installed linking it to the actuator. The solenoid valve when de-energized lets the pressure out of the actuator, and the spring forces the valve to a safe state. It should not be possible to manually control the solenoid valves.

A solenoid valve is installed between the positioner of the regulating valves and the actuator. In an interlock situation, the solenoid valve uses a spring to force the regulating valve to a safe position in accordance with the interlock instructions.

”Spring closes” actuators are used as fire valves and fast stop valves while “spring opens” actuators are used as ventilation/pressurization valves. Fire valves and fast stop valves must comply with the requirements of the medium.

Feed water valves (stop valves), main steam valves, dump valves, start valves, sprayer valves, jettison valves, cylinder reducing valves, chimney valves, and reducing valves for the distributing box are traditionally electrically driven and equipped with a secured auxiliary supply.

### 2.7.5 Pumps and blowers

The motor outputs used are standard outputs (no different colored internal wirings or different colored terminal blocks).

The operation details of pumps and blowers are obtained, with the help of closing auxiliary contacts, from motor contactors at the motor centre or, alternatively, from the frequency converter using the contact data at SIL 1 and in addition, for example, from the voltage or current monitoring or from some process variable starting from SIL2 integrity level.

Any possible seizing-up of a main output contactor is taken care of by oversizing the contractor. The dimensions of the contractors comply with the IEC60947-2 coordination class 2, AC3, (Simocode trigger class 10), so that $I_{CS}$ (measured breaking capacity for an extreme short circuit) is sufficiently high.

### 2.7.6 Motor valves

Auxiliary relays for SIS controls are added to the motor valves’ outputs. The relays used are auxiliary relays approved for safety and are, depending on the application, in parallel (start) or in series (stop).

The temperature control and torque limits for motor valves are bypassed in connection with the protective interlocking of SIS.

### 2.7.7 Safety switches

Both the motors and the motor valves are equipped with normal safety switches.

### 2.7.8 Voltage supply

For field equipment that require a 230 V external supply, the voltage feed must be wired from a UPS secured network.The network must be designed in such a way that it can keep the system running for 45 minutes.

The main supply for motor valves and for other safety related actuators must be arranged from a secured centre (e.g., diesel or by other means).

## 2.8 FIELD DESIGN

### 2.8.1 Installation targets

The installation targets must be designed and installed in such a way that tests can be performed without dismantling the installations.

### 2.8.2 Measurement points

In measurements related to SIS, the basic principle is that each measurement has its own process measurement point.

A separate pumping measurement point must be included in the measurement points of the measurement transmitters for deployment tests and for periodic testing. Pumping can be arranged, for example, through a 5/2 installation valve.

### 2.8.3 Root valves and installation valves

Both the root valves and the installation valves must be lockable, or the handles and hand wheels must be removed so that outsiders cannot change the valve positions. Clear indicators about the open/closed position must be installed in the valves once the handles and hand wheels have been removed.

### 2.8.4 Cabling

Measurements and controls connected with SIS can be realized using individual or main cabling. For analog signals protected cables are used.

SIS's redundant measurement messages are transferred to the SIS's logic solver through different cables and preferably through different routes.
If main cables are used in the installations, separate main cables that are exclusively reserved for SIS are used for signals connected with SIS.

There is not enough experience yet about field bus solutions to be able to recommend them for the transfer of measurement and control data in SIS.

### 2.8.5 Markings

Field equipment, root and installation valves, process measurement points and cabling must be distinguished by a different marking (red) from the rest of the field equipment (See Appendix 10).

## 2.9 SAFETY LOCKING FOR THE RECOVERY BOILER

It should be kept in mind that safety functions must always be based on the hazard and risk analysis made for the recovery boiler. Also, when assessing the significance of the risks, the integrity level must be defined. This has not been discussed in connection with the lockings presented below.
To achieve a adequate safety level, the work group ended up with the following model lockings.

### 2.9.1 Boiler protection

**Purpose:**

Boiler protection means all the necessary actions, from the viewpoint of safety, to prevent damage to the boiler. Boiler protection consists of several process values and device states for the boiler. These are defined values and states. When the boiler protection conditions have been complied with, the boiler can be ignited and firing can continue.

**Sources:**

**Fast stop button**

- The fast stop button pressed in the control room

**Cylinder surface**

- The cylinder surface is below the lower limit (dry boiling guard)
  3 pressure measurements
  - with2/3 selection
- The cylinder surface is above the upper limit (wet boiling guard)
  3 pressure measurements
  - with 2/3 selection

**Primary air**

- The amount of primary air below the lower limit
  2/3 selection, for example, of the following conditions:
    - the blower does not function
    - The amount of primary air below the lower limit
    - the pressure of the air tube below the lower limit

**Secondary air**

- The amount of secondary air below the lower limit
  2/3 selection, for example, of the following conditions:
  - the blower does not work
  - the amount of secondary air below the lower limit
  - the pressure of the air tube below the lower limit

**Furnace pressure**

- The pressure of the furnace above the upper limit
  3 pressure measurements
  - with 2/3 selection

**Flue gas outlet**

- The Flue gas outlet closed message (at least one gas outlet must be open)
- The Flue outlet open message is compiled from the blower's operation data and the input and output channel data related to open dampers.
  - the blower does not work
    Using the 2/3 selection about the blower's rotating speed data, electric drives on - data, and the vacuum pressure measurement after the electrostatic precipitator
    - the rotating speed of the blower below the lower limit
    - the blower works
    - the vacuum pressure of the channel above the lower limit
  - the income channel damper away from the open limit
    3 limit switches
    - 2/3 selection
  - the output channel damper away from the open limit
    3 limit switches
    - 2/3 selection

**Control air (when required)**

- the pressure of the control air below the lower limit
  3 pressure measurements
  - 2/3 selection

**The O2 content of the flue gas (when needed)**

- The content of O2 in the flue gas is below the minimum limit
  3 oxygen measurements
  - choose 2/3

**Targets**

**Liquor burning**

- liquor burning permit removed
  - liquor pumps stop
  - liquor feeder valves close

**Burning of auxiliary fuel**

- burning permits for auxiliary fuel systems are removed
  - the burners' fast stop valves close

- starting permits for auxiliary fuel systems are removed
    - the ignition gas valve closes

### Burning of mild stink gases

- the feeding permit for mild stink gases is removed
    - the feeder valves for mild stink gases close down
    - mild stink gases are lead to a chimney or to a spare burner

### Concentrated stink gases

- the feeding permit for concentrated stink gas is removed
  - the feeder valves for concentrated stink gas close down
  - concentrated stink gases are lead to a chimney or to a spare burner
  - the feeder valves for the auxiliary fuel of concentrated stink gas close down

**Blow gas from the dissolver (when required)**

- The dissolver's blow gas valves to the boiler close down
- The dissolvers blow gas valves to the chimney / roof open

**The boiler's bottom air**

- The boiler's bottom air stops
  - blowers stop
  - gates close

**Upper airways of the boiler**

- The upper airways of the boiler are left open

**Furnace ventilated**

- The Furnace ventilated message removed

### 2.9.2 Ventilation conditions for the burner

**Purpose**

Burner ventilation is an operation in which the burner is ventilated in order to ignite the auxiliary fuel. At the start of the ventilation the burner must be in a good condition so that the first burner can be started after the ventilation. Ventilation conditions are made up of many of the burner's process values and device states which must be at certain values and states.

**Sources**

**Fast stop button**

- Fast stop button not pressed in the control room

**Primary air**

- The amount of primary air above the lower limit
  2/3 selection, for example, of the following conditions:
  - the blower works
  - the amount of primary air over the minimum
  - the pressure of the air tube above the lower limit

**Secondary air**

- The amount of secondary air above the lower limit
  2/3 selection, for example, of the following conditions:
  - the blower works
  - the amount of secondary air above the minimum
  - the pressure of the air tube above the lower limit

**Furnace pressure**

- The pressure of the furnace below the upper limit
  3 pressure measurements
  - with 2/3 selection

**Flue gas outlet**

- The Flue-outlet-open message is compiled from the blower's operation data and the input and output channel data related to open dampers.
  - the blower does not work
    Using the 2/3 selection about the blower's rotating speed data, electric drives on - data, and the vacuum pressure measurement after the electrostatic precipitator
    - the rotating speed of the blower below the lower limit
    - the blower works
    - the vacuum pressure of the channel above the lower limit
  - the input channel damper on the open limit
    3 limit switches
    - 2/3 selection
  - the output channel damper on the open limit
    3 limit switches
    - 2/3 selection

**Control air**

- the pressure of the control air above the lower limit
  3 pressure measurements
  - 2/3 selection

**The emergency-stop for auxiliary fuel**

- The emergency-stop button for auxiliary fuel not pressed

**The emergency-stop for liquor burning**

- The emergency-stop button for the liquor burner not pressed

**liquor lines to the boiler**

- All firing liquor lines to the boiler closed

**Isolation of mild stink gases in the furnace**

- The isolation valves for mild stink gases closed

**Isolation of concentrated stink gases in the furnace**

- The isolation valves for concentrated stink gases closed and ventilation open

**Fuel lines for auxiliary fuel burners**

- The fast stop valves for the auxiliary fuel burner closed

**The furnace ventilated**

- Permitted time after the ventilation of the furnace exceeded

**Targets**

**Furnace ventilation**

- The ventilation permit for the furnace still valid

**Implementation**

The tripping condition “do not ventilate the boiler” is implemented in SIS. Monitoring related to the ventilation and ignition readiness is implemented in SIS.

The monitoring of the boiler ventilation is implemented in SIS. The safety logic controls that, after the ventilation order, the quantity of air has reached the required level and that the ventilation takes the time required. The time and the quantity of air needed for ventilation must be confirmed with the supplier of the boiler to ensure that the required quantity of air goes through the boiler.

### 2.9.3 Furnace ventilated

**Purpose:**

After the boiler has been ventilated for the required time, Furnace ventilated precondition message arrives, which means that the permit for the firing of the first burner has been obtained. The ventilated message is not needed when the liquor fire data is in effect in the furnace or when one of the burners is in operation.

**Sources**

**Boiler protection**
- Boiler protection in good condition

**The emergency-stop for auxiliary fuel**
- The emergency-stop button for auxiliary fuel not pressed

**The emergency-stop for liquor burning - off**

**Ventilated time**
- Furnace ventilated time below permitted

**Liquor lines to the boiler**
- All firing liquor lines to the boiler closed

**Auxiliary fuel burners in operation**
- No auxiliary fuel burner in operation

**Burner ignition attempts**
- Fewer than 2 attempts to ignite a burner with oil or fewer than 1 by gas

**Targets**

**Furnace ventilation**
- Furnace ventilated message still valid

**Implementation:**

The tripping conditions (do not ignite the boiler) are implemented in SIS. Monitoring of operations related to ventilation and ignition preparedness is implemented in SIS$_I$.
These monitoring processes include:

- Fire in the boiler signal creation
- Counting of ignition attempts

The counting of ignition attempts is implemented in SIS. A single ignition consists of a ignition order and the opening of the fast stop valve of the burner in question (the Closing-limits message – off).Two ignition attempts with oil are permitted, after which the ventilation of the boiler have to be repeated before any further ignition attempts.

### 2.9.4 Boiler burning permit for startup burners (furnace ready)

**Purpose**

The boiler burning permit for the startup burners ensures that the boiler condition is such that the startup burner can be set to work.

**Sources**

**Ventilation of the furnace**
- Furnace ventilated

OR
**Liquor firing**
- Liquor firing in operation
  - Liquor flow to the boiler above the lower limit, and
  - The amount of steam from the boiler above the lower limit

OR
**Auxiliary fuel burners**
- At least one auxiliary fuel burner in operation

**Targets**

Furnace burning permit for the startup burners in effect

### 2.9.5 Burning permit for the startup burner

**Purpose**

The burning permit for the startup burner ensures that both the furnace and the burner are in a state in which the burner can be started and that the process and state information related to both the auxiliary fuel to be burned and to other intermediate agents needed is correct.

**Sources**

**Boiler protection**
- Boiler protection in good condition

**The emergency-stop for auxiliary fuel**
- The emergency-stop button for auxiliary fuel not pressed

**Combustion air**
- The pressure of the combustion air above the lower limit

**The pressure of auxiliary fuel**
- The pressure of auxiliary fuel above the lower limit or below the upper limit

**The temperature of auxiliary fuel**
- The temperature of auxiliary fuel above the lower limit

**Burners’ control air pressure**
- The burners’ control air pressure above the lower limit

**The pressure of the dispersing agent intermediary**
- The pressure of the selected dispersing agent intermediary above the lower limit (oil firing)

**Boiler burning permit for the startup burners**
- Boiler burning permit for the startup burners in effect

**Burner in position**
- Burner in the chamber message in effect

**Air slide open**
- Air slide open message in effect

**Flame control**
- Flame message data exists (after a certain time from the ignition)

**Targets**

**Burning permit for the startup burner**
- Burning permit for the startup burners in effect

### 2.9.6 Boiler burning permit for load burners (furnace ready) (when required)

**Purpose**

The boiler burning permit for load burners ensures that the boiler conditions are such that the load burner can be started up.

**Sources**

**Liquor firing**
- Liquor firing in operation
  - Liquor flow to the boiler above the lower limit, and
  - The amount of steam from the boiler above the lower limit

OR

**Startup burners**
- At least the required number of auxiliary fuel burners in operation

**Targets**

Furnace burning permit for load burners in effect

### 2.9.7 Burning permit for the load burner

**Purpose**

The ignition permit for load burners ensures that the furnace and the burner are in a state in which the burner can be started and that the process and state information related to both the auxiliary fuel to be burned and to other intermediate agents needed is correct.

**Sources**

**Boiler protection**
- Boiler protection in good condition

**The emergency-stop for auxiliary fuel**
- The emergency-stop button for auxiliary fuel not pressed

**Furnace burning permit for load burners in effect (when required)**
- Liquor burning in operation - on

OR

- A sufficient number of startup burners on

**Combustion air**
- The pressure of the combustion air above the lower limit

**The pressure of auxiliary fuel**
- The pressure of auxiliary fuel above the lower limit or below the upper limit

**The temperature of auxiliary fuel**
- The temperature of auxiliary fuel above the lower limit

**Burners’ control air pressure (when required)**
- The burners’ control air pressure above the lower limit

**The pressure of the dispersing agent intermediary**

- The pressure of the selected dispersing agent intermediary above the lower limit (oil firing)

**Load burner in position**
- Load burner in the chamber message in effect

**Combustion air flow (when required)**
- The flow of the combustion air above the lower limit

**The proportion of combustion air and fuel (when required)**
- The proportion of combustion air and fuel correct

**The pressure of auxiliary fuel at the burner**
- The pressure of auxiliary fuel at the burner above the lower limit

**Flame control**
- Flame message data exists (after a certain time from the ignition)

**Targets**

**Burning permit for the load burner**
- Burning permit for the load burner in effect

### 2.9.8 The emergency-stop for auxiliary fuel

**Purpose**

The purpose of the emergency-stop buttons for the auxiliary fuel burners is to stop the auxiliary fuel burners and shut the feeding line valves as well as open the ventilation/pressurization valves in case of a possible disturbance such as fire.

**Sources**

**Fast stop button**
- Fast stop button pressed

**Emergency-stop buttons**
- Emergency-stop button pressed in the control room
- Emergency-stop buttons pressed in the field along the passages
- Emergency-stop buttons pressed in the burner control cabinets

**Targets**

**Fire stop valves for the burner's auxiliary fuel**
- Fire stop valves for the auxiliary fuel close

**Auxiliary fuel burners**
- Fast stop valves for the auxiliary fuel burners close
  - startup burners
  - load burners

**Ignition gas feed for the burners**
- The burners' fast stop valves for the ignition gas close

**Startup permit for the burners**
- The burners' ignition gas valves close

**Burner ventilation**
- The ventilation of the burner is interrupted and the "furnace ventilated" message disappears

**Implementation:**
Emergency-stop buttons must be equipped with opening contacts (closed current principle).

Pressing the emergency-stop buttons in the control room or along the passages closes all fire stop valves and the burners' fast stop valves either directly through the effect of the outputs of the safety logic or through the outputs of the basic process control system which are wired through relays controlled by the safety logic.

Pressing the emergency-stop buttons in the burner control cabinets closes the feeder valve and, when required, opens the ventilation valve at the burner concerned as well as closes the fast closing fuel valves at the burner.

### 2.9.9 Feeding permit for mild stink gases

**Purpose**

The feeding permit for mild stink gas ensures that the boiler is in a state in which stink gases can be safely brought in and that the gases burn properly.

**Sources**

**Boiler protection**
- Boiler protection in good condition

**The amount of steam in the flow (furnace ready)**
- The amount of steam in the boiler is below the minimum limit

**The level of the odorous gas condensate pocket (when needed)**
- The level of the odorous gas condensate pocket is below the maximum limit

**Odorous gas condensate content (when needed)**
- Content is below the minimum limit

**Targets**

**Feeding permit for mild stink gases**
- The feeding permit for mild stink gases is in effect
  - Mild stink gases to burn valve not locked
  - In targets, the collection valves not locked

### 2.9.10 Burning permit for concentrated stink gases

**Purpose**

The feeding permit for concentrated stink gas ensures that the boiler is in a state in which stink gases can be safely brought in and that the gases burn properly.

**Sources**

**Boiler protection**
- Boiler protection in good condition

**Liquor fire message to the stink gas feed**
- Liquor firing in operation
  - Liquor flow to the boiler above the lower limit, and
  - The amount of steam from the boiler above the lower limit

**Auxiliary firing in operation, oil/gas or methanol (when required)**
- Auxiliary firing in operation

**The pressure of the combustion air in the burner**
- The pressure of the combustion air above the lower limit

**The pressure of the burner's stink gas line**
- The pressure of the stink gas line above the minimum and below the maximum

**Condensate store surface**
- Condensate store surface below the upper surface

**The surface of the seal chamber**
- The surface of the seal chamber above the lower limit and below the upper limit

**Drop separator surface**
- The drop separator surface below the upper limit

**Explosion dampers in the stink gas line**
- Explosion dampers unbroken

**Targets**

**Burning permit for concentrated stink gases**
- Burning permit for concentrated stink gases in effect
  - <u>Concentrated stink gases to burn</u> valves and ventilation valve not locked

### 2.9.11 Start permit for liquor recycling

**Purpose**

In connection with liquor firing, it is important that the liquor to be fired does not enter the boiler in concentrations that are too low and that the state of the boiler is such that the liquor fed to the boiler burns and thus does not cause any melt water explosion hazard.

**Sources**

**Liquor feeding valves**
- All feeding valves for liquor nozzles closed

**Liquor nozzles / Safety gates**
- All liquor nozzles away from the boiler
- All safety gates closed

**Fast stop**
- Fast stop button not pressed

**Emergency-stop for liquor firing**
- The emergency-stop button for liquor firing not pressed

**Targets**

**Start permit for liquor recycling**
- Start permit for liquor recycling in effect
  - liquor pumps not locked
  - stop valves not locked

### 2.9.12 Liquor firing permit

**Purpose**

The liquor firing permit ensures that the boiler is in a state where liquor can be safely fed in and that the liquor burns properly. The aim is to prevent the entrance of wash water to the furnace at any stage.

**Sources**

**Boiler protection**
- Boiler protection in good condition

**Emergency-stop for liquor firing**
- The emergency-stop button for liquor firing not pressed

**Liquor solids %**
- Liquor solids % and/or its density above the lower limit
  - with 2/3 selection

**Cylinder pressure (when required)**
- Cylinder pressure above the lower limit of the liquor firing limit
  - 2/3 selection

**Auxiliary fuel burners in operation**
- Adequate number of auxiliary fuel burners in operation

OR

**Liquor fire message still valid**
- Liquor flow above the lower limit
- The amount of steam above the lower limit

**Washup for the liquor lines**
- Washup for the liquor lines not selected
- Wash measurement point not available
- Hand valve closed

**Targets**

**Liquor firing permit**
- Liquor firing permit in effect
  - Liquor pumps not locked
  - Stop valves/regulating valves not locked

### 2.9.13 Emergency-stop for liquor firing

**Purpose**

The purpose of the emergency-stop buttons for liquor firing is to stop liquor firing in case of a possible disturbance, e.g., a broken pipe or fire.

**Sources**

**Fast stop button**
- Fast stop button pressed

**Emergency-stop buttons**
- Emergency-stop button pressed in the control room
- A wall-specific emergency-stop button in the field at the liquor feeding levels pressed

**Targets**

**Liquor feeding valves for the boiler**
- Liquor feeding valves close

**Liquor feeding and recycling pumps**
- Liquor feeding and recycling pumps stop

**Liquor recycling valves**
- Liquor recycling valves close

**Impleme ntation**

Emergency-stop buttons must be equipped with opening contacts (closed circuit principle).

Pressing an Emergency-stop button in the control room closes all liquor feeding and recycling valves either directly through the effect of the outputs of the safety logic or through the outputs of the basic process control system which are wired through relays controlled by the safety logic. A wall-specific Emergency-stop button only closes the liquor feeding valve of the wall in question.

### 2.9.14 Start permit for liquor loop washup

**Purpose**

Washup means, in the first place, washing the liquor feeding lines into a collection tank and, in the second, washing up the nozzle lines and nozzles. The aim is to prevent the entrance of wash water to the furnace at any stage.

**Sources**

**Liquor feeding valves**

- All feeding valves for liquor nozzles closed

**Liquor nozzles / Safety gates**

- All liquor nozzles away from the boiler
- All safety gates closed

**Targets**

**Washup start permit**

- Washup start permit in effect
  - Liquor pumps not locked
  - Water stop valves not locked

### 2.9.15 Start permit for boiler floor washup

**Purpose**

The purpose of the start permit for boiler floor washup is to prevent the entry of washwater to a boiler that is too hot.

**Sources**

Boiler-specific definitions

**Targets**

**Start permit for floor washup**

- Washup start permit in effect
  - Water supply pump not locked
  - Water stop valves not locked

### 2.9.16 Stopping of air blowers

**Purpose:**

Stopping the air blowers when the flue outlets are closing prevents the entry of flue gases to the boiler room and high excess pressure in the boiler.

**Sources:**

- The flue gas outlet closed (at least one flue must be open)
- The flue open message is compiled from the blower's operation data and the input and output channel data related to open dampers.
  - the blower does not work
    Using the 2/3 selection regarding the blower's rotating speed data, electric drives on data, and the vacuum pressure measurement after the electrostatic precipitator
    - the rotating speed of the blower below the lower limit
    - the blower works
    - the vacuum pressure of the channel above the lower limit
  - the income channel damper away from the open limit
    3 limit switches
    - 2/3 selection

    OR
  - the output channel damper away from the open limit
    3 limit switches
    - 2/3 selection

**Targets**

**The boiler's bottom air**
- The boiler's bottom air stops
  - blowers stop
  - gates close

**The boiler's upper air**
- The boiler's upper air stops
  - blowers stop
  - gates close

### 2.9.17 Quick stop

**Purpose:** The purpose of the quick stop is to immediately stop the burning of lye and the stack by switching off the fuel feed and air supply to the lower part of the furnace. The quick stop is initiated from the control room using the quick stop switch.

**Source:**

**Quick stop switch in the control room**

- The quick stop switch has been pressed

**Targets:**

**Alarms**

- Voice alarms and alarms lights are activated

**The feed of burn lye**

- The burn lye pumps stop
- The fire shut-off valves of the burn lye feed close
- The feed valves of the burn lye close

**The auxiliary fuel burners**

- The quick shut-off valves of the auxiliary fuel burners close

**The auxiliary fuel feed**

- The fire shut-off valves of the auxiliary fuel feed close

**The feed of ignition gas to the burners**

- The shut-off valves of the ignition gas feed to the burners close

**The weak odorous gasses**

- The feed valves of weak odorous gasses close
- The weak odorous gasses are redirected to the smokestack or to the auxiliary burning location

**The strong odorous gasses**

- The feed valves of strong odorous gasses close
- The strong odorous gasses are redirected to the smokestack or to the auxiliary burning location

**The gasses of the dissolver (when needed)**

- The gas valves of the dissolver to the boiler close
- The gas valves leading from the dissolver to the smokestack / roof open

**The air feeds**

- The primary air feed to the furnace is prevented
  - the primary air blower stops
  - the primary air cut-off is activated
- The secondary air feed to the furnace is switched to the quick stop position
  - the closing plate of the secondary air feed is switched to the quick stop position
- The tertiary air feed to the furnace is switched to the quick stop position
  - the closing plate of the tertiary air feed is switched to the quick stop position

**The electrostatic precipitators**

- The electrostatic precipitators are switched off

**Sweeping**

- Sweeping is stopped and the sweepers driven from the furnace
- The sweeping steam valves close

**Ash and salt transporters**

- Ash and salt transporters stop

**Wait / consideration time for fast purge is started**

- The wait / consideration time (3 min) for fast purge is started

It will be jointly decided during the boiler risk assessment whether or not boiler bottling will also be automatically performed during a quick stop, in which case:

**Water and steam valves**
- Feed water pumps stop
- Feed water valves close
- The automatic start of the feed water turbine pump is prevented
- Injection water valves close
- Main steam valves close
- Startup closing valve opens
- Startup control valve opens 20%

**Implementation:**

The quick stop switch must be equipped with switches that open (stand by principle).

The quick stop valves of the auxiliary fuel lines are closed and if needed, the ventilation valves are opened using the safety automation system by switching the control signals of the logic part to no voltage. The quick stop valves and the ventilation valves switch to the safety state through spring operation.

Burner control itself is not necessarily a part of the safety automation system, but the burn control logic is given permission to burn from the safety automation system.

The switching of the burn valves, feed valves, air plates, motor valves, pumps, air blowers etc. to a safe state is implemented either through direct switches in the logic part or through separate relays that are controlled from the safety logic (SAS$_l$)

### 2.9.18 Fast purge

**Purpose:**

The purpose of the fast purge is to prevent water from getting in contact with the melt. Once quick stop has been triggered, a fast purge can be started at discretion using a switch in the control room.

**Source:**

**The fast purge switch**

- The fast purge switch has been pressed

**Targets:**

- Feed water pumps stop
- Feed water valves close
- The automatic start of the feed water turbine pump is prevented
- The steam cooling water line valves close

- Main steam valves close
- The startup close valve closes
- The startup control valve closes

After a set time (3 min) from the quick stop

- The fast purge valves open

**Implementation:**

The fast purge switch must be equipped with switches that open (stand by principle).

The safety logic controls separate closing relays that force the valves into the safe position. During safety control the moment limits and the temperature switch of the motor valves must be bypassed.

Releasing the fast purge switch stops the purge, causing the fast purge valves to close.

All fast purge valves are tested line by line at regular intervals during use by closing the hand valve located after the fast purge valves. Testing is done valve by valve on the view screen of the control room or locally. Testing can proceed once testing has been chosen on the view screen and the hand valve is closed.

The testing of the fast purge valves can also be done in the basic automation system. After testing the hand valves must be in the opened position. Testing will be logged. Any faults or inadequacies will be corrected immediately.

There must be an alarm or for instance a red signal light on the emergency stop panel for a closed hand valve.

## 2.10 TESTING

### 2.10.1 Factory acceptance testing

In factory acceptance testing (FAT) the emphasis is on program testing. Field equipment can be simulated by different means, for example, by wiring the sources to switch and light boards to speed up the testing.
The important thing is that all the sources and source combinations (2/3 measurement selections and other logical combinations) are examined and that the computational mA values for tripping limits are carefully scrutinized.

### 2.10.2 Deployment testing and periodic testing

When testing the deployment of the whole (SAT) and in periodic testing, it is recommended that the source signal simulations for field equipment are performed in a manner that is as real as possible. This means that pressure signals and pressure difference signals are simulated by pumping, temperature signals by warming, press buttons and limit switches by real devices, and that operation data is obtained from real data (the prevention of accidental start in case of a rotating apparatus must be taken into account).The real targets are also observed and identified in the field, valves by their movements, stopped motors by the contactors, by relay movements etc.

The tests of each testing phase are divided into two stages: safety logic tests and field circuit tests.

### 2.10.3 Testing of safety logic

In the preparatory stages of each testing, it should be ensured that the reason why the safety target goes into a safe state is due specifically to the operation of a safety interlock and not, for example, of a normal process lock.

For FAT testing, the system supplier draws up a safety logic related testing plan which covers all the system's fault and error situations that can be tested, taking into account also the redundancy in the different parts of the system. Moreover, the supplier draws up a checkup list about the system assembly, configuration and programming in accordance with the requirements of the manufacturer’s operation instructions. The functionality of different diagnostic alarms must be verified to make it possible to derive a full benefit from the system’s high diagnostics level.

In safety logics that are equipped with doubled processors, the stopping of one of the pair must be tested.

Fault testing of safety logic should include disconnections of cards, isolation of different connections and interruptions of voltage supply. These procedures are also applied in factory acceptance testing (FAT) so that the faults hidden by redundancies can also be revealed. When testing the whole (SAT) and in periodic tests during operation, however, the operating system inspection is not complete. Only some of the cards, connections and voltage interruptions are inspected according to the plan.

### 2.10.4 Testing of field circuits

In field testing for individual measurement transmitters, in addition to the testing of normal safety limits, also possible signal fault and transmitter failures must be taken into account. Depending on how a signal fault or transmitter failure is arranged in the transmitters, the safety logic must be constructed in such a way that the faults are discovered and the safety functions are implemented.

When testing the field circuits, one should be careful to ensure to that the real tripping value for a safety limit and the targets’ observed safe states are recorded.

In 2/3 of the optional measurements the testings should be arranged so that the measurements would be dealt with individually and in 1/3 the safety alarms and fault alarms would be identified and trippings in pairs would be identified.

When drawing up tripping limits based on analog measurements, it should be remembered that a deviation caused by a possible magnetic lag should be taken into account downward and that the tripping limit is not to be exceeded at any stage.This applies in cases where the tripping source is the process measurement’s upper limit.

The starting point for the testings is always that, for example, in the case of boiler protection, it is simulated initially as being in a sound condition. The tripping of the boiler protection will be caused by the signal pairs under testing either by using mA simulators (FAT testing) or by pumping in the field (deployment and periodic tests). In the same way, the transmitters’ signal and transmitter faults must be inspected in pairs, taking into account all the possibilities.

# 3 PART 2

## 3.1 GENERAL

This part presents model documents connected with the SIS lifecycle. There may be plant-specific digressions from the model documents. For example, there are two different ways to present logic diagrams and, in addition or as an alternative to these, there are also verbal explanations with which these diagrams can be supplemented.

### 3.1.1 General risk graph

Appendix 1 shows, with the help of a risk graph, the safety integrity definition for a recovery boiler. The definition is based on the risk graph diagram which complies with the SFS-IEC 61508 standard. The calibration of the diagram was adjusted to make it suitable for the definition of the integrity levels for personal, environmental, property and stoppage damage in connection with the recovery boiler. The appendix also has a model of the hazard and risk analysis form and shows how to fill it out.

### 3.1.2 Verification of the integrity level for safety instrumented systems

Appendix 2 presents the methods for verifying the integrity level (the required risk reduction) achieved by safety instrumentation.

The appendix employs mathematics based on failure probabilities. The values of different safety protection factors are added up, and the conclusion is that the overall probability of failure on demand (PFD) of the protective equipment comes up to the required integrity level.

The appendix also has formulae from Appendix B of the IEC 61508-6 standard. When applying the formulae, attention should be paid to the assumptions and limitations discussed in the standard. The formulae presented are not suitable for calculations of diverse channels.

### 3.1.3 Interlock diagrams

In interlock diagrams, a format similar to that in Appendix 3 can be used. Either the safety interlocks and basic control process lockings are presented in the same diagram, in which case the SIS interlocks are shown with two parallel lines, one continuous and the other one broken, or they are shown in their own diagram.

Appendix 4 shows SIS basic circuit models designed with the 1/2 principle. These illustrate the functional structure of the entire SIS circuit from the sources to the logic solver and further on to the targets. The diagrams detail the sources, I/Os, auxiliary relays, dependencies to the basic process control system and the targets to control.

An example of a verbalized SIS circuit operation is shown in Appendix 5.

### 3.1.4 Display images

Appendix 6 consists of examples of display images related to the recovery boiler's safety interlock operations.

### 3.1.5 Circuit design and wiring diagrams

Model diagrams of the circuit and wiring diagrams are shown in Appendix 7.

### 3.1.6 Testing documents

Appendix 8 shows the SIS model documents for factory acceptance testing (FAT) and periodic testing. Periodic testing documents can be adapted for the use as deployment testing documents.

### 3.1.7 Operation and maintenance guidelines

Appendix 9 shows the model for an operation and maintenance plan. It gives details about the persons responsible for SIS, maintenance of the documentation, training, requirement definitions, and about exceptional situations.

The appendix also contains a model guide for SIS modification procedures in case a need arises for them. Such a guide should give the instructions about who has the authority to order application, wiring, device, and testing modifications as well as about the reporting of the modifications. In cases where the modifications change requirements definitions or are otherwise considerable, the whole safety lifecycle must be looked over thoroughly, starting from the hazard and risk analysis.

# SUMMARY

The members of the Finnish Recovery Boiler Committee have inquired for a clear set of instructions about the implementation of safety instrumentation for recovery boilers. This is due to a concern about safety and the variety of implementations between different manufacturing plants.

The enforcement of the SFS-IEC 61508 reference standard as the Finnish national standard has forced the manufacturing plants in all their processes related to functional safety to refer to that standard and use its methods. This, in turn, has created confusion about implementations and handling of functional safety.

The recommendation aims to inform on hardware solutions, both about the selection as well as installation, and thus give the practitioner as clear a picture as possible about the implementation. The recommendation cannot take a position on whether the selected hardware solutions, as far as the measurements and controls are concerned, comply with the integrity level required in each particular case. This matter will be brought to the fore in the future development of the recommendation, once failure probabilities that are more reliable have been obtained from the equipment manufacturers in the future. This will allow quantitative (computational) examination of integrity levels for different equipment solutions.

The aim of this recommendation is to present a clear example with the help of guidelines and model documents, to clarify and standardize the practice in the future. The interlocks that the work group listed as candidates to be included in SIS are example interlocks from implemented boiler projects. The definition of final safety interlocks should always be based on a hazard and risk analysis, which should take into account, in a case-specific manner, the equipment and process solutions as well as environmental factors such as location, movement and unfamiliar equipment at the plant.

The carrying thought behind the model documents is that the practitioner should have as good a starting point as possible to implement the required documents. The objective is that the documents and instructions, by their clarity and consistency, would enable efficiency of operation and maintenance in the activities during operation and in periodic testings.

The recovery boiler is subject to many different guidelines and instructions. The implementation and operation of safety instrumentation has required its own recommendation to increase its clarity and unity to a decent level. Even at its first stage, the recommendation has received an enthusiastic and encouraging welcome from different quarters, among them many competent authorities. The feedback obtained has been very useful in the subsequent scrutiny of the recommendation. The work group would like to get feedback in the future also from the practitioners. That would make it possible to update and further develop the recommendation to make it serve in the task for which the work group created it as well as possible in the future.

# APPENDIX 1

## RISK GRAPH

**Definition of the safety integrity level for a recovery boiler with the help of a risk graph**

# General
# Hazard and risk analysis

The purpose of the hazard and risk analysis is to chart and define the hazards related to the operation of a recovery boiler and to define the magnitude of the risks caused by them. The general objective is that the analysis deals separately with personal, environmental, material and stoppage hazards.

The authors of the analysis, however, make their decision case by case about whether to deal with the material and stoppage hazards in addition to personal and environmental hazards, which according to the general standards and regulations must be dealt with. See EN61508 and EN61511.

A common way to proceed in the Hazard and risk analysis is to start by charting the hazards. An example of this is the Potential Problem Analysis (POA). The charting of hazards continues with the help of hazard recognition methods, the best-known of which is the HAZOP method. HAZOP is based on the examination of the reasons and consequences of the deviations in processes. After the hazards have been recognized, they are categorized, and non-tolerable hazards are then brought to a tolerable level.

Dangers, reasons for those dangers, their consequences, as well as the current preparation and the extent of the risk are presented in an analysis form of which there is a model as an appendix. The management of the hazards must be recorded in the form and in relation to the subprocesses of the boiler. This ensures readability and also that any possible later examination, modifications and additions can be done easily.

The magnitude of the risk (the required risk reduction) related to the risks that can be protected against with safety instrumentation, are defined with the help of the risk graph, which is presented in the following pages. The parameters of the risk graph used in the definition are shown separately for different hazards (personal, environment, material and stoppage hazards.

## The factors of the hazard and risk analysis

The persons who participate in the authoring of the hazard and risk analysis, must know, among other things, the operation of the boiler (operations supervisor), measurements, different subprocesses, chemicals to be employed, and the boiler's electrics, instrumentation, control and mechanics.

The leader of the analysis must be cognizant with the analysis method and also adequately know the process to be dealt with.

## Documentation

One must ensure that all the documents that are necessary for dealing with the matter are up-to-date and available, in order that the identification of hazards became as successful as possible (the plant's layout drawings, PI charts, process descriptions, etc.).

## Hazard management

When dealing with hazard items in the hazard analysis, at least the following matters listed below must be considered. The list can be used as a checklist, though only possible real hazards need to be recorded.

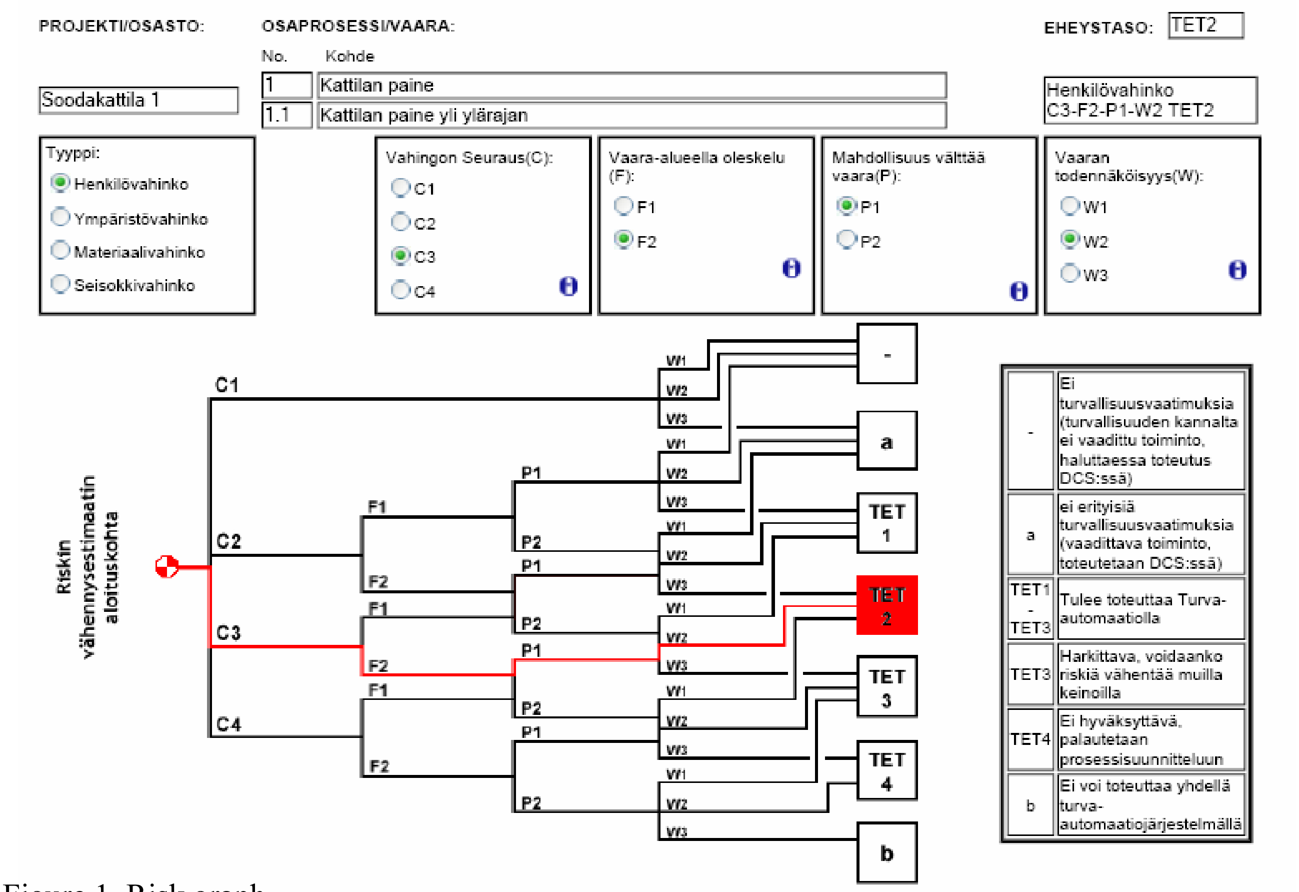
Process hazards / Process deviations:
- water access to the furnace
- high / low temperature
- high / low pressure
- high / low surface
- flow deviations (no flow, large flow, backflow)
- fire
- explosion
- leak
- failure (for example, DCS, critical measurement, valve)
- mechanical damage
- interruption in the auxiliary energy supply
- human errors
- startup / shutdown
- stoppage / maintenance
- others

Hazard factors related to the operation environment of the equipment and machines
- moving machine parts
- squeezing
- become entangled
- become trapped
- hazards due to high pressure gas or liquid spray
- electrical hazards
- hazards due to temperature (hot surfaces, for example)
- noise
- radiation
- touching or breathing of harmful substances
- biological or microbiological hazards
- disregard to ergonomic principles
- unexpected startup
- human errors
- falling or thrown parts
- slipping, stumbling or falling
- hazards associated with lifting
- others

## Classification of damage

The authors of the analysis (the owner of the plant) can decide case by case whether to classify the material and stoppage hazards as risks related to safety or whether they should be dealt with as so-called device protections, in which case the markings would follow the normal practice and the protection circuits would also come under the periodic testing programs the way safety instrumentation does.

# Risk graph



PROJEKTI/OSASTO: Soodakattila 1

OSAPROSESSI/VAARA:

| No. | Kohde |
|---|---|
| 1 | Kattilan paine |
| 1.1 | Kattilan paine yli ylärajan |

EHEYSTASO: TET2

Henkilövahinko
C3-F2-P1-W2 TET2

Tyyppi:
● Henkilövahinko
○ Ympäristövahinko
○ Materiaalivahinko
○ Seisokkivahinko

Vahingon Seuraus(C):
○ C1
○ C2
● C3
○ C4

Vaara-alueella oleskelu (F):
○ F1
● F2

Mahdollisuus välttää vaara(P):
● P1
○ P2

Vaaran todennäköisyys(W):
○ W1
● W2
○ W3

| | |
|---|---|
| - | Ei turvallisuusvaatimuksia (turvallisuuden kannalta ei vaadittu toiminto, haluttaessa toteutus DCS:ssä) |
| a | ei erityisiä turvallisuusvaatimuksia (vaadittava toiminto, toteutetaan DCS:ssä) |
| TET1 - TET3 | Tulee toteuttaa Turva-automaatiolla |
| TET3 | Harkittava, voidaanko riskiä vähentää muilla keinoilla |
| TET4 | Ei hyväksyttävä, palautetaan prosessisuunnitteluun |
| b | Ei voi toteuttaa yhdellä turva-automaatiojärjestelmällä |

Figure 1. Risk graph

# Integrity levels and the calibration of the parameters in risk graphs

## Risk graph parameters

## Result parameter, C

### Personal safety

Result parameter C is divided in four levels: C1, C2, C3 and C4. In risk assessment, the result parameter is defined according to the table below:

| Result parameter | Calibration | For example |
|---|---|---|
| C1 | Little harm done | Small wound, bruise or mild burn. No sickness leave |
| C2 | Disablement or sickness, no permanent effect on working capacity | Results in, for example, a medical examination and sickness leave |
| C3 | Death or serious injuries | |
| C4 | Death of several people | Disablement |

## Environmental safety

| | | |
|---|---|---|
| **Result parameter** | **Calibration** | **For example** |
| C1 | No damage, hazard or harm to residents nearby<br>No negative publicity | - Slight smell inconvenience<br>- Mild and concentrated stink gas conduction to the chimney for a short duration only<br>- Small amount of alkaline liquor to the channel |
| C2 | Slight environmental contamination that can be fixed. Slight contaminant emission to the environment | - Smell inconvenience<br>- Concentrated stink gas conduction to the chimney for a longer duration<br>- Alkaline liquor to the channel<br>- Emission which requires an emission notification to be made |
| C3 | Considerable contaminant emission extending outside the plant area and exceeding the permitted limit for the environment | - A large scale alkaline liquor or other emission which causes the destruction of the bacterial strain in the biological filter |
| C4 | Catastrophic emission outside the plant area | Serious contamination of the ground, ground water or waterway<br>- Serious destruction of plant or animal life nearby |

## Material safety

When estimating the parameter for material damages, equipment damage and repair work, costs are taken into account.

| **Result parameter** | **Calibration** | **For example** |
|---|---|---|
| C1 | <50 000 Eur | Replacement of the blower motor |
| C2 | 0,05 - 1 M Eur | Tube leak, breakdown of a combustible air blower |
| C3 | 1 - 5 M Eur | Stink gas thud |
| C4 | >5 M Eur | Melt water explosion |

### Stoppage safety

When assessing the result parameter of stoppage damages, other plants' stoppage damages must be considered also.

| Result parameter | Calibration | For example |
|---|---|---|
| C1 | <8h | Interruption in liquor firing |
| C2 | 8h – 1 wk | - Tube leak<br>- Breakdown of a combustible air blower |
| C3 | 1 wk – 2 mth | Stink gas thud |
| C4 | >2 mth | Melt water explosion |

## Stay parameter F

### Personal safety

| Stay parameter | Calibration | For example |
|---|---|---|
| F1 | The hazard centered on a limited area, and movement around the area is irregular | Electrostatic precipitator area, cylinder level |
| F2 | The hazard centers on the entire boiler room or levels where movement is commonplace | Liquor feeding level, burner level and lowest level |

### Environmental, material and stoppage safety

Environmental, material and stoppage risks are not time dependent, for which reason the parameter that is always used is F2.

## Hazard avoidance probability parameter P

The hazard avoidance parameter, P, describes the possibility to avoid an event in a situation where there is no electric safety function or when it is not operational. Timewise, the area of influence of parameter P is between the safety function and the hazardous event.

To discover a non-functionality of the protection, there must be an alarm that is not dependent on safety instrumentation, and the non-functionality of the protection must be detectable from process variables and/or state information.

**Personal safety**

| Possibility to avoid a hazard | Calibration | For example |
|---|---|---|
| P1 | - Possible in certain circumstances<br>- The operator has a sufficient time to act<br>- The persons in the area have the possibility to move to a safe area | - The hazard can be spotted and avoided in time<br>- Discovered with measurements and alarms<br>- Shutting up of different combustibles, fast stop |
| P2 | Otherwise, select P2 | |

**Environmental, material and stoppage safety**

The procedures employed, in case of parameter P for hazard avoidance probability, are the same for environmental, material and stoppage safety risks.

| Possibility to avoid a hazard | Calibration | For example |
|---|---|---|
| P1 | - Possible in certain circumstances<br>- The operator has a sufficient time to act | - The hazard can be spotted and avoided in time<br>- Discovered with measurements and alarms<br>- Emission of green liquor or other combustibles to the channel<br>- Closure, fast stop |
| P2 | Otherwise P2 | |

## Hazard existence probability W

The hazard existence probability parameter, W, describes the appearance probability of a hazard when protection by safety instrumentation is not taken into account. When estimating the probability of an event, the effect of other means to reduce risks is also considered.

Other risk reduction means include, for example:
- planning, design
- normal basic process control interlocks, controls, etc.
- safety valves
- rupture disks
- explosion relief panels
- gas and fire detectors
- training, instructions, etc.

**Personal, environmental, material and stoppage safety**

The procedures employed, in case of parameter P for hazard existence probability, are the same for personal, environmental, material and stoppage safety risks.

| Hazard existence probability parameter | Calibration | For example |
|---|---|---|
| W1 | Very small<br>(occurrence interval more than 33 years) | Occurrence of damage not probable in this plant under the present practice |
| W2 | Small (occurrence interval 3 – 33 years) | Damage has occurred in a comparable plant elsewhere and there is a reason to believe that it can happen in this plant within the next 3 – 33 years |
| W3 | Probable<br>(occurrence interval 4mth – 3 years) | It is probable that damage will occur in this plant during the next 3 years |

With the help of the occurrence intervals above, a generally tolerable individual risk level can be achieved.

## Hazard and risk analysis form

Annex 1 of Appendix 1 shows the form for hazard and risk analysis.

The front page of the form is to be filled out with the details of the plant and the project, the system being analyzed, the drawings used (e.g., PI diagrams), the participants in the analysis, the date, place and possible observations, which later on must be attended to, for example, if the analysis proves inadequate for some reason.

Real hazard situations should be entered in the **Hazard** section. This applies, for example, to excessive pressure in the boiler. All possible hazards due to hazard situations that can cause at least personal or environmental hazards are recorded. The work group decides, whether to record also possible material and stoppage hazards.

All possible reasons that can cause the hazard to be dealt with or start a possible chain of events that leads to the hazard in question should be entered in the **Hazard causes** section.

In the **Consequences** section, first the cause-specific general consequences are entered and, under that, the damage-specific consequences for personal, environmental, material and stoppage damages. Their possible magnitude is also estimated here.

The **Preparation (without SRS)** section is used to record all possible preparation, whether mechanical or electrical, handled by instruction or by education, that can affect the possible occurrence of damage.

The **Risk (without SRS)** section records the parameter path (e.g., C3-F2-P1-W2) obtained from the risk graph's estimation of the magnitude of the risk reduction requirement and the risk reduction requirement itself (-, a, SIL1 – SIL4 or b). See Figure 1 of the risk graph.

The **SRS/Actions/Comments** section is used to enter the work group's proposals about possible safety operations in SRS and other possibly needed additional clarifications.

ANNEX 1

# HAZARD AND RISK ANALYSIS FORM

| **HAZARD** | **HAZARD CAUSES** | **CONSEQUENCES**<br>**-Personal damage**<br>**-Environmental damage**<br>**-Material damage**<br>**-Stoppage damage** | **PREPARATION**<br>**(without SIS)** | **RISK**<br>**(without SIS)** | **SIS/ACTIONS**<br>**COMMENTS** |
|---|---|---|---|---|---|

## 1. BOILER WATER SYSTEM

| | | | | | | |
|---|---|---|---|---|---|---|
| **1.1** | **Cylinder surface too low** | • a big leak in the furnace<br>• | • boiling dry<br>• pipe damage<br>• melt water explosion | • surface measurements (2/3)<br>• local water glasses 2 + camera<br>• instructions for operation and maintenance<br>• regular periodic inspections and strength measurements for boiler pipes | Person:<br>C4-F2-P2-W1<br>SIL3<br>Environment:<br>-C2-F2-P2-W1<br>SIL1<br>Material:<br>-C4-F2-P2-W1<br>SIL3<br>Stoppage:<br>-C4-F2-P2-W1<br>SIL3 | Regular periodic inspections and strength measurements for boiler pipes.Tripping from a low surface 2/3 react (LI-7312, -13, -22)<br>SIL2 implemented |
| **1.2** | **Cylinder surface too low** | • a leak in the boiler<br>• | • boiling dry<br>• pipe damage<br>• melt water explosion hazard | • surface measurements (2/3)<br>• local water glasses, 2 + camera<br>• difference measurement for the water feed and amount of steam causing an alarm<br>• instructions for operation and maintenance<br>• regular periodic inspections and strength measurements for boiler pipes | Person:<br>C4-F2-P1-W1<br>SIL2<br>Environment:<br>-C2-F2-P1-W1<br>a<br>Material:<br>C1-F2-P2-W2<br>-<br>Stoppage<br>:<br>-C2-F2-P1-W2<br>SIL1 | Tripping from a low surface 2/3 react (LI-7312, -13, -22)<br>• closing of the auxiliary fuel burners<br>• ventilation discarded<br>• liquor firing stopped<br>• feeding of mild stink gases stopped |

| | HAZARD | HAZARD CAUSES | CONSEQUENCES<br>-Personal damage<br>-Environmental damage<br>-Material damage<br>-Stoppage damage | PREPARATION<br>(without SIS) | RISK (without SIS) | SIS/ACTIONS COMMENTS |
|---|---|---|---|---|---|---|
| | **1.3 Cylinder surface too low** | • feed water flow prevented<br>• | • boiling dry<br>• pipe damage<br>• melt water explosion hazard | • surface measurements (2/3)<br>• local water glasses, 2 + camera<br>• instructions for operation and maintenance<br>• feed water flow measurement | Person:<br>C4-F2-P1-W1<br>SIL2<br>Environment:<br>- C2-F2-P1-W1<br>a<br>Material:<br>C1-F2-P2-W1<br>-<br>Stoppage<br>:<br>C2-F2-P1-W2<br>SIL1 | SIL2 implemented<br>Tripping from a low surface 2/3 react (LI-7312, -13, -22)<br>• closing of the auxiliary fuel burners<br>• ventilation discarded<br>• liquor firing stopped<br>• feeding of mild stink gas stopped |
| | **1.4 Cylinder surface too low** | • a sudden increase in pressure<br>• | • the surface of the cylinder falls momentarily | • surface measurements (2/3)<br>• local water glasses, 2 + camera<br>• instructions for operation and maintenance | Person:<br>C1<br>-<br>Environment:<br>-C1<br>- Material:<br>C1<br>-<br>Stoppage<br>: C1<br>- | No safety requirements |

# APPENDIX 2

# VERIFICATION OF INTEGRITY LEVELS FOR SAFETY INSTRUMENTATION

## General

When verifying the integrity level for a protection built within SIS, one must consider separately the adequacy of the device architecture as well as the mathematical probability of failure due to hardware failure. The examination of both the device architecture as well as that of the probability of failure must be conducted for each of the protection's structural part (subsystems) separately. The interlocks that are built for the safety instrumentation consist mainly of the source part or normally transmitters, of safety logic, and of the target part or normally valves and motors (see Figure 1).

## Hardware structures

In safety instrumented systems, the functional protections are built of different device structures, so that a single field device, for example, at the source side is replaced by several field devices. This provides additional security for safety operations and in certain structures also more usability for the plant. The most common device structures are:

1/1 structure (1oo1, 1 –out-of-1)

- one component (e.g., measurement), SIS is activated by the component demand or failure

1/2 structure (1oo2, 1 –out-of-2)

- two components connected parallel, SIS is activated by a separate demand or failure from each component

2/2 structure (2oo2, 2 –out-of-2)

- two components connected parallel, SIS is activated by a simultaneously occurring demand or failure from both of the components Thus, a failure of only one of the components does not activate SIS.

2/3 structure (2oo3, 2 –out-of-3)

- three components are connected parallel, SIS is activated by a simultaneously occurring demand or failure of two of the components Thus, a failure of only one of the components does not activate SIS.

## Dangerous and safe failures

Components' failure modes can be divided into safe and dangerous failures. The classification of the failure modes is based on the examination of the system state after the failure.

Dangerous failure refers to a situation, where a safety related system is prevented from responding to a potentially dangerous situation. Dangerous failures may be caused by, for example, an incorrect system definition, systematic or random equipment failures, a programming or human error or changes that have taken place in the system's operating environment.

A failure in a safety related system can lead to an accident if SIS does not correctly function in that exigency. The mathematical failure probability examination due to hardware failures is based on dangerous failures in practice.

In the case of a safe failure, the system incorrectly interprets the process to be in a dangerous state and thus often performs a shutdown for the failed system.

**Undetected and detected failures**

To anticipate failures, it is of the utmost importance that the system or the operator notices a possible failure situation. Based on this, failures can be further classified into undetected and detected failures.

A detected failure is a failure which can be discovered with the internal system diagnostics or in connection with normal operations, for example, from the control room. An undetected failure refers to a situation in which the system experiences a failure but the failure remains unnoticed. Undetected failures are normally found in periodic testing.

**Examination of hardware architecture**

In the examination of hardware architecture, hardware fault tolerance and safe failure fraction are brought under inspection. The examination of hardware architecture brings added demands to the complexity of the hardware in some cases where a higher SIL could theoretically be achieved if the mathematical examination approach only were used in the examination.

Table 1 shows the permissible hardware safety integrity according to the fault tolerance of the hardware and safe failure fraction of a device for so-called simple devices. Simple devices are assumed to be devices whose

- all failure modes are known
- behavior in a fault situation can be completely defined
- failure rate track record for detected and undetected dangerous failures is sufficiently well known to be regarded as reliable failure information based on practice.

| Safe failure fraction | Hardware fault tolerance N | | |
|---|---|---|---|
| | 0 | 1 | 2 |
| < 60 % | SIL1 | SIL2 | SIL3 |
| 60 % - 90 % | SIL2 | SIL3 | SIL4 |
| 90 % - 99 % | SIL3 | SIL4 | SIL4 |
| > 99 % | SIL3 | SIL4 | SIL4 |

Table 1

Table 2 shows the permissible hardware safety integrity according to the fault tolerance of the hardware and safe failure fraction of a device for other than so-called simple devices.

| Safe failure fraction | Hardware fault tolerance N | | |
|---|---|---|---|
| | 0 | 1 | 2 |
| < 60 % | not permissible | SIL1 | SIL2 |
| 60 % - 90 % | SIL1 | SIL2 | SIL3 |
| 90 % - 99 % | SIL2 | SIL3 | SIL4 |
| > 99 % | SIL3 | SIL4 | SIL4 |

Table 2

In the tables, fault tolerance N means that N+1 faults can result in losing the safety function. In different hardware architecture examinations it is important to consider, e.g., the safe failure fraction for process measurement transmitters. Once that is, for example, between 60-90 %, SIL1 can be achieved with a single transmitter. Employing two transmitters of the same transmitter type, SIL2 can be achieved. Here we need to assume that the quality requirements for the hardware, software and the project to be implemented are of SIL2 level.

If the components have not been given their safe failure fraction (SFF), these can be calculated with the equation:

$SFF = (\lambda_S + \lambda_{DD}) / (\lambda_S + \lambda_D)$
where
$\lambda_S$ = combined safe failures probability
$\lambda_{DD}$ =the probability of dangerous failures detected by diagnostics
$\lambda S$ = combined dangerous failures probability

## Failure probability examination

In the integrity level verification, each part of the protection is examined separately or, in normal situations, the source (e.g., a transmitter), the logic, and the target (e.g., valve). See Figure 1. In failure probability examination the average probability of failure on demand ($PFD_{AVG}$) is calculated, once the exigent condition appears, for the protection built in SIS as a whole by adding up the failure probabilities for the different part factors (source, logic, target) as follows:

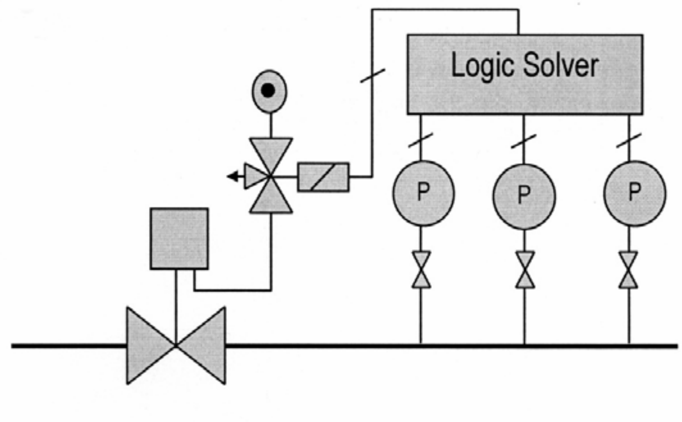


Figure 1. Example basic structure for safety automation

$PFD_{AVG} = PFD_{SENSOR} + PFD_{LOG} + PFD_{ACTUATOR}$
where

- $PFD_{AVG}$ is the average failure probability for the SIS safety function when an exigent situation occurs

- $PFD_{SENSOR}$ is the failure probability of a sensor (e,g., transmitter) or an input connection unit when an exigent situation occurs

- $PFD_{LOG}$ is the failure probability of the logic solver when an exigent situation occurs

- $PFD_{ACTUATOR}$ is the failure probability of an output connection unit or actuator (e.g., valve) when an exigent situation occurs.

**Integrity levels and the probability of dangerous failure**

Table 3 shows the correspondence between the integrity levels (SIL) and the average probability of dangerous failure on demand (PFD) as well as the achieved risk reduction. The data on the table is based on PFD values for a small number of demands, which means that the safety function demand is less than once a year or at most twice during the interval between periodic testing.
For example, in SIL2 the average probability for the total number of failures should be between $10^{-2}$ - $10^{-3}$. The risk reduction will then be of 100 – 1000 magnitude.

| Integrity level (SIL) | Average probability failure on demand | Risk reduction |
|---|---|---|
| 4 | $\geq 10^{-5}$ $< 10^{-4}$ | >10000 ≤ 100000 |
| 3 | $\geq 10^{-4}$ $< 10^{-3}$ | >1000 ≤ 10000 |
| 2 | $\geq 10^{-3}$ $< 10^{-2}$ | >100 ≤ 1000 |
| 1 | $\geq 10^{-2}$ $< 10^{-1}$ | >10 ≤ 100 |
| | | |
| | | |

Table 3

## PFD formulae for hardware structures

The formulae are from Appendix B of the IEC 61508-6 standard.
Note: When applying the formulae, attention must be paid to the assumptions and limitations expressed in the standard. The formulae presented are not suitable for calculations of diverse channels.

Table 4 explains the parameters for the formulae employed:

| | |
|---|---|
| MTTR (h) | Mean time to restoration (hours) |
| TI (h) | Periodic testing interval (hours) |
| $PFD_G$ | The average probability of failure on demand for a device |
| $PFD_{SYS}$ | The average probability of failure on demand for safety functions |
| ▮$_D$ (1/h) | The probability of dangerous failure (per hour) |
| ▮$_{DD}$ | The probability of detected dangerous failures (per hour) |
| ▮$_{DU}$ | The probability of undetected dangerous failures (per hour) |
| $b_D$ | The fraction of the detected dangerous failures that have a common origin |
| b | The fraction of the undetected dangerous failures that have a common origin |
| $t_{CE}$ | Device’s mean equivalent down time (h) |
| $t_{GE}$ | System’s mean equivalent down time (h) |

Table 4

### Structure 1oo1

$\lambda_D = \lambda_{DU} + \lambda_{DD}$

$PFD_{SENSOR} =( \lambda_{DU} + \lambda_{DD} ) t_{CE}$

where
$t_{CE} = (\lambda_{DU} / \lambda_D) ((T_1 / 2) + MTTR) + (\lambda_{DD} / \lambda_D) MTTR$, thus

$PFD_{SENSOR} = \lambda_{DU} (T_1 / 2 + MTTR) + \lambda_{DD} MTTR$

### Structure 1oo2

$\lambda_D = \lambda_{DU} + \lambda_{DD}$

$PFD_{SENSOR} =2( (1- \beta_D )\lambda_{DD} + (1- \beta )\lambda_{DU})^2 t_{CE} t_{GE} + \beta_D \lambda_{DD}MTTR + \beta\lambda_{DU}(T_1 / 2 + MTTR)$

where
$t_{CE}$ = as in structure 1oo1

$t_{GE} = (\lambda_{DU} / \lambda_D) ((T_1 / 3) + MTTR) + (\lambda_{DD} / \lambda_D) MTTR$

### Structure 2oo2

$\lambda_D = \lambda_{DU} + \lambda_{DD}$

$PFD_{SENSOR} = 2(\lambda_{DU} + \lambda_{DD})\, t_{CE}$

where
$t_{CE}$ = as in structure 1oo1

### Structure 2oo3

$\lambda_D = \lambda_{DU} + \lambda_{DD}$

$$PFD_{SENSOR} = 6((1-\beta_D)\lambda_{DD} + (1-\beta)\lambda_{DU})^2\, t_{CE}\, t_{GE} + \beta_D\, \lambda_{DD} MTTR + \beta\lambda_{DU}(T_1 / 2 + MTTR)$$

where
$t_{CE}$ = as in structure 1oo1

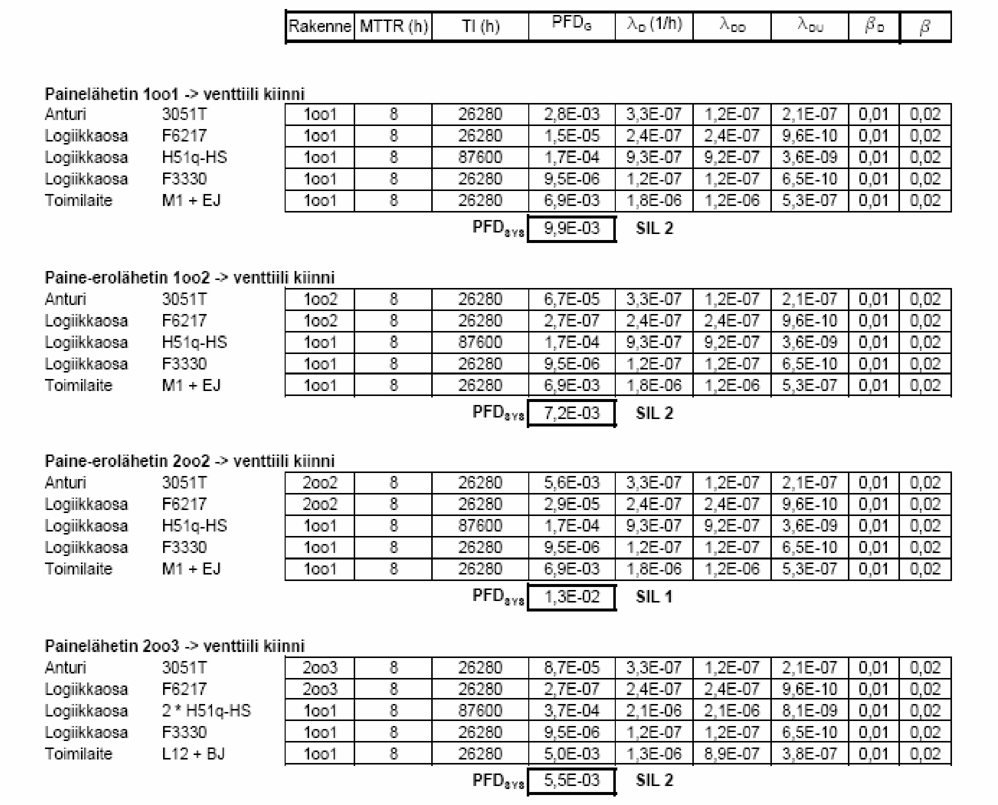
$t_{GE}$ = as in structure 1oo2

## PFD calculation examples for different device structures

Table 5 shows some obtained PFD values for different device structures using the formulae presented above. The calculation example uses a pressure transmitter whose:

- $\lambda_D$ = 3,3E-07 1/h
- $\lambda_{DD}$ = 1,2E-07 1/h, of which
- $\lambda_{DU}$ = 2,1E-07 1/h
- $\beta$ = 2%
- $\beta_D$ = 1%

In the calculation, the value of MTTR is 8 h and the periodic testing interval (TI) 3 years.



|  |  | Rakenne | MTTR (h) | TI (h) | $PFD_G$ | $\lambda_D$ (1/h) | $\lambda_{DD}$ | $\lambda_{DU}$ | $\beta_D$ | $\beta$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **Painelähetin 1oo1 -> venttiili kiinni** |  |  |  |  |  |  |  |  |  |  |
| Anturi | 3051T | 1oo1 | 8 | 26280 | 2,8E-03 | 3,3E-07 | 1,2E-07 | 2,1E-07 | 0,01 | 0,02 |
| Logiikkaosa | F6217 | 1oo1 | 8 | 26280 | 1,5E-05 | 2,4E-07 | 2,4E-07 | 9,6E-10 | 0,01 | 0,02 |
| Logiikkaosa | H51q-HS | 1oo1 | 8 | 87600 | 1,7E-04 | 9,3E-07 | 9,2E-07 | 3,6E-09 | 0,01 | 0,02 |
| Logiikkaosa | F3330 | 1oo1 | 8 | 26280 | 9,5E-06 | 1,2E-07 | 1,2E-07 | 6,5E-10 | 0,01 | 0,02 |
| Toimilaite | M1 + EJ | 1oo1 | 8 | 26280 | 6,9E-03 | 1,8E-06 | 1,2E-06 | 5,3E-07 | 0,01 | 0,02 |
|  |  |  |  | **$PFD_{SYS}$** | 9,9E-03 | **SIL 2** |  |  |  |  |
| **Paine-erolähetin 1oo2 -> venttiili kiinni** |  |  |  |  |  |  |  |  |  |  |
| Anturi | 3051T | 1oo2 | 8 | 26280 | 6,7E-05 | 3,3E-07 | 1,2E-07 | 2,1E-07 | 0,01 | 0,02 |
| Logiikkaosa | F6217 | 1oo2 | 8 | 26280 | 2,7E-07 | 2,4E-07 | 2,4E-07 | 9,6E-10 | 0,01 | 0,02 |
| Logiikkaosa | H51q-HS | 1oo1 | 8 | 87600 | 1,7E-04 | 9,3E-07 | 9,2E-07 | 3,6E-09 | 0,01 | 0,02 |
| Logiikkaosa | F3330 | 1oo1 | 8 | 26280 | 9,5E-06 | 1,2E-07 | 1,2E-07 | 6,5E-10 | 0,01 | 0,02 |
| Toimilaite | M1 + EJ | 1oo1 | 8 | 26280 | 6,9E-03 | 1,8E-06 | 1,2E-06 | 5,3E-07 | 0,01 | 0,02 |
|  |  |  |  | **$PFD_{SYS}$** | 7,2E-03 | **SIL 2** |  |  |  |  |
| **Paine-erolähetin 2oo2 -> venttiili kiinni** |  |  |  |  |  |  |  |  |  |  |
| Anturi | 3051T | 2oo2 | 8 | 26280 | 5,6E-03 | 3,3E-07 | 1,2E-07 | 2,1E-07 | 0,01 | 0,02 |
| Logiikkaosa | F6217 | 2oo2 | 8 | 26280 | 2,9E-05 | 2,4E-07 | 2,4E-07 | 9,6E-10 | 0,01 | 0,02 |
| Logiikkaosa | H51q-HS | 1oo1 | 8 | 87600 | 1,7E-04 | 9,3E-07 | 9,2E-07 | 3,6E-09 | 0,01 | 0,02 |
| Logiikkaosa | F3330 | 1oo1 | 8 | 26280 | 9,5E-06 | 1,2E-07 | 1,2E-07 | 6,5E-10 | 0,01 | 0,02 |
| Toimilaite | M1 + EJ | 1oo1 | 8 | 26280 | 6,9E-03 | 1,8E-06 | 1,2E-06 | 5,3E-07 | 0,01 | 0,02 |
|  |  |  |  | **$PFD_{SYS}$** | 1,3E-02 | **SIL 1** |  |  |  |  |
| **Painelähetin 2oo3 -> venttiili kiinni** |  |  |  |  |  |  |  |  |  |  |
| Anturi | 3051T | 2oo3 | 8 | 26280 | 8,7E-05 | 3,3E-07 | 1,2E-07 | 2,1E-07 | 0,01 | 0,02 |
| Logiikkaosa | F6217 | 2oo3 | 8 | 26280 | 2,7E-07 | 2,4E-07 | 2,4E-07 | 9,6E-10 | 0,01 | 0,02 |
| Logiikkaosa | 2 * H51q-HS | 1oo1 | 8 | 87600 | 3,7E-04 | 2,1E-06 | 2,1E-06 | 8,1E-09 | 0,01 | 0,02 |
| Logiikkaosa | F3330 | 1oo1 | 8 | 26280 | 9,5E-06 | 1,2E-07 | 1,2E-07 | 6,5E-10 | 0,01 | 0,02 |
| Toimilaite | L12 + BJ | 1oo1 | 8 | 26280 | 5,0E-03 | 1,3E-06 | 8,9E-07 | 3,8E-07 | 0,01 | 0,02 |
|  |  |  |  | **$PFD_{SYS}$** | 5,5E-03 | **SIL 2** |  |  |  |  |

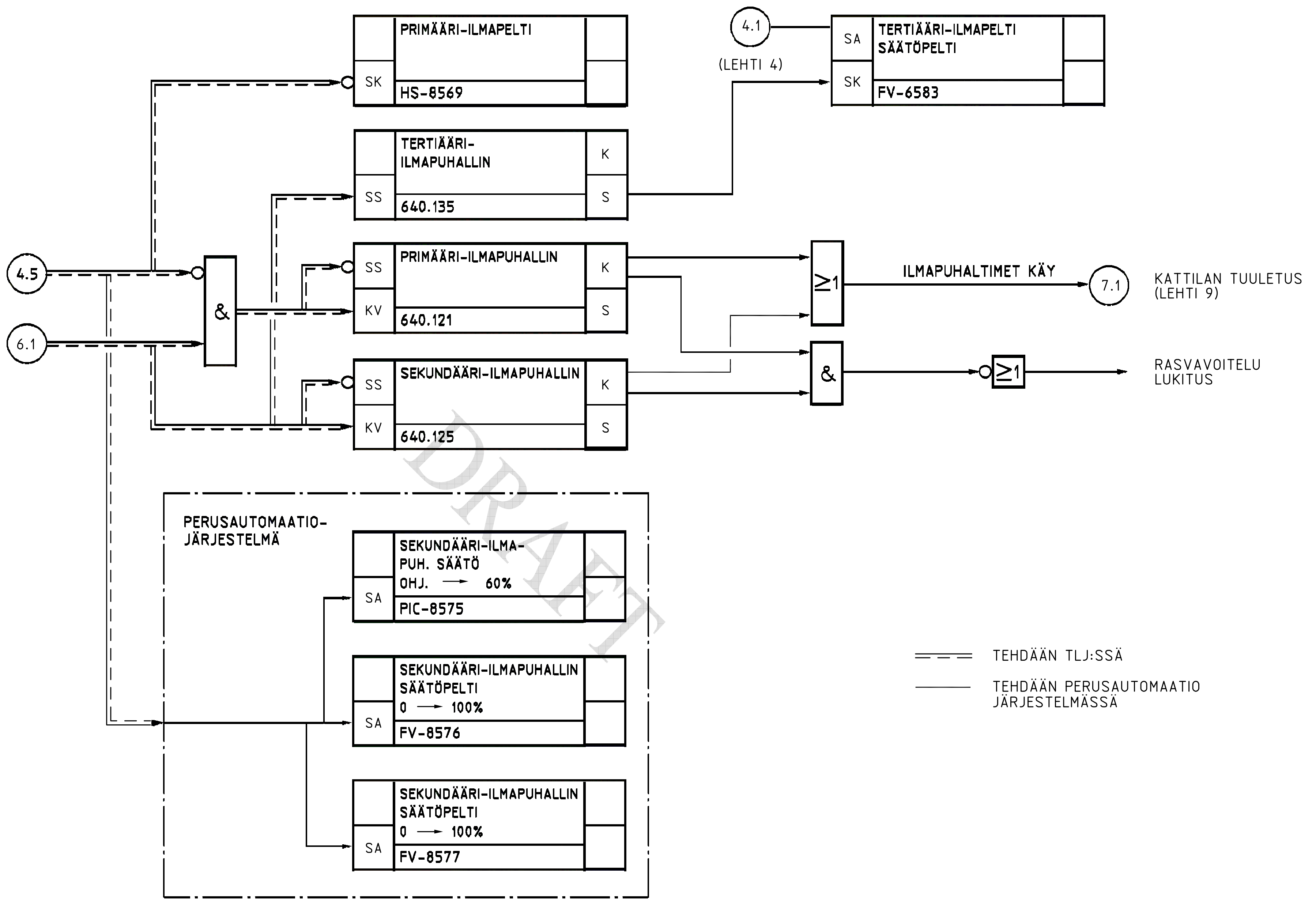
Table 5

# APPENDIX 3

## INTERLOCK DIAGRAMS

### Examples of implemented interlock diagrams

Muutos Muutos Muutos



| | | | | | | |
|---|---|---|---|---|---|---|
| Toimittaja/no. | Toim.piir.no. | Pvm. | | Piir. nimi<br>SOODAKATTILAN TLJ<br>LOGIIKKAKAAVIO<br>ESIMERKKI | Laji | Sovellus | 
| Ark.no. | | Suunn. | | | Keskus | Lähtö |
| PÖYRY | | Tark. | Osasto | No. | Piir.no. | Lehti |
| | | Hyv. | Tekn.kok. | No. | | Rev. |

Laitepaikka

Vaihe

Muutos

Muutos

Muutos

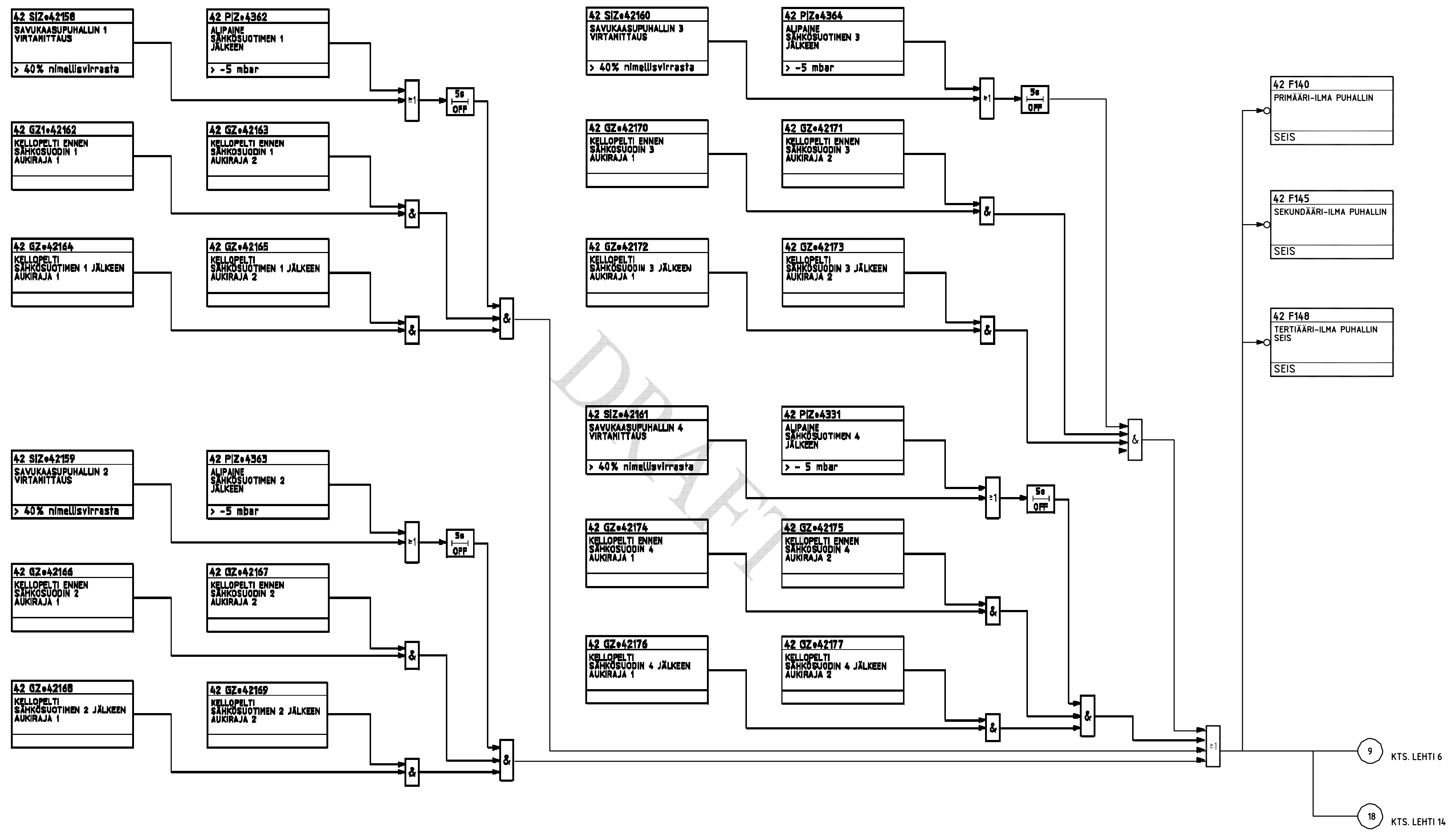
PIKAPYSÄYTYS

VÄH. 1 SAVUKAASUKANAVA AUKI

Muutos
Muutos

Muutos
Muutos

Muutos
Muutos

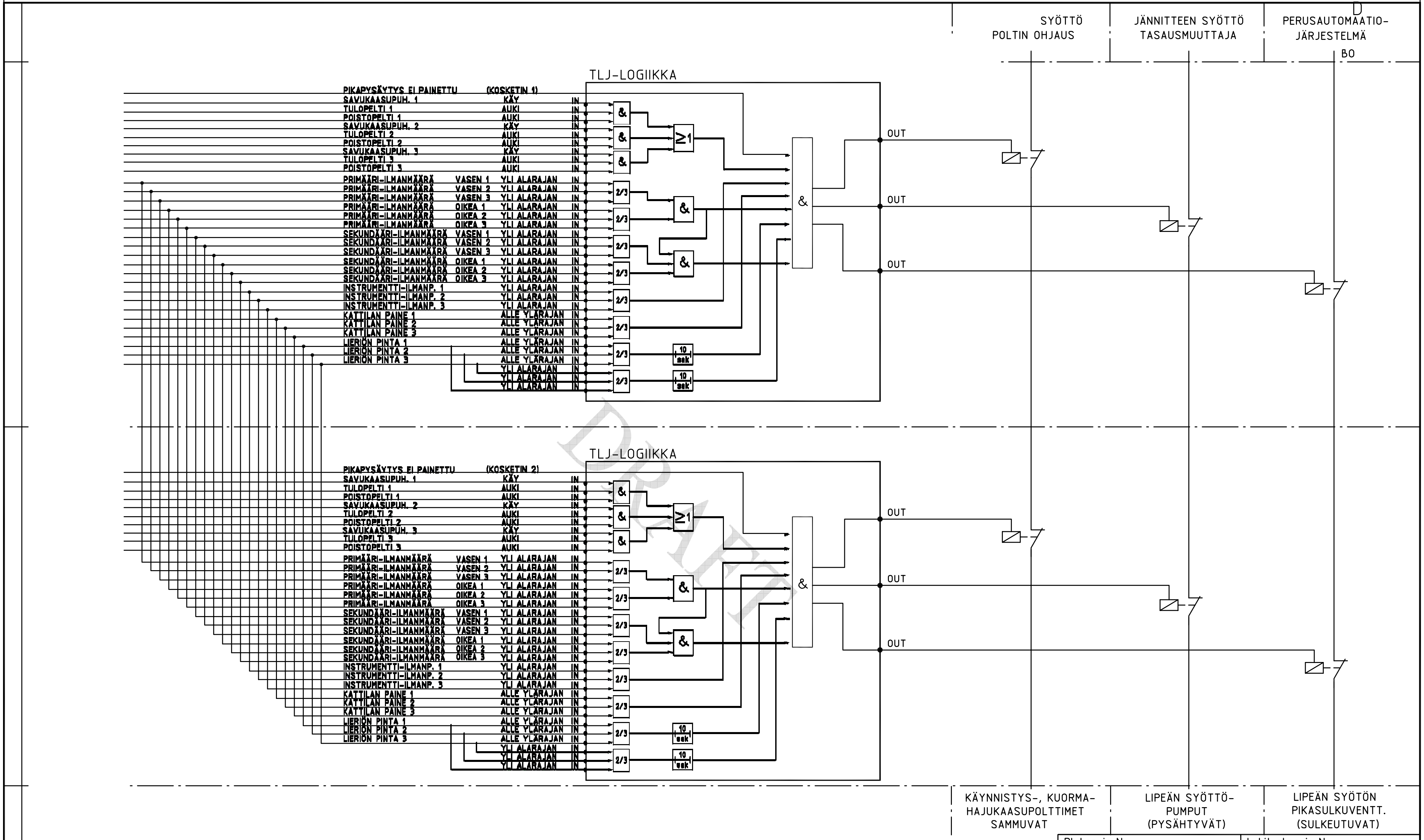


| | | | | | | |
|---|---|---|---|---|---|---|
| Toimittaja/no. | Toim.piir.no. | Pvm. | | | Piir. nimi<br>SOODAKATTILA,<br>TURVA-AUTOMAATIO<br>SAVUKAASUTIE AUKI | Laji | Sovellus | Laitepaikka |
| Ark.no. | | Suunn. | | | | Keskus | Lähtö | Vaihe |
| PÖYRY | | Tark. | Osasto | No. | | Piir.no. | Lehti | Rev. |
| | | Hyv. | Tekn.kok. | No. | | | | |

51726112__03.dwg 29.01.2008 09:28 /prs16

# APPENDIX 4

# BASIC DIAGRAMS Exampes of a logic solver (1/2 principle)



PI-kaavio No.
Lukituskaavio No.

Toimittaja/no.
Toim.piir.no.
Ark.no.
PÖYRY

Pvm.
Suunn.
Tark.
Hyv.
Osasto
Tekn.kok.
No.
No.

Piir. nimi
SOODAKATTILAN TLJ
LOGIIKKAKAAVIO
KATTILASUOJA

Laji
Sovellus
Laitepaikka
Keskus
Lähtö
Vaihe
Piir.no.
Lehti
Rev.

Muutos

Muutos

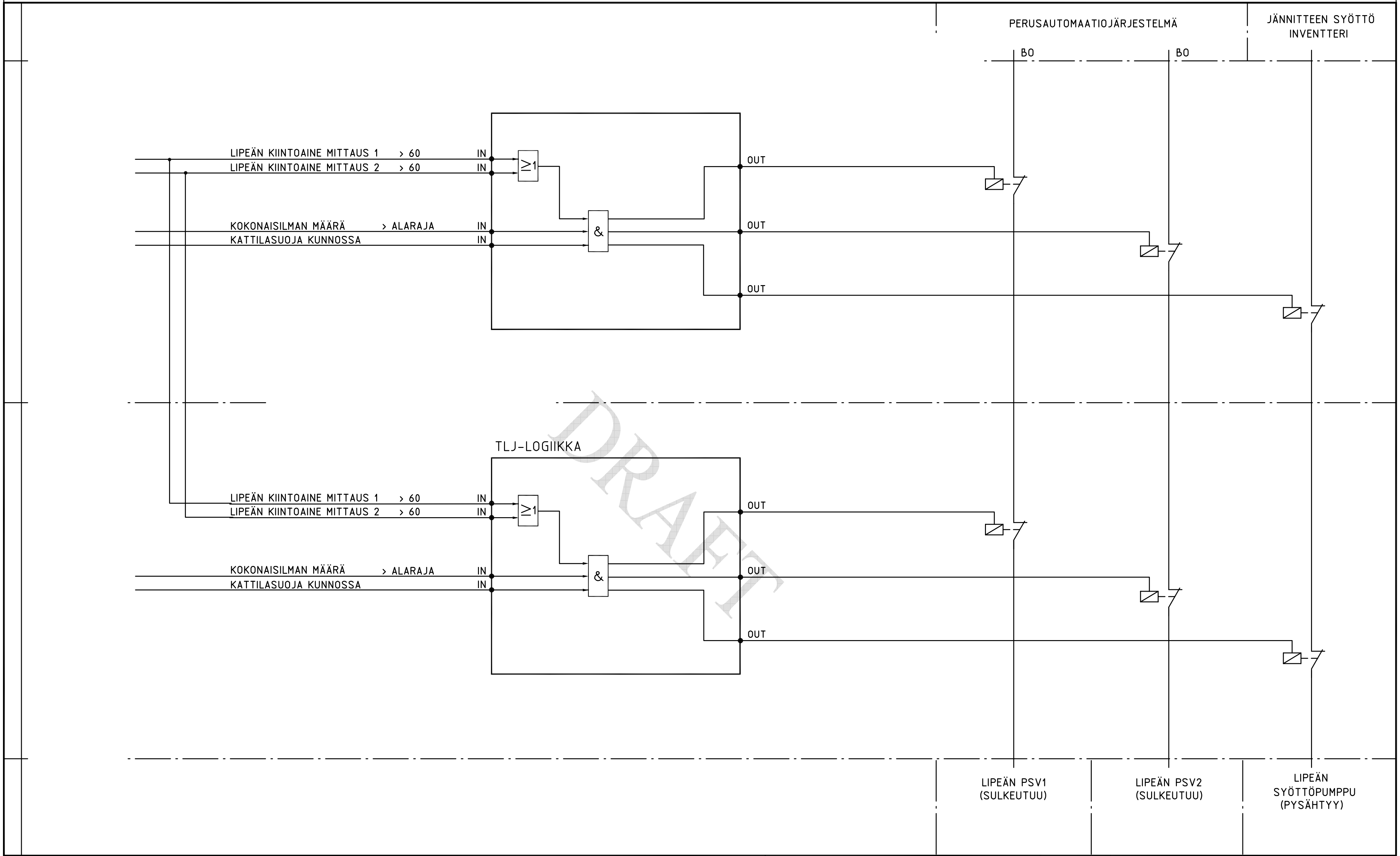
Muutos

JÄNNITTEEN

KANAVA A

KANAVA B

MALLI8.dwg 29.01.2008 10:04 /prs16



Toimittaja/no.
Toim.piir.no.
Ark.no.
**PÖYRY**
Pvm.
Suunn.
Tark.
Hyv.
Osasto
Tekn.kok.
No.
No.
Piir. nimi
SOODAKATTILAN TLJ
LOGIIKKAKAAVIO
LIPEÄN POLTON VALVONTA
Laji
Sovellus
Laitepaikka
Keskus
Lähtö
Vaihe
Piir.no.
Lehti
Rev.

Muutos Muutos Muutos

KANAVA A

TLJ-LOGIIKKA

KANAVA B

# APPENDIX 5

# EXAMPLE OF A CIRCUIT-SPECIFIC OPERATION DESCRIPTION

# 93HS0001 Fire valve for natural gas:

## Use:

It functions as a fire valve for natural gas

## Operation:

The valve is opened and closed by the operator.
The circuit is connected to safety interlocks. Pressing the Fast stop button or the emergency-stop button closes the valve through SRS.

## Alarms:

## Interlocks:

## Safety interlocks:

Interlocks close the valve 93HV0001 when:

Fast stop button 93XZ0001 is pressed in the control room.

Emergency-stop button 93XZ0002 is pressed in the control room.

Emergency-stop button 93XZ0003 is pressed at the burner level.

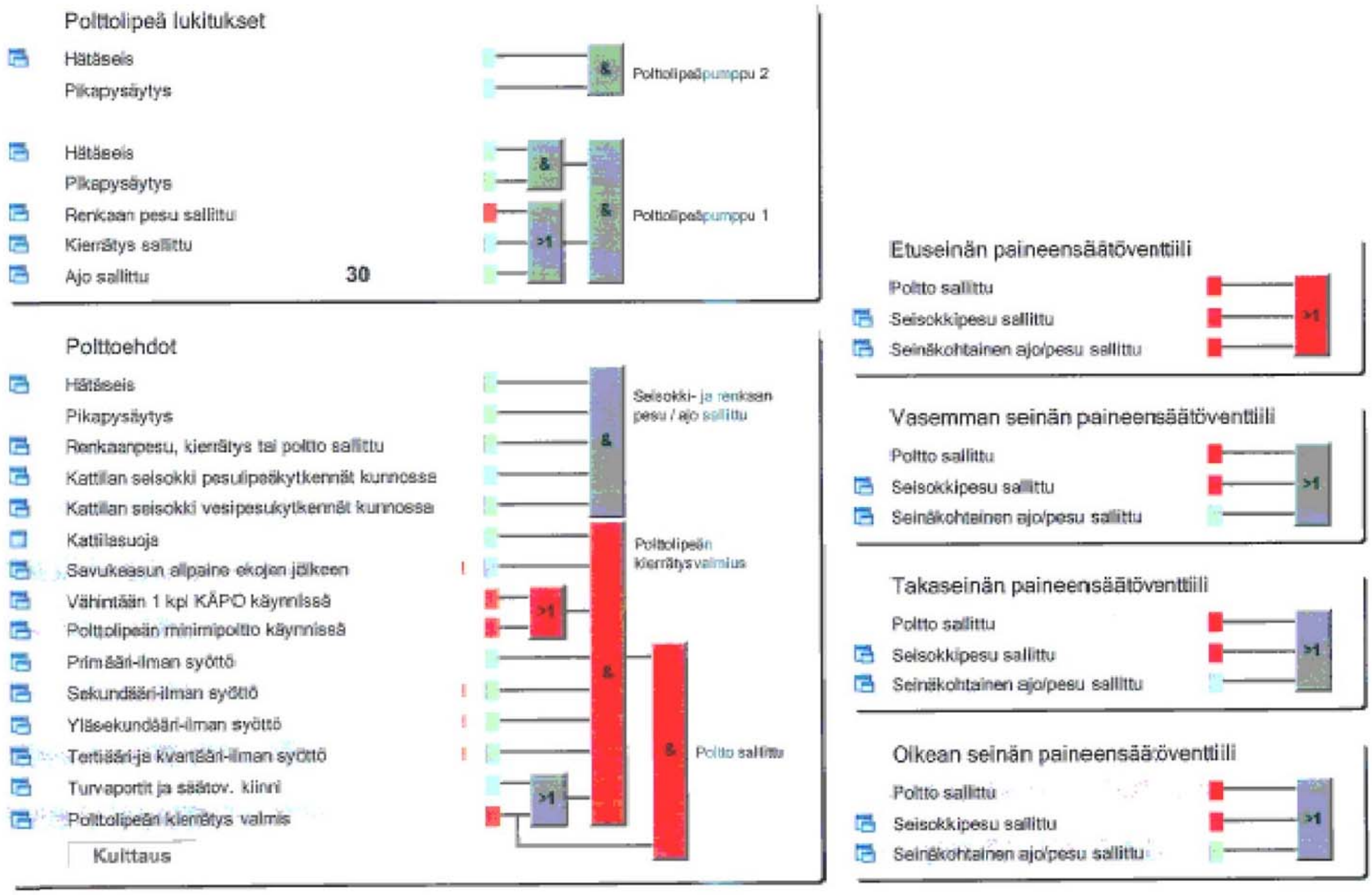
Emergency-stop button 93XZ0004 is pressed at the melt channel level.

Emergency-stop button 93XZ0005 is pressed by the auxiliary burners on the roof.

## Data to other circuits:

# APPENDIX 6

# EXAMPLES OF DISPLAY IMAGES



## Polttolipeä lukitukset

Hätäseis
Pikapysäytys

Hätäseis
Pikapysäytys
Renkaan pesu sallittu
Kierrätys sallittu
Ajo sallittu

30

## Polttoehdot

Hätäseis
Pikapysäytys
Renkaanpesu, kierrätys tai poltto sallittu
Kattilan seisokki pesulipeäkytkennät kunnossa
Kattilan seisokki vesipesukytkennät kunnossa
Kattilasuoja
Savukaasun alipaine ekojen jälkeen
Vähintään 1 kpl KÄPO käynnissä
Polttolipeän minimipoltto käynnissä
Primääri-ilman syöttö
Sekundääri-ilman syöttö
Yläsekundääri-ilman syöttö
Tertiääri-ja kvartääri-ilman syöttö
Turvaportit ja säätov. kiinni
Polttolipeän kierrätys valmis

Kuittaus

## Etuseinän paineensäätöventtiili

Poltto sallittu
Seisokkipesu sallittu
Seinäkohtainen ajo/pesu sallittu

## Vasemman seinän paineensäätöventtiili

Poltto sallittu
Seisokkipesu sallittu
Seinäkohtainen ajo/pesu sallittu

## Takaseinän paineensäätöventtiili

Poltto sallittu
Seisokkipesu sallittu
Seinäkohtainen ajo/pesu sallittu

## Oikean seinän paineensäätöventtiili

Poltto sallittu
Seisokkipesu sallittu
Seinäkohtainen ajo/pesu sallittu

| Toimittaja/no. | Toim.piir.no. | Pvm. | | Piir. nimi<br>LIPEÄNPOLTTO | Laji | Sovellus | Laitepaikka |
|---|---|---|---|---|---|---|---|
| Ark.no. | | Suunn. | | | Keskus | Lähtö | Vaihe |
| PÖYRY | | Tark. | Osasto | No. | Piir.no. | Lehti | Rev. |
| | | Hyv. | Tekn.kok. | No. | | | |

Savukaasutie auki

| | | | | | | |
|---|---|---|---|---|---|---|
| Savukaasupuhallin 1 | 6282716501 | | | | | |
| Savukaasu sähkösuotimelta 1 | 82PCZ-44634 | -3099 | Pa | < | -500 | Pa |
| Kellopelti 1 auki 1 | 82GZ-44631 | | | | | |
| Kellopelti 1 auki 2 | 82GZ-44632 | | | | | |
| Kellopelti 4 auki 1 | 82GZ-44639 | | | | | |
| Kellopelti 4 auki 2 | 82GZ-44640 | | | | | |
| Savukaasupuhallin 2 | 6282716502 | | | | | |
| Savukaasu sähkösuotimelta 2 | 82PCZ-44624 | -4412 | Pa | < | -500 | Pa |
| Kellopelti 2 auki 1 | 82GZ-44621 | | | | | |
| Kellopelti 2 auki 2 | 82GZ-44622 | | | | | |
| Kellopelti 5 auki 1 | 82GZ-44629 | | | | | |
| Kellopelti 5 auki 2 | 82GZ-44630 | | | | | |
| Savukaasupuhallin 3 | 6282716503 | | | | | |
| Savukaasu sähkösuotimelta 3 | 82PCZ-44613 | 426 | Pa | < | -500 | Pa |
| Kellopelti 3 auki 1 | 82GZ-44610 | | | | | |
| Kellopelti 3 auki 2 | 82GZ-44611 | | | | | |
| Kellopelti 6 auki 1 | 82GZ-44619 | | | | | |
| Kellopelti 6 auki 2 | 82GZ-44620 | | | | | |

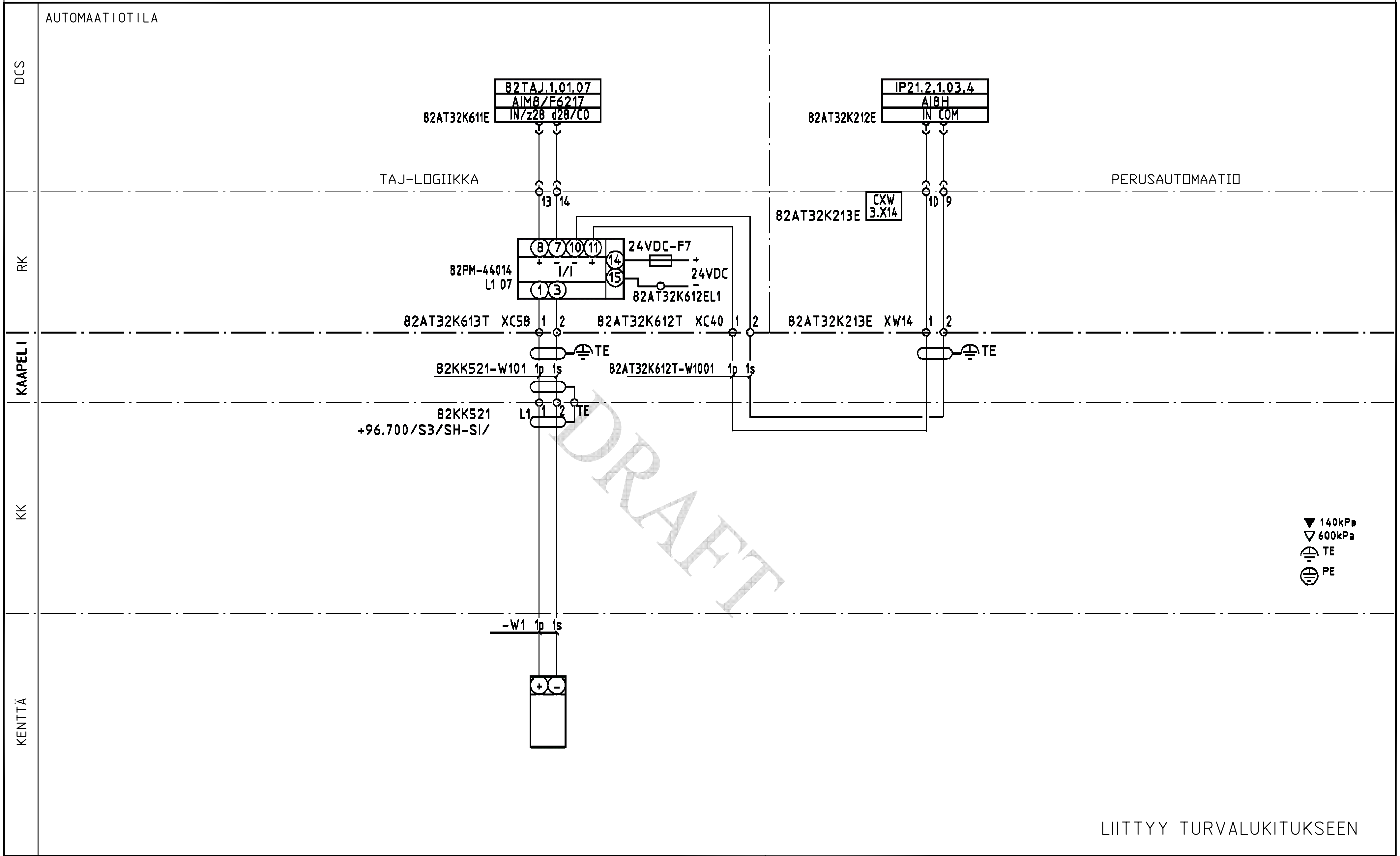
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Toimittaja/no. | Toim.piir.no. | Pvm. | | Piir. nimi<br>SAVUTIEAUKI | Laji | Sovellus | Laitepaikka |
| Ark.no. | | Suunn. | | | Keskus | Lähtö | Vaihe |
| PÖYRY | | Tark. | Osasto | No. | Piir.no. | Lehti | Rev. |
| | | Hyv. | Tekn.kok. | No. | | | |

SAVUTIE AUKI.dwg 29.01.2008 12:08 /prs16

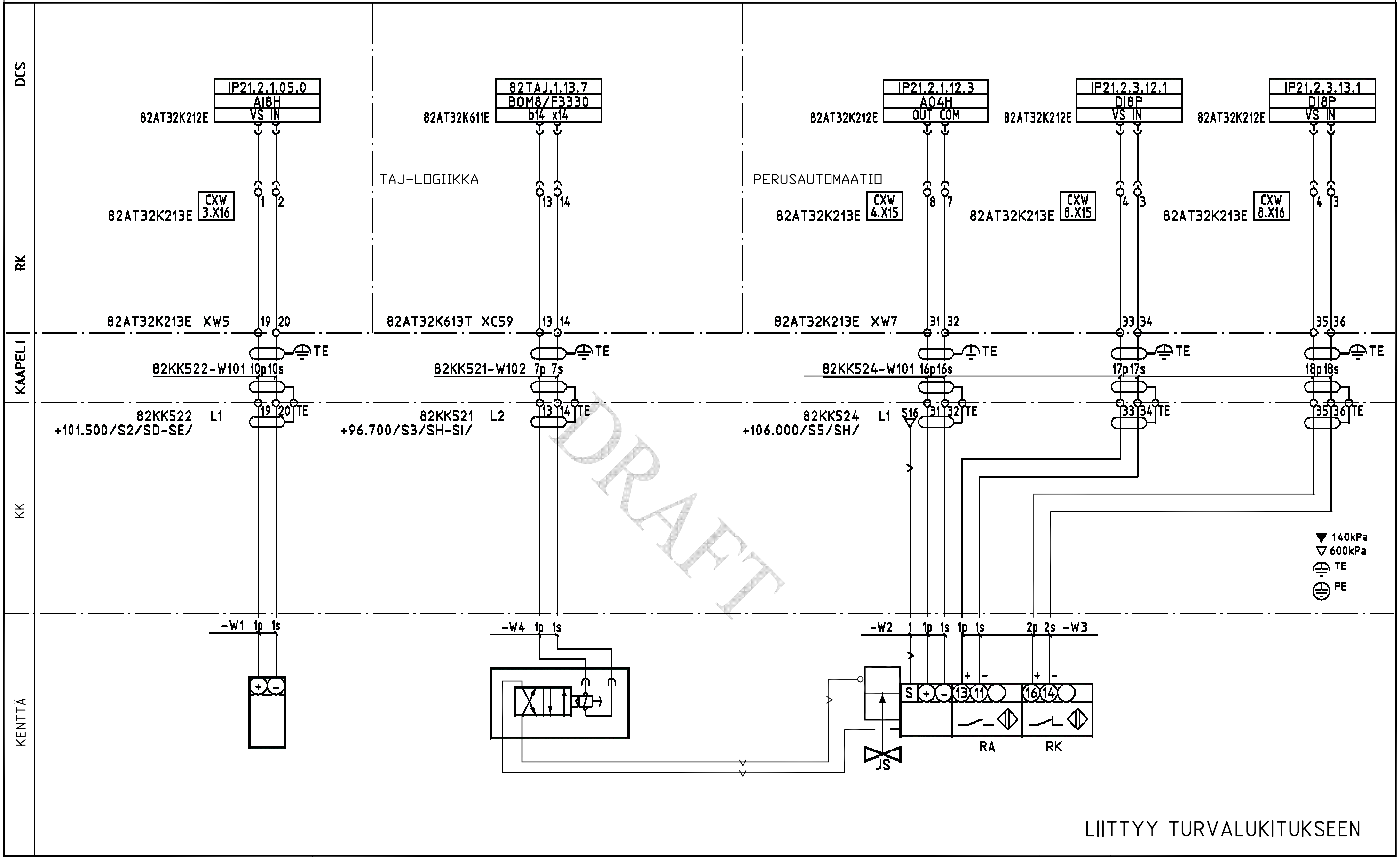
# APPENDIX 7

# MODEL CIRCUIT DESIGN AND WIRING DIAGRAMS

Muutos
Muutos
Muutos
Muutos
Muutos
Muutos



Toimittaja/no.
Toim.piir.no.
Ark.no.
PÖYRY
Pvm.
Suunn.
Tark.
Hyv.
Osasto
Tekn.kok.
No.
No.
Piir. nimi
MITTAUS
Laji
Sovellus
Laitepaikka
Keskus
Lähtö
Vaihe
Piir.no.
Lehti
Rev.



LIITTYY TURVALUKITUKSEEN

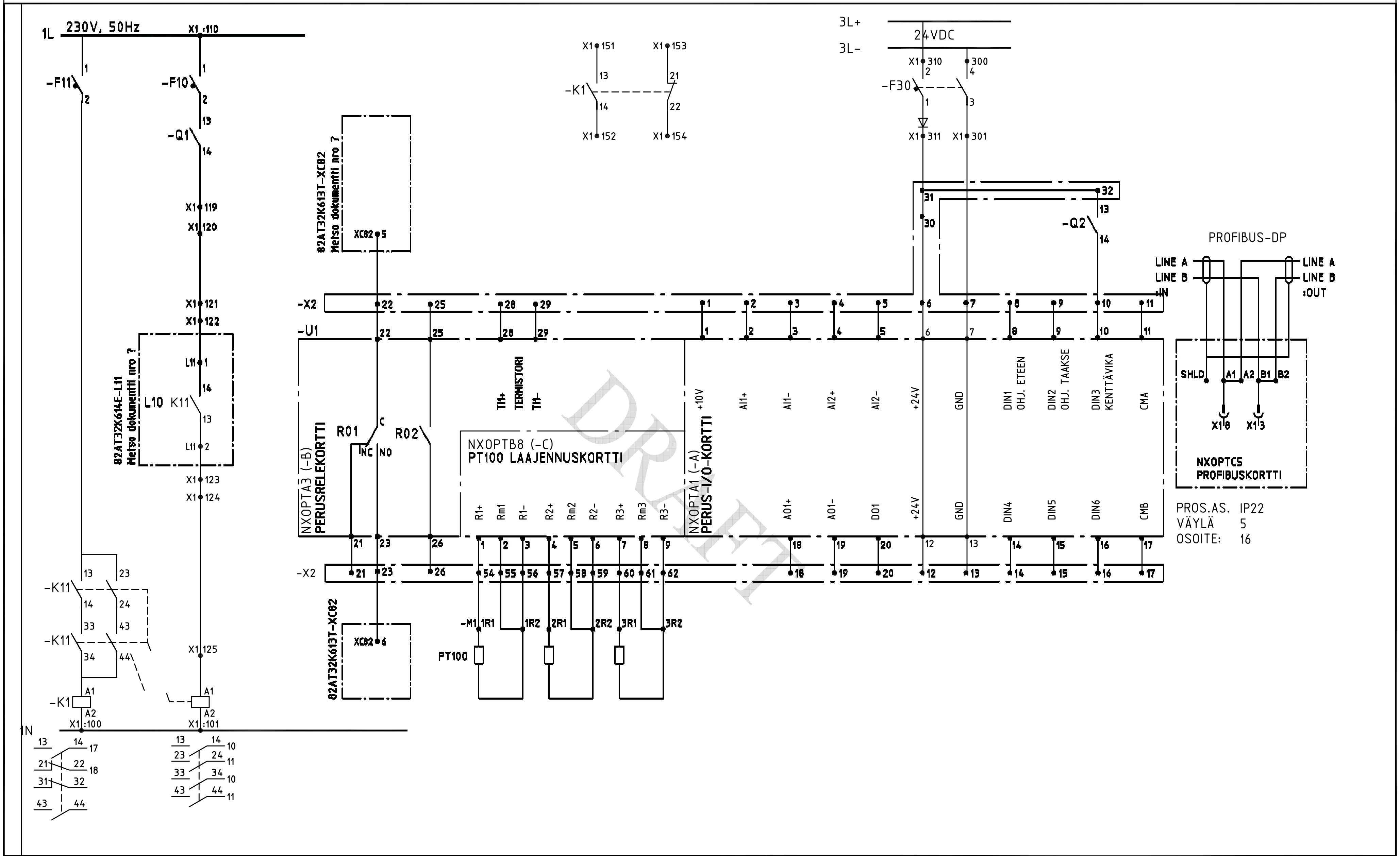
Toimittaja/no.
Toim.piir.no.
Ark.no.

PÖYRY

Pvm.
Suunn.
Tark.
Hyv.
Osasto
Tekn.kok.
No.
No.

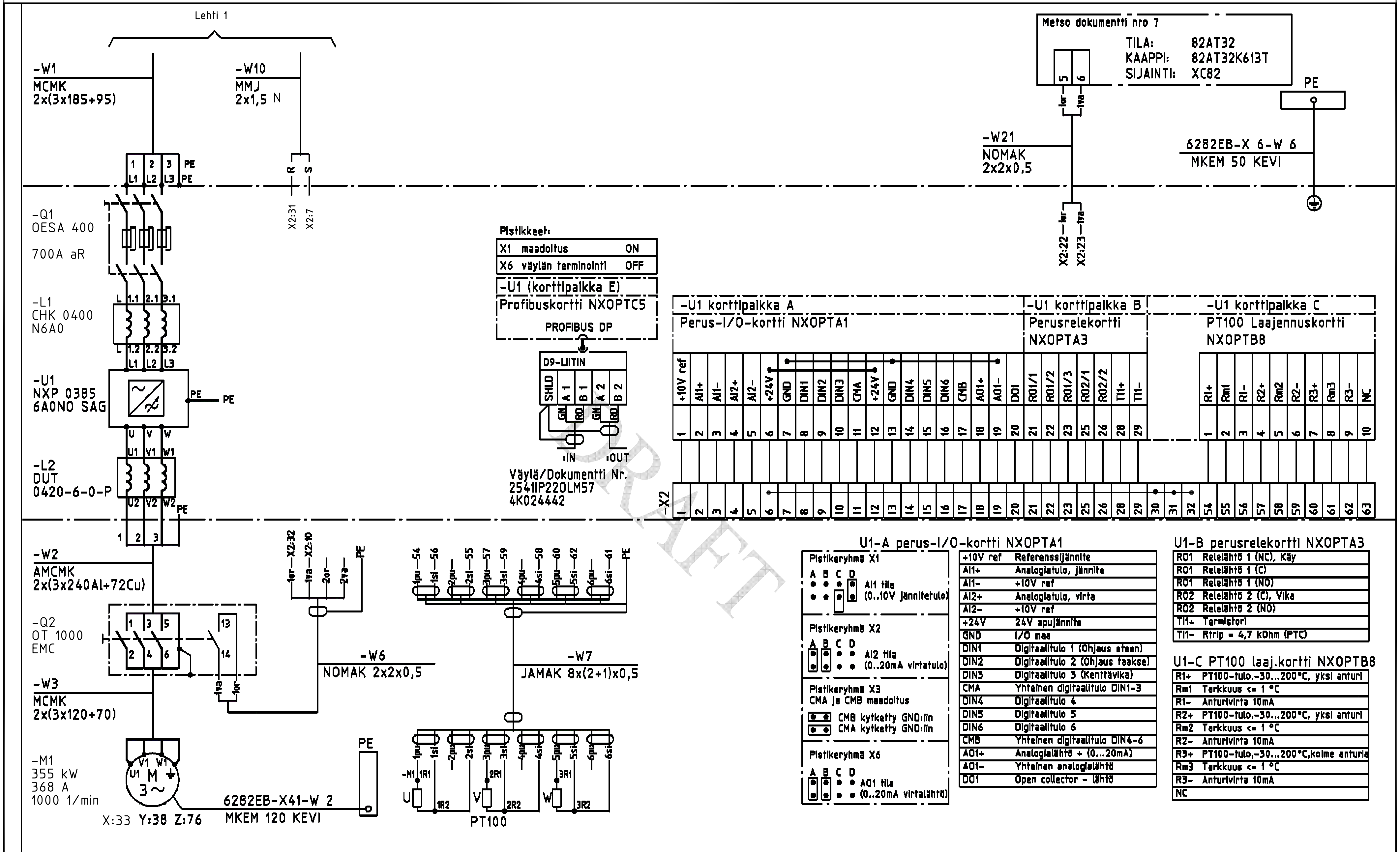
Piir. nimi
SÄÄTÖVENTTIILI

Laji
Sovellus
Laitepaikka
Keskus
Lähtö
Vaihe
Piir.no.
Lehti
Rev.



PROS.AS. IP22
VÄYLÄ 5
OSOITE: 16

Toimittaja/no.
Toim.piir.no.
Ark.no.
PÖYRY
Pvm.
Suunn.
Tark.
Hyv.
Osasto
Tekn.kok.
No.
No.
Piir. nimi
TAAJUUSMUUTTAJA
Laji
Sovellus
Laitepaikka
Keskus
Lähtö
Vaihe
Piir.no.
Lehti 3/3
Rev.



U1-A perus-I/O-kortti NXOPTA1

| | |
|---|---|
| +10V ref | Referenssijännite |
| AI1+ | Analogiatulo, jännite |
| AI1- | +10V ref |
| AI2+ | Analogiatulo, virta |
| AI2- | +10V ref |
| +24V | 24V apujännite |
| GND | I/O maa |
| DIN1 | Digitaalitulo 1 (Ohjaus eteen) |
| DIN2 | Digitaalitulo 2 (Ohjaus taakse) |
| DIN3 | Digitaalitulo 3 (Kenttävika) |
| CMA | Yhteinen digitaalitulo DIN1-3 |
| DIN4 | Digitaalitulo 4 |
| DIN5 | Digitaalitulo 5 |
| DIN6 | Digitaalitulo 6 |
| CMB | Yhteinen digitaalitulo DIN4-6 |
| AO1+ | Analogialähtö + (0...20mA) |
| AO1- | Yhteinen analogialähtö |
| DO1 | Open collector - lähtö |

U1-B perusrelekortti NXOPTA3

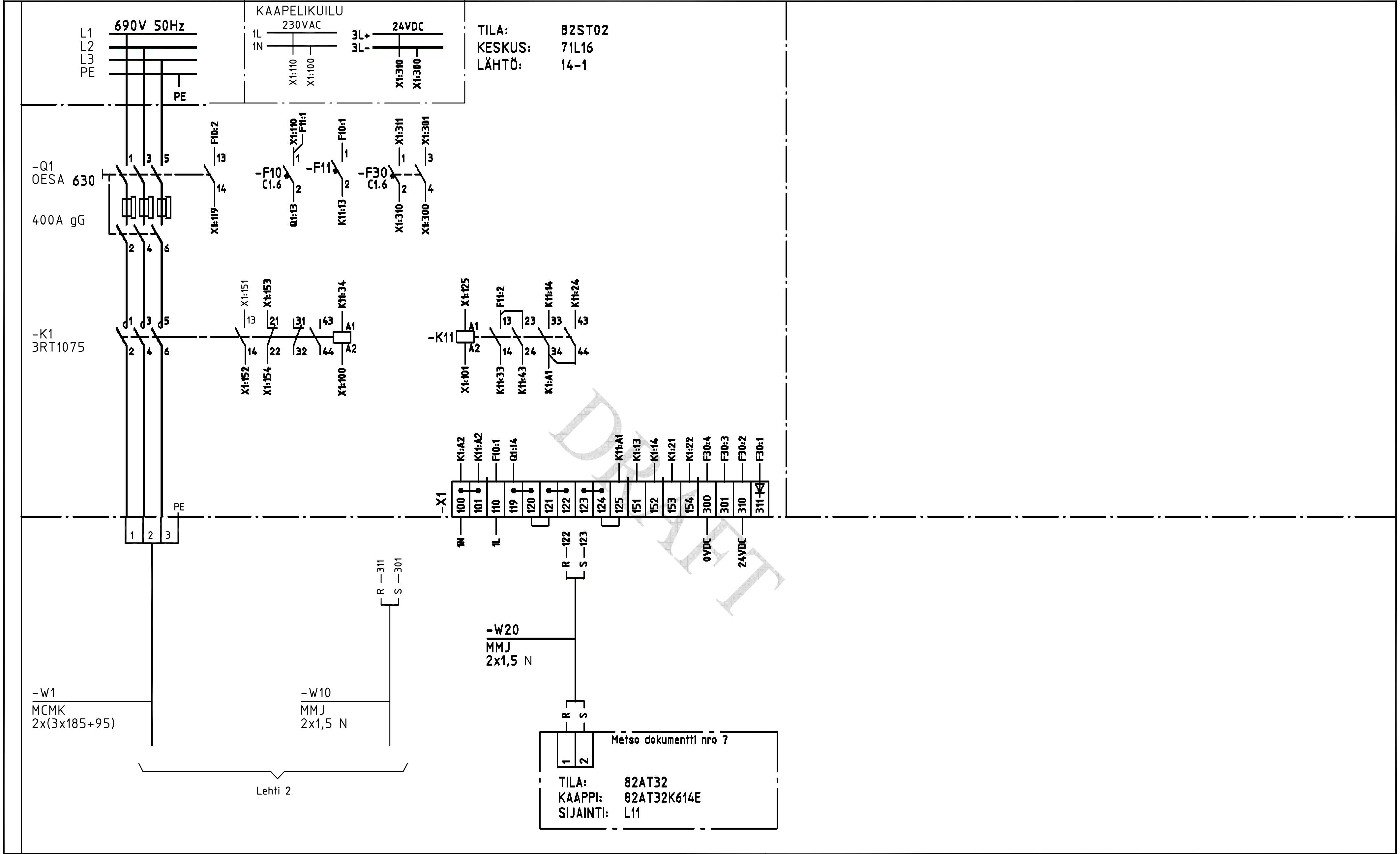
| | |
|---|---|
| RO1 | Relelähtö 1 (NC), Käy |
| RO1 | Relelähtö 1 (C) |
| RO1 | Relelähtö 1 (NO) |
| RO2 | Relelähtö 2 (C), Vika |
| RO2 | Relelähtö 2 (NO) |
| TI1+ | Termistori |
| TI1- | Rtrip = 4,7 kOhm (PTC) |

U1-C PT100 laaj.kortti NXOPTB8

| | |
|---|---|
| R1+ | PT100-tulo,-30...200°C, yksi anturi |
| Rm1 | Tarkkuus <= 1 °C |
| R1- | Anturivirta 10mA |
| R2+ | PT100-tulo,-30...200°C, yksi anturi |
| Rm2 | Tarkkuus <= 1 °C |
| R2- | Anturivirta 10mA |
| R3+ | PT100-tulo,-30...200°C,kolme anturia |
| Rm3 | Tarkkuus <= 1 °C |
| R3- | Anturivirta 10mA |
| NC | |

3K081908_002.dwg 29.01.2008 11:23 /prs16

Toimittaja/no.
Toim.piir.no.
Ark.no.
PÖYRY
Pvm.
Suunn.
Tark.
Hyv.
Osasto
Tekn.kok.
No.
No.
Piir. nimi
TAAJUUSMUUTTAJA
Laji
Sovellus
Laitepaikka
Keskus
Lähtö
Vaihe
Piir.no.
Lehti
2/3
Rev.



Toimittaja/no.
Toim.piir.no.
Ark.no.
PÖYRY
Pvm.
Suunn.
Tark.
Hyv.
Osasto
No.
Tekn.kok.
No.
Piir. nimi
TAAJUUSMUUTTAJA
Laji
Sovellus
Laitepaikka
Keskus
Lähtö
Vaihe
Piir.no.
Lehti
1/3
Rev.

3K081908_001.dwg 29.01.2008 10:51 /prs16

# APPENDIX 8

## MODELS OF TESTING DOCUMENTS

## Examples of implemented projects

Testing instructions, FAT testing, 8A
Testing record, FAT testing, 8B
Testing report, FAT testing, 8C

Testing instructions, periodic testing, 8D
Testing record, periodic testing, 8E
Testing report, periodic testing, 8F

**Recovery Boiler Ltd**
**SRS project**

**RECOVERY BOILER**

## A TESTING OF THE FIELD CIRCUITS

**EXAMPLE**

## 1 Fast stop

### 1.1 Preparations

1.1.1 Ensure that the process is simulated in such a way that it can be tested.
1.1.2 Using the simulating connectors, put the fast stop button to an OK state in both A and B channels.
1.1.3 Prevent programmable interlocks and mark the changes in the logbook.
1.1.4 Control valves 93HV0001, 93HV0002, 93HV0003, 93HV0004, 93FV0005, 93FV0006, 93HV007 and 93HV0008 to an open state and valves 93HV0009, and 93HV0010 to a closed state and start pumps 930001 and 930002 and pumps 930003 and 930004.

### 1.2 Fast stop 93XZ0001.Z1 (Channel A)

1.2.1 Simulate the fast stop button 93XZ0001 by opening the switch in channel A and record the acknowledgement for channel A.
1.2.2 Verify that the interlocks function with light and sound alarms (card output stops), with the boiler protection (tripped, LED turns off), valves 93HV0001, 93HV0002, 93HV0003, 93HV0004, 93FV0005, 93FV0006, 93HV0007 and 93HV0008 (close) and 93HV0009 and 93HV0010 (open) and pumps 930001 and 930002 (stop) and pumps 930003 and 930004 (stop).Also verify that the startup, load and stink gas burners are turned off (auxiliary relays disengage).
1.2.3 Acknowledge, on the testing record, that the targets' interlocks function on channel A.
1.2.4 Turn the simulation switch to an OK state on channel A.

### 1.3 Fast stop 93XZ0001.Z2 (Channel B)

1.3.1 Do the preparations as in 1.1.
1.3.2 Simulate the fast stop button 93XZ0001 by opening the switch in channel B and record the acknowledgement for channel B.
1.3.3 Verify that the interlocks function with light and sound alarms (card output stops), with the boiler protection (tripped, LED turns off), valves 93HV0001, 93HV0002, 93HV0003, 93HV0004, 93FV0005, 93FV0006, 93HV0007 and 93HV0008 (close) and 93HV0009 and 93HV0010 (open) and pumps 930001 and 930002 (stop) and pumps 930003 and 930004 (stop).
Also verify that the startup, load and stink gas burners are turned off (auxiliary relay disengages).
1.3.4 Acknowledge, on the testing record, that the targets' interlocks function on channel B.
1.3.5 Turn the simulation switch to an OK state on channel B.

### 1.4 Finalization

1.4.1 If you do not test other interlock circuits at the same time, reset the circuits' programmable interlocks and acknowledge the repairs done on the logbook.

## 2 Burner protection (presented only partially)

### 2.1 Preparations

2.1.1 Ensure that the process is simulated in such a way that it can be tested.
2.1.2 Prevent programmable interlocks and control valves 93HV0007, 93HV0008 to an open state and start pumps 930003 and 930004.

### 2.2 Boiler pressure below 25mbar (Channel A) Transmitters 93PT0001 and 93PT0002

2.2.1 On channel B, simulate the limit value data of pressure transmitters 93PT0001, 0002 and 0003 to a good state and in such a way that channel B does not receive the limit exceeded information.
2.2.2 Bring the boiler protection to an OK state as follows:
-Flue open -simulate valves 93GZ0001.01 and 02 in an open position and blower 930005 to an operating state (one flue open)
-Primary air blower - simulate the primary air blower into an operating state
-Secondary air blower - simulate the secondary air blower into an operating state
-Cylinder surface ok - use potentiometers to simulate, from the terminal blocks to two cylinder surface measuring circuits, those values that are between the wet and dry boiling limits.
-Instrument – air measuring circuit ok
- use potentiometers to simulate, from the terminal blocks to two instrument-air measuring circuits, those values that are over the tripping limit.

2.2.3 Increase "pressure" 93PT0001 with a simulator, at the same time observing, on the display, the slow increase of the pressure over the tripping limit (above 12 mA).
2.2.4 Verify the alarm "Safety limit exceeded on the circuit and no boiler protection tripped".
2.2.5 Decrease the "pressure" back below the tripping limit.
2.2.6 Increase "pressure" 93PT0002 with a simulator, at the same time observing, on the display, the slow increase of the pressure over the tripping limit (above 12mA).
2.2.7 Verify the alarm "Safety limit exceeded on the circuit" and "No boiler protection tripped".
2.2.8 Increase also "pressure" 93PT0001 with a simulator, at the same time observing, on the display, the slow increase of the pressure over the tripping limit (above 12mA).
2.2.9 Verify that interlocks function with the boiler protection (trips), and that the startup, load and stink gas burners stop (auxiliary relays disengage), with valves 93HV0003 and 93HV0004 (close) as well as with pumps 930003 and 930004 (stop).
2.2.10 Acknowledge, on the testing record, that the target's interlocks function on channel A.
2.2.11 Decrease, with simulators, the "pressures" from both measurements below the tripping limits.

## 2.3 Broken message operations

2.3.1 Break the measurement message circuit at transmitter 93PT0001 by detaching the simulator cable.
2.3.2 Verify the alarm “Signal fault on the circuit and no safety interlocks”.
2.3.3 Reconnect the signal cable.
2.3.4 Break the measurement message circuit at transmitter 93PT0002 by detaching the simulator cable.
2.3.5 Verify the alarm “Signal fault on the circuit and no safety interlocks”.
2.3.6 Break the measurement message circuit also at transmitter 93PT0001.
2.3.7 Verify that interlocks function with the boiler protection (trips), and that the startup, load and stink gas burners stop (auxiliary relays disengage), with valves 93HV0003 and 93HV0004 (close) as well as with pumps 930003 and 930004 (stop).
2.3.8 Acknowledge, on the testing record, that the target’s interlocks function on channel A.
2.3.9 Reconnect the simulators to the circuits.

## 2.4 Boiler pressure below 25mbar (Channel B) Transmitters 93PT0001 and 93PT0002

2.4.1 On channel A, simulate the limit value data of pressure transmitters 93PT0001, 0002 and 0003 to a good state and in such a way that channel A does not receive the limit exceeded information.
2.4.2 Bring the boiler protection to an OK state as follows:
-Flue open -simulate valves 93GZ0001.01 and 02 in an open position and blower 930005 to an operating state (one flue open)
-Primary air blower - simulate the primary air blower into an operating state
-Secondary air blower - simulate the secondary air blower into an operating state
-Cylinder surface ok - use potentiometers to simulate, from the terminal blocks to two cylinder surface measuring circuits, those values that are between the wet and dry boiling limits.
-Instrument – air measuring circuit ok
- use potentiometers to simulate, from the terminal blocks to two instrument-air measuring circuits, those values that are over the tripping limit.
2.4.3 Increase “pressure” 93PT0001 with a simulator, at the same time observing, on the display, the slow increase of the pressure over the tripping limit (above 12 mA).
2.4.4 Verify the alarm “Safety limit exceeded on the circuit and no boiler protection tripped”.
2.4.5 Decrease the “pressure” back below the tripping limit.
2.4.6 Increase “pressure” 93PT0002 with a simulator, at the same time observing, on the display, the slow increase of the pressure over the tripping limit (above 12mA).
2.4.7 Verify the alarm “Safety limit exceeded on the circuit and no boiler protection tripped”.
2.4.8 Increase also “pressure” 93PT0001 with a simulator, at the same time observing, on the display, the slow increase of the pressure over the tripping limit (above 12mA).
2.4.9 Verify that interlocks function with the boiler protection (trips), and that the startup, load and stink gas burners stop (auxiliary relays disengage), with valves 93HV0003 and 93HV0004 (close) as well as with pumps 930003 and 930004 (stop).
2.4.10 Acknowledge, on the testing record, that the target’s interlocks function on channel B.
2.4.11 Decrease, with simulators, the “pressures” from both measurements below the tripping

limits.

## 2.5 Broken message operations

2.5.1 Break the measurement message circuit at transmitter 93PT0001 by detaching the simulator cable.
2.5.2 Verify the alarm “Signal fault on the circuit and no safety interlocks”.
2.5.3 Reconnect the signal cable.
2.5.4 Break the measurement message circuit at transmitter 93PT0002 by detaching the simulator cable.
2.5.5 Verify the alarm “Signal fault on the circuit and no safety interlocks”.
2.5.6 Break the measurement message circuit also at transmitter 93PT0001.
2.5.7 Verify that interlocks function with the boiler protection (trips), and that the startup, load and stink gas burners stop (auxiliary relays disengage), with valves 93HV0003 and 93HV0004 (close) as well as with pumps 930003 and 930004 (stop).
2.5.8 Acknowledge, on the testing record, that the target’s interlocks function on channel B.
2.5.9 Reconnect the simulators to the circuits.

**Repeat the same testing also for measurements 93PT0002 and 93PT0003 as well as 93PT0001 and 93PT0003**.

**Recovery Boiler Ltd**
**SRS project**
**15.1.2007**

APPENDIX 8 B
**EXAMPLE**
**FAT TESTING RECORD**

16A0913-E0044

| SOURCE | NAME | VERIFIED | CHANNEL | TARGET | NAME | VERIFIED | ACKNOWLEDGEMENT | COMMENTS |
|---|---|---|---|---|---|---|---|---|
| **1. FAST STOP** | | | | | | | | |
| 93XZ0001.Z1 | Button, control room | | | | Light alarm | | | |
| | Pressed | Pressed | A | | -starts functioning | Relay checked | MTe | |
| | checked | | | | | | | |
| | | | | | Sound alarm | | | |
| | | | A | | -starts functioning | Relay checked | MTe | |
| | | | | | Boiler protection | | | |
| | | | A | | -activates | LED off | MTe | |
| | | | Tester in charge: | | | | | |
| | | | MTe | | | | | |
| | | | Signature | Name clarification | | | | |
| | | | FUEL VALVES | | | | | |
| | | | | 93HV0001 | Fire valve for natural gas | | | |
| | | | A | | -closes | Relay disengaged | | |
| | | | | 93HV0002 | Fire valve for natural gas | | | |
| | | | A | | -closes | Relay disengaged | MTe | |
| | | | | 93HV0003 | Methanol gate | | | |
| | | | A | | -closes | Relay disengaged | MTe | |
| | | | | 93HV0004 | Stink gas gate | | | |
| | | | A | | -closes | Relay disengaged | MTe | |
| | | | | 93FV0005 | Primary air slide | | | |
| | | | A | | -closes | Relay disengaged | MTe | |
| | | | | 93FV0006 | Primary air slide | | | |
| | | | A | | -closes | Relay disengaged | MTe | |

| | | | | |
|---|---|---|---|---|
| | 93HV0007 | Stop valve for firing liquor 1 | | |
| A | | -closes | Relay disengaged | MTe |
| | 93HV0008 | Stop valve for firing liquor 1 | | |
| A | | -closes | Relay disengaged | MTe |
| | 93HV0009 | Main steam valve | | |

| SOURCE | NAME | VERIFIED | CHANNEL | TARGET | NAME | VERIFIED | ACKNOWLEDGEMENT | COMMENTS |
|---|---|---|---|---|---|---|---|---|
| | | | A | | -closes | Relay disengaged | MTe | |
| | | | | 93HV0010 | Main steam valve bypass | | | |
| | | | A | | -closes | Relay disengaged | MTe | |

Tester in charge:

Martin Tester

Signature Name clarification

APPENDIX 8 B

## EXAMPLE

## FAT TESTING RECORD

| SOURCE | NAME | VERIFIED | CHANNEL | TARGET | NAME | VERIFIED | ACKNOWLEDGEMENT | COMMENTS |
|---|---|---|---|---|---|---|---|---|
| | | | | 93HV0009 | Ventilation of natural gas | | | |
| | | | A | | -opens | Relay disengaged | MTe | |
| | | | | 93HV0010 | Stink gases to pipe | | | |
| | | | A | | -opens | Relay disengaged | MTe | |
| | | | | | BURNERS | | | |
| | | | | | Startup burners | | | |
| | | | A | | -stop | Relay disengaged | MTe | |
| | | | | | Load burners | | | |
| | | | A | | -stop | Relay disengaged | MTe | |
| | | | | | Stink gas burners | | | |
| | | | A | | -stop | Relay disengaged | MTe | |
| | | | | | BLOWERS | | | |
| | | | | 930001 | Primary blower | | | |
| | | | A | | -stops | Relay disengaged | MTe | |
| | | | | 930002 | Mild stink gas blower | | | |
| | | | A | | -stops | Relay disengaged | MTe | |
| | | | | | PUMPS | | | |
| | | | | 930003 | Firing liquor pump 1 | | | |
| | | | A | | -stops | Relay disengaged | MTe | |
| | | | | 930004 | Firing liquor pump 2 | | | |
| | | | A | | -stops | Relay disengaged | MTe | |

Tester in charge:

| | |
|---|---|
| | Martin Tester |
| Signature | Name clarification |

APPENDIX 8 B

## EXAMPLE
## FAT TESTING RECORD

| SOURCE | NAME | VERIFIED | CHANNEL | TARGET | NAME | VERIFIED | ACKNOWLEDGEMENT | COMMENTS |
|---|---|---|---|---|---|---|---|---|
| 93XZ0001.Z2 | Button, control room | | | | Light alarm | | | |
| | Pressed | Pressed | B | | -starts functioning | Relay checked | MTe | |
| | | | | | Sound alarm | | | |
| | | | B | | -starts functioning | Relay checked | MTe | |
| | | | | | Boiler protection | | | |
| | | | B | | -activates | LED off | MTe | |
| | | | | | FUEL VALVES | | | |
| | | | | 93HV0001 | Fire valve for natural gas | | | |
| | | | B | | -closes | Relay disengaged | MTe | |
| | | | | 93HV0002 | Fire valve for oil | | | |
| | | | B | | -closes | Relay disengaged | MTe | |
| | | | | 93HV0003 | Methanol gate | | | |
| | | | B | | -closes | Relay disengaged | MTe | |
| | | | | 93HV0004 | Stink gas gate | | | |
| | | | B | | -closes | Relay disengaged | MTe | |
| | | | | 93FV0005 | Primary air slide | | | |
| | | | B | | -closes | Relay disengaged | MTe | |
| | | | | 93FV0006 | Primary air slide | | | |
| | | | B | | -closes | Relay disengaged | MTe | |
| | | | | 93HV0007 | Stop valve for firing liquor 1 | | | |
| | | | B | | -closes | Relay disengaged | MTe | |
| | | | | 93HV0008 | Stop valve for firing liquor 1 | | | |
| | | | B | | -closes | Relay disengaged | MTe | |
| | | | | 93HV0009 | Main steam valve | | | |
| | | | B | | -closes | Relay disengaged | MTe | |
| | | | | 93HV0010 | Main steam valve bypass | | | |

-closes Relay disengaged MTe Tester in charge:

MTe Martin Tester

Signature Name clarification

APPENDIX 8 B

**EXAMPLE**

**FAT TESTING RECORD**

| SOURCE | NAME | VERIFIED | CHANNEL | TARGET | NAME | VERIFIED | ACKNOWLEDGEMENT | COMMENTS |
|---|---|---|---|---|---|---|---|---|
| | | | | 93HV0009 | Ventilation of natural gas | | | |
| | | | B | | -opens | Relay disengaged | MTe | |
| | | | | 93HV0010 | Stink gases to pipe | | | |
| | | | B | | -opens | Relay disengaged | MTe | |
| | | | | | BURNERS | | | |
| | | | | | Startup burners | | | |
| | | | B | | -stop | Relay disengaged | MTe | |
| | | | | | Load burners | | | |
| | | | B | | -stop | Relay disengaged | MTe | |
| | | | | | Stink gas burners | | | |
| | | | B | | -stop | Relay disengaged | MTe | |
| | | | | | BLOWERS | | | |
| | | | | 930001 | Primary blower | | | |
| | | | B | | -stops | Relay disengaged | MTe | |
| | | | | 930002 | Mild stink gas blower | | | |
| | | | B | | -stops | Relay disengaged | MTe | |
| | | | | | PUMPS | | | |
| | | | | 930003 | Firing liquor pump 1 | | | |
| | | | B | | -stops | Relay disengaged | MTe | |
| | | | | 930004 | Firing liquor pump 2 | | | |
| | | | B | | -stops | Relay disengaged | MTe | |

Tester in charge:

MTe Martin Tester

Signature Name clarification

| **SOURCE** | **NAME** | **VERIFIED** | **CHANNEL** | **TARGET** | **NAME** | **VERIFIED** | **ACKNOWLEDGEMENT** | **COMMENTS** |
|---|---|---|---|---|---|---|---|---|
| **2. BOILER PROTECTION** | | | | | | | | |
| | | | | | | | | |
| FURNACE PRESSURE | | | | | | | | |
| 93PI0001 | Furnace pressure | | | | | | | |
| | - pressure above 25.0 mba | 12,0 mA | A | | 1/3 alarm | | | 25 mbar = 12.0 mA |
| 93PI0002 | Furnace pressure | | A | | -activates | Activated | MTe | |
| | - pressure above 25.0 mba | 12,1 mA | | | | | | |
| 93PI0003 | Simulated to an OK state | OK | | | BURNERS Startup | | | |
| | | | | | burners | | | |
| | | | A | | -stop | Relay disengaged | MTe | |
| | | | | | Load burners | | | |
| | | | A | | -stop | Relay disengaged | MTe | |
| | | | | | | | | |
| | | | Stink gas burnersA | | -stop | Relay disengaged | MTe | |
| | | | | | | | | |
| | | | | | LIQUOR FEEDING VALVE | | | |
| | | | | 93HV0007 | Liquor feeding fast stop valve | | | |
| | | | A | | -closes | Relay disengaged | MTe | |
| | | | | 93HV0008 | Liquor feeding fast stop valve | | | |
| | | | A | | -closes | Relay disengaged | MTe | |
| | | | | | | | | |
| | | | | | PUMPS | | | |
| | | | | 930003 | Firing liquor pump 1 | | | |
| | | | A | | -stops | Relay disengaged | MTe | |
| | | | | 930004 | Firing liquor pump 2 | | | |
| | | | A | | -stops | Relay disengaged | MTe | |

Tester in charge:

MTe Martin Tester

Signature Name clarification

**Recovery Boiler Ltd**
**SRS project**
**15.1.2007**

APPENDIX 8 B

## EXAMPLE
## FAT TESTING RECORD

| SOURCE | NAME | VERIFIED | CHANNEL | TARGET | NAME | VERIFIED | ACKNOWLEDGEMENT | COMMENTS |
|---|---|---|---|---|---|---|---|---|
| 93PI0001 | Furnace pressure | | | | | | | |
| | - signal broken | Broken | A | | 1/3 alarm | | | |
| 93PI0002 | Furnace pressure | | | | BOILER PROTECTION | | | |
| | - signal broken | Broken | A | | -activates | Activated | MTe | |
| 93PI0003 | Simulated to an OK | state OK | | | | | | |
| | | | | | BURNERS | | | |
| | | | | | Startup burners | | | |
| | | | A | | -stop | Relay disengaged | MTe | |
| | | | | | Load burners | | | |
| | | | A | | -stop | Relay disengaged | MTe | |
| | | | | | Stink gas burners | | | |
| | | | A | | -stop | Relay disengaged | MTe | |
| | | | | | LIQUOR FEEDING VALVE | | | |
| | | | | 93HV0007 | Liquor feeding fast stop valve | | | |
| | | | A | | -closes | Relay disengaged | MTe | |
| | | | | 93HV0008 | Liquor feeding fast stop valve | | | |
| | | | A | | -closes | Relay disengaged | MTe | |
| | | | | | PUMPS930003 | | | |
| | | | | | Firing liquor pump 1 | | | |
| | | | A | | -stops | Relay disengaged | MTe | |
| | | | | 930004 | Firing liquor pump 2 | | | |
| | | | A | | -stops | Relay disengaged | MTe | |

Tester in charge:

MTe Martin Tester

Signature Name clarification

APPENDIX 8 B

**EXAMPLE**

**FAT TESTING RECORD**

| SOURCE | NAME | VERIFIED | CHANNEL | TARGET | NAME | VERIFIED | ACKNOWLEDGEMENT | COMMENTS |
|---|---|---|---|---|---|---|---|---|
| FURNACE PRESSURE | | | | | | | | |
| 93PI0001 | Furnace pressure | | | | | | | |
| | - pressure above 25.0 mba 12,03 mA B | | | | 1/3 alarm | | | 25 mbar = 12.0 mA |
| 93PI0002 | Furnace pressure | | | | BOILER PROTECTION | | | |
| | - pressure above 25.0 mba 12,05 mA B | | | | -activates | Activated | MTe | |
| 93PI0003 | Simulated to an OK state OK | | | | | | | |
| | | | | | BURNERS | | | |
| | | | | | Startup burners | | | |
| | | | B | | -stop | Relay disengaged | MTe | |
| | | | | | Load burners | | | |
| | | | B | | -stop | Relay disengaged | MTe | |
| | | | | | Stink gas burners | | | |
| | | | B | | -stop | Relay disengaged | MTe | |
| | | | | | LIQUOR FEEDING VALVE | | | |
| | | | | 93HV0007 | Liquor feeding fast stop valve | | | |
| | | | B | | -closes | Relay disengaged | MTe | |
| | | | | 93HV0008 | Liquor feeding fast stop valve | | | |
| | | | B | | -closes | Relay disengaged | MTe | |
| | | | | | PUMPS | | | |
| | | | | 930003 | Firing liquor pump 1 | | | |
| | | | B | | -stops | Relay disengaged | MTe | |
| | | | | 930004 | Firing liquor pump 2 | | | |
| | | | B | | -stops | Relay disengaged | MTe | |

Tester in charge:

MTe Martin Tester

Signature Name clarification

**Recovery Boiler Ltd**
**SRS project**
**15.1.2007**

APPENDIX 8 B

**EXAMPLE**

**FAT TESTING RECORD**

16A0913-E0044

| SOURCE | NAME | VERIFIED | CHANNEL | TARGET | NAME | VERIFIED | ACKNOWLEDGEMENT | COMMENTS |
|---|---|---|---|---|---|---|---|---|
| 93PI0001 | Furnace pressure | | | | | | | |
| | - signal broken | Broken | B | | 1/3 alarm | | | |
| 93PI0002 | Furnace pressure | | | | BOILER PROTECTION | | | |
| | - signal broken | Broken | B | | -activates | Activated | MTe | |
| 93PI0003 | Simulated to an OK state | OK | | | | | | |
| | | | | | BURNERS | | | |
| | | | | | Startup burners | | | |
| | | | B | | -stop | Relay disengaged | MTe | |
| | | | | | Load burners | | | |
| | | | B | | -stop | Relay disengaged | MTe | |
| | | | | | Stink gas burnersB | | | |
| | | | | | -stop | Relay disengaged | MTe | |
| | | | | | LIQUOR FEEDING VALVE | | | |
| | | | | 93HV0007 | Liquor feeding fast stop valve | | | |
| | | | B | | -closes | Relay disengaged | MTe | |
| | | | | 93HV0008 | Liquor feeding fast stop valve | | | |
| | | | B | | -closes | Relay disengaged | MTe | |
| | | | | | PUMPS | | | |
| | | | | 930003 | Firing liquor pump 1 | | | |
| | | | B | | -stops | Relay disengaged | MTe | |
| | | | | 930004 | Firing liquor pump 2 | | | |
| | | | B | | -stops | Relay disengaged | MTe | |

Tester in charge:

MTe Martin Tester

Signature Name clarification

**Recovery Boiler Ltd**
**SRS project**

MODEL

# FACTORY ACCEPTANCE TEST REPORT ON SAFETY INTERLOCKS (SIS) OF A RECOVERY BOILER

## 1 TARGET

A safety related system for a recovery boiler (SIS)

## 2 TIME AND PLACE

01-02.01.2005 Recovery Boiler Ltd

## 3 PARTICIPANTS

| | |
|---|---|
| N. N. | Plant operator |
| N. N. | Person responsible for the plant's SIS |
| N. N. | Automation installer |
| N. N. | Head designer |
| Inspection office/ Y. Y. | Inspector |

## 4 TESTING METHODS

The testing was conducted in accordance with the testing plan and testing instructions.

## 5 TESTING ACCEPTANCE

On the basis of the testing, we state that the interlocks that form a part of the safety related system for the section function correctly and safely. Therefore, the testing can be accepted.

The testing summary in Appendix 1 presents some alarm deficiencies as well as some parts that were left untested.

| | |
|---|---|
| Recovery Boiler Ltd | Recovery Boiler Ltd |
| ________________________ | ________________________ |
| Plant operator | Person in charge of SIS |
| Recovery Boiler Ltd | Recovery Boiler Ltd |
| ________________________ | ________________________ |
| Inspector | Head designer |

**APPENDICES**

1. Testing summary

APPENDIX I 1(2)

**Recovery Boiler Ltd**
**SIS project**

# MODEL SUMMARY OF THE FACTORY ACCEPTANCE TEST (FAT) FOR A RECOVERY BOILER'S SAFETY INTERLOCKS (SIS)

## 1 TESTING ARRANGEMENTS

### 1.1 Safety system

The system as a whole was installed and connected.

Hardware:

- the system was energized and switched on.

Software:

- the programs had been loaded on the system, and, for individual circuits, the normal process control procedures at the process stations had been tested beforehand.

Documentation:

- the following documentation was used in testing: SIS connection diagrams, SIS operation descriptions, SIS display images, circuit diagrams and wiring diagrams as well as I/O and hardware layout drawings, testing instructions and testing records.

Testing equipment:

- Measurement channels had been wired to a separate potentiometer board, with which the simulation of individual measurements was easy to implement. During measurement simulations, the measuring circuits were connected to mA measuring instruments, which allowed the measurement of accurate mA signals. The measurements were performed by a Beamex MIC 10 calibrator. The calibration certificates for the measuring instruments are in Appendix 6.

## 2 TESTING

In the testing, the process interlocks at the process station for all targets (valves and motors) were removed, to ensure that SIS operations were the reason for the valves and motors to get to a safe state.

The testing was performed in a straightforward manner, by following the testing instructions, which had been made beforehand and where the testing was divided into possible interlock failures and field equipment and process faults.

The field equipment and process faults were tested in full. (the emergency-stop switch as well as each process measurement value of the boiler protection were simulated and tested for each channel).
In addition to the functioning of the interlocks, alarm messages and interlock indications on SIS displays were examined. Appended there is also a copy of the page of the alarm printer and a display page both related to tripping situations.

## 3 COMMENTS ON TESTING

### 3.1 Testing of the safety system

The testing was performed according to the plan. The programs and the system functioned well. Some observations related to the testing:

- A signal fault did not trigger measurement 93PI0001 to send a circuit-specific alarm. It was a programming fault, which was then repaired, and a retesting took place.

- System alarms were generally missing. These alarms had not yet been created for the system. The alarms are tested during the first periodic testing.

## 4 DOCUMENTATION

The testing plan can be found in the testing folder’s interleaf Section 1. Functioning of the sources as well as that of interlocks is marked in the testing record (interleaf 4). The same interleaf divider holds the printouts of the alarm pages for the interlock functions. The final safety interlock connection diagrams for the recovery boiler, SIS display images, program diagrams related to interlocks as well as the hardware layout images are in the same folder.

**Recovery Boiler Ltd**
**SRS project**

**EXAMPLE**

## RECOVERY BOILER

## A TESTING OF THE FIELD CIRCUITS

## 1 Fast stop

### 1.1 Preparations

1.1.1 Ensure that the process is in such a state that it can be tested.

1.1.2 Shut hand valves 1000 (natural gas), 1001 (oil), 1002 (methanol), 1010, 1011, 1012 and 1013 (liquor for firing).

1.1.3 Remove the main fuses from blowers 930001 (Primary blower), 930002 (Blower for mild stink gases) as well as from pumps 930003 (Firing liquor pump1), and 930004 (Firing liquor pump 2).

1.1.4 Change the connection to fast stop button 93XZ0001-Z2 (channel B) with terminal blocks 93CR11.12 AX1:1-3, so that 1 and 2 come together.

1.1.5 Prevent programmable interlocks and mark the changes in the logbook.

1.1.6 Control valves 93HV0001, 93HV0002, 93HV0003, 93HV0004, 93FV0005, 93FV0006, 93HV007 and 93HV0008 to an open state and valves 93HV0009, and 93HV0010 to a closed state and start blowers 930001 and 930002 and pumps 930003 and 930004.

### 1.2 Fast stop 93XZ0001.Z1 (Channel A)

1.2.1 In the control room, press fast stop button 93XZ0001 in and acknowledge for channel A in the records.

1.2.2 Verify that interlocking takes place for light and sound alarms (activate), boiler burner (trips, LED goes off), valves 93HV0001, 93HV0002, 93HV0003, 93HV0004, 93FV0005, 93FV0006, 93HV0007 and 93HV0008 (close) and 93HV0009 and 93HV0010 (open) and blowers 930001 and 930002 (stop) and pumps 930003 and 930004 (stop).
Also verify that the startup, load and stink gas burners become turned off when cutting the 230V control voltage by relays in the burner control cabinet 93CR05.10.1.2.3
Acknowledge, on the testing record, that the targets' interlocks function on channel A.

1.2.4 Lift the fast stop button back to the upper position.

1.2.5 Change the connection to fast stop button 93XZ0001.Z2 (channel B) back as it was.

## 1.3 Fast stop 93XZ0001.Z2 (Channel B)

1.3.1 Change the connection to fast stop button 93XZ0001.Z1 (channel A) with terminal blocks 93CR11.08 AX1:1-3, so that 3 and 4 are brought together.

1.3.2 Do the other preparations as in 1.1.
1.3.3 In the control room, press fast stop button 93XZ0001 in and acknowledge for channel B in the records.
1.3.4 Verify that interlocking takes place for light and sound alarms (activate), boiler burner (trips, LED goes off), valves 93HV0001, 93HV0002, 93HV0003, 93HV0004, 93FV0005, 93FV0006, 93HV0007 and 93HV0008 (close) and 93HV0009 and 93HV0010 (open) and blowers 930001 and 930002 (stop) and pumps 930003 and 930004 (stop).Also verify that the startup, load and stink gas burners become turned off when cutting the 230V control voltage by relays in the burner control cabinet 93CR05.10.
1.3.5 Acknowledge, on the testing record, that the targets' interlocks function on channel B.
1.3.6 Lift the fast stop button back to the upper position.
1.3.7 Change the connection to fast stop button 93XZ0001.Z2 (channel A) back as it was

## 1.4 Finalization

1.4.1 If you do not test other interlock circuits at the same time, reset the circuits' programmable interlocks and acknowledge the repairs done on the logbook.

## 2 Burner protection (presented only partially)

## 2.1 Preparations

2.1.1 Ensure that the process is in such a state that it can be tested.
2.1.2 Shut hand valves 1010, 1011, 1012 and 1013 (liquor for firing).
2.1.3 Remove the main fuses from blowers 930001 (Primary air blower), 930008 (Secondary air blower), 930005 (Flue gas blower 1), 930006 (Flue gas blower 2) and 930007 (Flue gas blower 3) as well as pumps 930003 (Firing liquor pump 1) and 930004 (Firing liquor pump 2).
2.1.4 Prevent programmable interlocks and control valves 93HV0007, 93HV0008 to an open state and smoke dampers 93GZ0001.01, 93GZ0001.02, 93GZ0002.01, 93GZ0002.02, 93GZ0003.01 and 93GZ0003.02 to a closed state and stop blowers 930005, 930006 and 930007.

## 2.2 Boiler pressure below 25mbar (Channel A)
## Transmitters 93PT0001 and 93PT0002

2.2.1 On channel B, simulate the limit value data of pressure transmitters 93PT0001, 0002 and 0003 to a good state in such a way that the B channel does not receive the limit exceeded information.

2.2.2 Bring the boiler protection to an OK state as follows:

| | |
|---|---|
| -Flue open | -open dampers 93GZ0001.01 and 02 and start blower 930005 (one flue open) |
| -Primary air blower | - start the primary air blower |
| -Secondary air blower | –start the secondary air blower |
| -Cylinder surface ok | -simulate, from the terminal blocks to two cylinder surface measuring circuits, values that are between the wet and dry boiling limits. |
| -Instrument-air pressure | – ensure that the pressure in the network is above 3,5 bar. If not, simulate, from the terminal blocks to two instrument-air measuring circuits, values that are over 3,5 bar. |

2.2.3 Lift the pressure by pumping with transmitter 93PT0001. At the same time observe, on the display terminal, the slow increase in the pressure above the tripping limit (above 25 mbar).

2.2.4 Verify the alarm “Safety limit exceeded on the circuit and no boiler protection tripped”.

2.2.5 Decrease the pressure back below 25 mbars.

2.2.6 Lift the pressure by pumping from transmitter 93PT0002. At the same time observe, on the display terminal, the slow increase in the pressure above the tripping limit (above 25 mbar).

2.2.7 Verify the alarm “Safety limit exceeded on the circuit and no boiler protection tripped”.

2.2.8 Increase also pressure from transmitter 93PT0001, at the same time observing, on the display terminal, the slow increase of the pressure over the tripping limit (above 25mbar).

2.2.9 Verify that interlocks function with the boiler protection (trips), with valves 93HV0003 and 93HV0004 (close) as well as with pumps 930003 and 930004 (stop) and that the startup, load and stink gas burners stop (the relays in the burner control cabinet disengage).

2.2.10 Acknowledge, on the testing record, that the target’s interlocks function on channel A.

2.2.11 Decrease the pressures from both measurements below the tripping limits.

## 2.3 Broken message operations

2.3.1 Break the measurement message circuit at transmitter 93PT0001 by detaching the signal cable.

2.3.2 Verify the alarm “Signal fault on the circuit and no safety interlocks”.

2.3.3 Reconnect the signal cable.

2.3.4 Break the measurement message circuit at transmitter 93PT0002 by detaching the signal cable.

2.3.5 Verify the alarm “Signal fault on the circuit and no safety interlocks”.

2.3.6 Break the measurement message circuit also at transmitter 93PT0001.

2.3.7 Verify that interlocks function with the boiler protection (trips), with valves 93HV0003 and 93HV0004 (close) as well as with pumps 930003 and 930004 (stop) and that the startup, load and stink gas burners stop (the relays in the burner control cabinet disengage).

2.3.8 Acknowledge, on the testing record, that the target’s interlocks function on channel A.

2.3.9 Reconnect the signal cables with the transmitters.

## 2.4 Boiler pressure below 25mbar (Channel B) Transmitters 93PT0001 and 93PT0002

2.4.1 On channel A, simulate the limit value data of pressure transmitters 93PT0001, 0002 and 0003 to a good state in such a way that the A channel does not receive the limit exceeded information.

2.4.2 Bring the boiler protection to an OK state as follows:

-Flue open -open dampers 93GZ0001.01 and 02 and start blower 930005 (one flue open)

-Primary air blower - start the primary air blower

-Secondary air blower - start the secondary air blower

-Cylinder surface ok -simulate, from terminal blocks to two cylinder surface measuring circuits, values that are between the wet and dry boiling limits.

-Instrument-air pressure – ensure that the pressure in the network is above 3,5 bars. If not, simulate, from the terminal blocks to two instrument-air measuring circuits, values that are over 3,5 bar.

2.4.3 Lift the pressure by pumping from transmitter 93PT0001. At the same time observe, on the display terminal, the slow increase in the pressure above the tripping limit (above 25 mbar).

2.4.4 Verify the alarm “Safety limit exceeded on the circuit and no boiler protection tripped”.

2.4.5 Decrease the pressure back below 25 mbars.

2.4.6 Lift the pressure by pumping from transmitter 93PT0002. At the same time observe, on the display terminal, the slow increase in the pressure above the tripping limit (above 25 mbar).

2.4.7 Verify the alarm “Safety limit exceeded on the circuit and no boiler protection tripped”.

2.4.8 Increase also pressure from transmitter 93PT0001, at the same time observing, on the display terminal, the slow increase of the pressure over the tripping limit (above 25mbar).

2.4.9 Verify that interlocks function with the boiler protection (trips), with valves 93HV0003 and 93HV0004 (close) as well as with pumps 930003 and 930004 (stop) and that the startup, load and stink gas burners stop (the relays in the burner control cabinet disengage).

2.4.10 Acknowledge, on the testing record, that the target’s interlocks function on channel B.

2.4.11 Decrease the pressures from both measurements below the tripping limits.

## 2.5 Broken message operations

2.5.1 Break the measurement message circuit at transmitter 93PT0001 by detaching the signal cable.

2.5.2 Verify the alarm “Signal fault on the circuit and no safety interlocks”.

2.5.3 Reconnect the signal cable.

2.5.4 Break the measurement message circuit at transmitter 93PT0002 by detaching the signal cable.

2.5.5 Verify the alarm “Signal fault on the circuit and no safety interlocks”.

2.5.6 Break the measurement message circuit also at transmitter 93PT0001.

2.5.7 Verify that interlocks function with the boiler protection (trips), with valves 93HV0003 and 93HV0004 (close) as well as with pumps 930003 and 930004 (stop) and that the startup, load and stink gas burners stop (the relays in the burner control cabinet disengage).

2.5.8 Acknowledge, on the testing record, that the target’s interlocks function on channel B.

2.5.9 Reconnect the signal cables with the transmitters.

**Repeat the same testing also for measurements 93PT0002 and 93PT0003 as well as 93PT0001 and 93PT0003.**

**Recovery Boiler Ltd**
**SRS project**
**15.1.2007**

APPENDIX 8 E

**EXAMPLE**

**PERIODIC TESTING RECORD**

16A0913-E0044

**EXAMPLE**

| SOURCE | NAME | VERIFIED | CHANNEL | TARGET | NAME | VERIFIED | ACKNOWLEDGEMENT | COMMENTS |
|---|---|---|---|---|---|---|---|---|
| **1. FAST STOP** | | | | | | | | |
| | | | | | | | | |
| 93XZ0001.Z1 | Button, control room | | | | Light alarm | | | |
| | Pressed | *Pressed* | A | | -starts functioning | | | |
| | | *Functioned* | | | | | | |
| | | | | | Sound alarm | | | |
| | | | A | | -starts functioning | *Functioned* | *M Ta* | |
| | | | | | Boiler protectionA | | | |
| | | | | | -activates | *Activated* | *M Ta* | |
| | | | | | | | | |
| | | | | | FUEL VALVES | | | |
| | | | | 93HV0001 | Fire valve for natural gas | | | |
| | | | A | | -closes | *Closed* | *M Ta* | |
| | | | | 93HV0002 | Fire valve for oil | | | |
| | | | A | | -closes | *Closed* | *M Ta* | |
| | | | | 93HV0003 | Methanol gate | | | |
| | | | A | | -closes | *Closed* | *M Ta* | |
| | | | | 93HV0004 | Stink gas gate | | | |
| | | | A | | -closes | | | Not tested |
| | | | | 93FV0005 | Primary air slide | | | |
| | | | A | | -closes | *Closed* | *M Ta* | |
| | | | | 93FV0006 | Primary air slide | | | |
| | | | A | | -closes | *Closed* | *M Ta* | |
| | | | | 93HV0007 | Stop valve for firing liquor 1 | | | |
| | | | A | | -closes | *Closed* | *M Ta* | |
| | | | | 93HV0008 | Stop valve for firing liquor 2 | | | |
| | | | A | | -closes | *Closed* | *M Ta* | |

Tester in charge:

|  |  |
|---|---|
| M Ta | Mark Tally |
| Signature | Name clarification |

APPENDIX 8 E

**EXAMPLE**

**PERIODIC TESTING RECORD**

| SOURCE | NAME | VERIFIED | CHANNEL | TARGET | NAME | VERIFIED | ACKNOWLEDGEMENT | COMMENTS |
|---|---|---|---|---|---|---|---|---|
| | | | | 93HV0009 | Ventilation of natural gas | | | |
| | | | A | | -opens | *Opened* | *M Ta* | |
| | | | | 93HV0010 | Stink gases to pipe | | | |
| | | | A | | -opens | *Opened* | *M Ta* | |
| | | | | | | | | |
| | | | | | BURNERS | | | |
| | | | | | Startup burners | | | |
| | | | A | | -stop | *Stopped* | *M Ta* | |
| | | | | | Load burners | | | |
| | | | A | | -stop | *Stopped* | *M Ta* | |
| | | | | | Stink gas burners | | | |
| | | | A | | -stop | *Stopped* | *M Ta* | |
| | | | | | | | | |
| | | | | | BLOWERS | | | |
| | | | | 930001 | Primary blower | | | |
| | | | A | | -stops | *Stopped* | *M Ta* | |
| | | | | 930002 | Mild stink gas blower | | | |
| | | | A | | -stops | *Stopped* | *M Ta* | |
| | | | | | | | | |
| | | | | | PUMPS | | | |
| | | | | 930003 | Firing liquor pump 1 | | | |
| | | | A | | -stops | *Stopped* | *M Ta* | |
| | | | | 930004 | Firing liquor pump 2 | | | |
| | | | A | | -stops | *Stopped* | *M Ta* | |
| | | | | | | | | |

Tester in charge:
M Ta Mark Tally

Signature Name clarification

**Recovery Boiler Ltd**
**SRS project**
**15.1.2007**

APPENDIX 8 E

16A0913-E0044

## EXAMPLE
## PERIODIC TESTING RECORD

| SOURCE | NAME | VERIFIED | CHANNEL | TARGET | NAME | VERIFIED | ACKNOWLEDGEMENT | COMMENTS |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | |
| 93XZ0001.Z2 | Button, control room | | | | Light alarm | | | |
| | Pressed | *Pressed* | B | | -starts functioning | *Functioned* | *M Ta* | |
| | | | | | Sound alarm | | | |
| | | | B | | -starts functioning | *Functioned* | *M Ta* | |
| | | | | | Boiler protection | | | |
| | | | B | | -activates | *Activated* | *M Ta* | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | FUEL VALVES | | | |
| | | | | 93HV0001 | Fire valve for natural gas | | | |
| | | | B | | -closes | *Closed* | *M Ta* | |
| | | | | 93HV0002 | Fire valve for oil | | | |
| | | | B | | -closes | *Closed* | *M Ta* | |
| | | | | 93HV0003 | Methanol gate | | | |
| | | | B | | -closes | *Closed* | *M Ta* | |
| | | | | 93HV0004 | Stink gas gate | | | |
| | | | B | | -closes | | | Not tested |
| | | | | 93FV0005 | Primary air slide | | | |
| | | | B | | -closes | *Closed* | *M Ta* | |
| | | | | 93FV0006 | Primary air slide | | | |
| | | | B | | -closes | *Closed* | *M Ta* | |
| | | | | 93HV0007 | Stop valve for firing liquor 1 | | | |
| | | | B | | -closes | *Closed* | *M Ta* | |
| | | | | 93HV0008 | Stop valve for firing liquor 1 | | | |
| | | | B | | -closes | *Closed* | *M Ta* | |
| | | | | 93HV0009 | Ventilation of natural gas | | | |
| | | | B | | -opens | *Opened* | *M Ta* | |
| | | | | 93HV0010 | Stink gases to pipe | | | |
| | | | B | | -opens | *Opened* | *M Ta* | |
| | | | | | | | | |

Tester in charge:

M Ta Mark Tally
Signature Name clarification

APPENDIX 8 E
**EXAMPLE**
**PERIODIC TESTING RECORD**

| SOURCE | NAME | VERIFIED | CHANNEL | TARGET | NAME | VERIFIED | ACKNOWLEDGEMENT | COMMENTS |
|---|---|---|---|---|---|---|---|---|
| | | | | | BURNERS | | | |
| | | | | | Startup burners | | | |
| | | | B | | -stop | *Stopped* | *M Ta* | |
| | | | | | Load burners | | | |
| | | | B | | -stop | *Stopped* | *M Ta* | |
| | | | | | Stink gas burners | | | |
| | | | B | | -stop | *Stopped* | *M Ta* | |
| | | | | | | | | |
| | | | | | BLOWERS | | | |
| | | | | 930001 | Primary blower | | | |
| | | | B | | -stops | *Stopped* | *M Ta* | |
| | | | | 930002 | Mild stink gas blower | | | |
| | | | B | | -stops | *Stopped* | *M Ta* | |
| | | | | | | | | |
| | | | | | PUMPS | | | |
| | | | | 930003 | Firing liquor pump 1 | | | |
| | | | B | | -stops | *Stopped* | *M Ta* | |
| | | | | 930004 | Firing liquor pump 2 | | | |
| | | | B | | -stops | *Stopped* | *M Ta* | |
| | | | | | | | | |

Tester in charge:

| | |
|---|---|
| M Ta | Mark Tally |
| Signature | Name clarification |

APPENDIX 8 E
EXAMPLE
PERIODIC TESTING RECORD

| SOURCE | NAME | VERIFIED | CHANNEL | TARGET | NAME | VERIFIED | ACKNOWLEDGEMENT | COMMENTS |
|---|---|---|---|---|---|---|---|---|
| **2. BOILER PROTECTION** | | | | | | | | |
| | | | | | | | | |
| FURNACE PRESSURE | | | | | | | | |
| 93PI0001 | Furnace pressure | | | | | | | |
| | - pressure above 25mbar | *25,1 mbar* | A | | 1/3 alarm | | | |
| 93PI0002 | Furnace pressure | | | | BOILER PROTECTION | | | |
| | - pressure above 25mbar | *25,0 mbar* | A | | -activates | *Activated* | *M Ta* | |
| 93PI0003 | Furnace pressure | | | | | | | |
| | - Simulated to an OK state | *Simulated* | | | BURNERS | | | |
| | | | | | Startup burners | | | |
| | | | A | | -stop | *Stopped* | *M Ta* | |
| | | | | | Load burners | | | |
| | | | A | | -stop | *Stopped* | *M Ta* | |
| | | | | | Stink gas burners | | | |
| | | | A | | -stop | *Stopped* | *M Ta* | |
| | | | | | | | | |
| | | | | | LIQUOR FEEDING VALVE | | | |
| | | | | 93HV0007 | Liquor feeding fast stop valve | | | |
| | | | A | | -closes | *Closed* | *M Ta* | |
| | | | | 93HV0008 | Liquor feeding fast stop valve | | | |
| | | | A | | -closes | *Closed* | *M Ta* | |
| | | | | | | | | |
| | | | | | PUMPS | | | |
| | | | | 930003 | Firing liquor pump 1 | | | |
| | | | A | | -stops | *Stopped* | *M Ta* | |
| | | | | 930004 | Firing liquor pump 2 | | | |
| | | | A | | -stops | *Stopped* | *M Ta* | |
| | | | | | | | | |

Tester in charge:

M Ta Mark TallySignature Name clarification

APPENDIX 8 E

## EXAMPLE
## PERIODIC TESTING RECORD

| SOURCE | NAME | VERIFIED | CHANNEL | TARGET | NAME | VERIFIED | ACKNOWLEDGEMENT | COMMENTS |
|---|---|---|---|---|---|---|---|---|
| 93PI0001 | Furnace pressure | | | | | | | |
| | - signal broken | *Broken* | A | | 1/3 alarm | | | |
| 93PI0002 | Furnace pressure | | | | BOILER PROTECTION | | | |
| | - signal broken | *Broken* | A | | -activates | *Activated* | *M Ta* | |
| 93PI0003 | Furnace pressure | | | | | | | |
| | - Simulated to an OK state | *Simulated* | | | BURNERS | | | |
| | | | | | Startup burners | | | |
| | | | A | | -stop | *Stopped* | *M Ta* | |
| | | | | | Load burners | | | |
| | | | A | | -stop | *Stopped* | *M Ta* | |
| | | | | | Stink gas burners | | | |
| | | | A | | -stop | *Stopped* | *M Ta* | |
| | | | | | | | | |
| | | | | | LIQUOR FEEDING VALVE | | | |
| | | | | 93HV0007 | Liquor feeding fast stop valve | | | |
| | | | A | | -closes | *Closed* | *M Ta* | |
| | | | | 93HV0008 | Liquor feeding fast stop valve | | | |
| | | | A | | -closes | *Closed* | *M Ta* | |
| | | | | | | | | |
| | | | | | PUMPS | | | |
| | | | | 930003 | Firing liquor pump 1 | | | |
| | | | A | | -stops | *Stopped* | *M Ta* | |
| | | | | 930004 | Firing liquor pump 2 | | | |
| | | | A | | -stops | *Stopped* | *M Ta* | |
| | | | | | | | | |

Tester in charge:
M Ta Mark Tally
Signature Name clarification

APPENDIX 8 E

## EXAMPLE

## PERIODIC TESTING RECORD

| SOURCE | NAME | VERIFIED | CHANNEL | TARGET | NAME | VERIFIED | ACKNOWLEDGEMENT | COMMENTS |
|---|---|---|---|---|---|---|---|---|
| FURNACE PRESSURE | | | | | | | | |
| 93PI0001 | Furnace pressure | | | | | | | |
| | - pressure above 25mbar | *25,05 mbar* | B | | 1/3 alarm | | | |
| 93PI0002 | Furnace pressure | | | | BOILER PROTECTION | | | |
| | - pressure above 25mbar | *25,04 mbar* | B | | -activates | *Activated* | *M Ta* | |
| 93PI0003 | Furnace pressure | | | | | | | |
| | - Simulated to an OK state | *Simulated* | | | BURNERS | | | |
| | | | | | Startup burners | | | |
| | | | B | | -stop | *Stopped* | *M Ta* | |
| | | | | | Load burners | | | |
| | | | B | | -stop | *Stopped* | *M Ta* | |
| | | | | | Stink gas burners | | | |
| | | | B | | -stop | *Stopped* | *M Ta* | |
| | | | | | | | | |
| | | | | | LIQUOR FEEDING VALVE | | | |
| | | | | 93HV0007 | Liquor feeding fast stop valve | | | |
| | | | B | | -closes | *Closed* | *M Ta* | |
| | | | | 93HV0008 | Liquor feeding fast stop valve | | | |
| | | | B | | -closes | *Closed* | *M Ta* | |
| | | | | | | | | |
| | | | | | PUMPS | | | |
| | | | | 930003 | Firing liquor pump 1 | | | |
| | | | B | | -stops | *Stopped* | *M Ta* | |
| | | | | 930004 | Firing liquor pump 2 | | | |
| | | | B | | -stops | *Stopped* | *M Ta* | |
| | | | | | | | | |

Tester in charge:

M Ta Mark Tally
Signature Name clarification

**Recovery Boiler Ltd**
**SRS project**
**15.1.2007**

APPENDIX 8 E

**EXAMPLE**

**PERIODIC TESTING RECORD**

| SOURCE | NAME | VERIFIED | CHANNEL | TARGET | NAME | VERIFIED | ACKNOWLEDGEMENT | COMMENTS |
|---|---|---|---|---|---|---|---|---|
| 93PI0001 | Furnace pressure | | | | | | | |
| | - signal broken | *Broken* | B | | 1/3 alarm | | | |
| 93PI0002 | Furnace pressure | | | | BOILER PROTECTION | | | |
| | - signal broken | *Broken* | B | | -activates | *Activated* | *M Ta* | |
| 93PI0003 | Furnace pressure | | | | | | | |
| | - Simulated to an OK state | *Simulated* | | | BURNERS | | | |
| | | | | | Startup burners | | | |
| | | | B | | -stop | *Stopped* | *M Ta* | |
| | | | | | Load burners | | | |
| | | | B | | -stop | *Stopped* | *M Ta* | |
| | | | | | Stink gas burners | | | |
| | | | B | | -stop | *Stopped* | *M Ta* | |
| | | | | | | | | |
| | | | | | LIQUOR FEEDING VALVE | | | |
| | | | | 93HV0007 | Liquor feeding fast stop valve | | | |
| | | | B | | -closes | *Closed* | *M Ta* | |
| | | | | 93HV0008 | Liquor feeding fast stop valve | | | |
| | | | B | | -closes | *Closed* | *M Ta* | |
| | | | | | | | | |
| | | | | | PUMPS | | | |
| | | | | 930003 | Firing liquor pump 1 | | | |
| | | | B | | -stops | *Stopped* | *M Ta* | |
| | | | | 930004 | Firing liquor pump 2 | | | |
| | | | B | | -stops | *Stopped* | *M Ta* | |

Tester in charge:

M Ta Mark Tally
Signature Name clarification

**Recovery Boiler Ltd**
**SIS project**

MODEL

## MODEL PERIODIC TESTING REPORT ON THE SAFETY INTERLOCKS (SIS) OF A RECOVERY BOILER

### 1 TARGET

A safety related system for a recovery boiler (SIS)

### 2 TIME AND PLACE

01-02.01.2005 Recovery Boiler Ltd

### 3 PARTICIPANTS

| | |
|---|---|
| N. N. | Plant operator |
| N. N. | Person responsible for the plant’s SIS |
| N. N. | Automation installer |
| N. N. | Electric fitter |
| Inspection office/Y. Y. | Inspector (part time) |

### 4 TESTING METHODS

The testing was conducted in accordance with the testing plan and testing instructions.

### 5 TESTING ACCEPTANCE

On the basis of the testing, we state that the interlocks that form a part of the safety related system for the section function correctly and safely. Therefore, the testing can be accepted.

The testing summary in Appendix 1 presents some alarm deficiencies as well as some parts that were left untested.

| | |
|---|---|
| Recovery Boiler Ltd | Recovery Boiler Ltd |
| _________________________ | _________________________ |
| Plant operator<br>SIS | Person responsible for the plant’s |
| Recovery Boiler Ltd | Recovery Boiler Ltd |
| _________________________ | _________________________ |
| Automation installer | Electric fitter |

Recovery Boiler Ltd

_________________________

Inspector

**APPENDICES**

1. Testing summary

APPENDIX I 1(2)

**Recovery Boiler Ltd**
**SIS project**

## PERIODIC TESTING REPORT ON THE SAFETY INTERLOCKS (SIS) OF THE RECOVERY BOILER
## SUMMARIZING MODEL

## 1 TESTING ARRANGEMENTS

### 1.1 Safety system

The system as a whole was in operation.

Before the testing was started, the central unit cards in the safety system's logic part were replaced with new ones. In this way, also new cards can be tested during periodic testing.

Documentation

- the following documentation was used in testing: SIS connection diagrams, SIS operation descriptions, SIS display images, circuit diagrams and wiring diagrams as well as I/O and hardware layout drawings, testing instructions and testing records.

## 2 TESTING

The test objects in the field testing regarded as belonging to so-called SIS were

-Fast stop
-Jettisoning
-Boiler protection (from several field variables)
-Emergency-stop (from the control room of the recovery boiler (3))

All the trippings were arranged in such a manner that the tripping in question affects at a time only the SIS's channel (A or B) to be tested. The testing instructions explain how to block each tripping signal away from the channel that is not to be tested.

Analog measurements (sources in the boiler protection part) were simulated in accordance with real process conditions: a calibration pump was used to pump the necessary pressure to the pressure and surface transmitters for creating the SIS tripping limit there. The required activity from the 2/3 operations was generated by always pumping two transmitters to the same state. In this way the whole circuit from the transmitter to the safety system could be tested. The calibration certificates for the equipment used in the testing are in the testing folder at tab 9 interleaf.

The testing, as usual, included the valves, and their movements to a safe state were verified on a monitor and on the field.

The safety switches of the motors were turned to 0 position and the main fuses were removed. That the motors were stopped by interlocks was verified by contractors.

In the testing, the process interlocks at the process station for all targets (valves and motors) were removed, to ensure that SIS operations were the reason for the valves and motors to get to a safe state.

The testing was performed in a straightforward manner, by following the testing instructions, which had been made beforehand and where the testing was divided into possible interlock failures and field equipment and process faults.

The field equipment and process faults were tested in full.
(the emergency-stop switch as well as each process measurement value of the boiler protection were simulated and tested for each channel).
The fault testing for safety interlocks was not done in full, because that had already been performed to completion with the factory acceptance test (FAT). Only some sporadic tests were undertaken. The following fault cases were tested:

-I/O card no. 5 was removed from frame 0
-I/O card no. 7 was removed from frame 1
-the supply of electricity was cut for frame 0
-expansion bus no. 5 was removed from frame 1
-frame 1 was removed from the field connection
-process station 60 was stopped

In addition to the functioning of the interlocks, alarm messages and interlock indications on SIS displays were examined. Appended there is also a copy of the page of the alarm printer and a display page both related to tripping situations.

# 3 COMMENTS ON TESTING

## 3.1 Testing of the safety system

The testing was performed according to the plan. The programs and the system functioned well. Some observations related to the testing:

- For some reason, part of the markings of the field equipment and cabling had come loose. The markings were attached by the client during testing.

- On pressing the 93XZ0015 Emergency-switch (B channel), valve 93HV0007 started closing slowly, resulting in a wrong-limit alarm.
  It was noticed that the air pipes by the valve were bent in some places and slowed down the movement of pressure air in the piping system.
  The pipes were straightened and the valve's closing time became normal. The client will replace the air tubes during the next stoppage.

# APPENDIX 9

# GUIDE FOR OPERATION AND MAINTENANCE

## Plan for operation and maintenance, 9A
## Guide for modification procedures, 9B

**Recovery Boiler Ltd**
**SIS project**

**MODEL**

## PLAN FOR OPERATION AND MAINTENANCE

## HISTORY

The first version was written on 15th January 2003.

## 1 PLAN TARGET

This recommendation applies to the operation and maintenance of a Safety Related System (SRS) for recovery boilers of Recovery Boilers Ltd.

## 2 PERSONS IN CHARGE

The person responsible for the safety of the recovery boiler is the operations supervisor.

The responsibility for the maintenance of automation and SIS belongs to the plant's automation maintenance where the person in charge for SIS is the automation master for the recovery boiler.

## 3 DOCUMENTATION

The entire documentation related to SIS has been collected in section-specific folders, which can be found with the day master, in the archive, in the automation configuration space for the liquor line or with the SIS person in charge.

The operation and maintenance instructions are kept in the SIS documentation folder. The plant's SIS person in charge has the master documentation (clause 2). That person is also responsible for updating the folder and for its distribution to the parties involved.

# 4 TRAINING

## 4.1 Training plan

The head operator of the plant and its SIS person in charge draw up a plan of continuous training for the operation and maintenance personnel. The plan pays attention to:

- the training of the technical personnel on fault diagnostics and repair as well as on testing of the system
- the training of the operation personnel
- the introduction of SIS to those unfamiliar with it
- a separate retraining of the personnel when the need arises, for example, during the periodic testing or other changes

## 4.2 Training register

A register is being maintained on training and competency. All the training events are entered to the training register that is maintained by the personnel administration. These events include participation in training events organized by an equipment supplier or a client.

# 5 REQUIREMENTS DEFINITIONS

## 5.1 Routine activities

The daily duties of the maintenance personnel in relation to the operation and maintenance of SIS are the following:

- Tidiness of the areas
- Prevention of entry from outsiders to the areas concerned (own key for the areas of electrical and automation equipment and processes)
- Keeping the SIS cabinet doors closed
- Updating of the SIS document folders
- Monitoring of air quality in SIS areas (temperature, pressure difference, moisture)
- Keeping the alarm lists under observation and responding to repeated alarms
- Observing the state of installations during factory visits and initiating preventive actions against hazard conditions possibly caused by temporary placing of foreign objects at the plant.

## 5.2 Operation instructions

The operation and maintenance instructions for different processing situations are presented in process-specific operation instructions, which include the operations before startup, during startup, running, and shutdown and the actions during a stoppage.

The operation instructions also show the SIS related circuits that are in the section and their operation.

The instructions also discuss possible faults/failures and how to remove them, thus trying to prevent a hazardous state or decrease the consequences of the hazard.

## 5.3 Periodic testing and records

Due to the nature of processes and the structure of SIS, in which all SIS's field and system devices form part of the process control equipment, all field and system devices are under constant operation and being supervised. For example, if one of the connections for duplicated limit information breaks, the limit signal disappears and causes thus the tripping of interlocks and the process shutdown. In measurements based on the 2/3 principle, one can be temporarily removed for calibration or maintenance, but the remaining transmitters then operate as if part of an 1/2 arrangement.

The portion of undetected faults based on the above is small in normal process run situations. It is regarded as reasonable to schedule periodic testing in 18 - 24 - 26 intervals depending on the hardware structure.

The periodic testing plan, the testing instructions and records for periodic testing are in the SIS periodic testing folder. The records drawn up during testing must also be included in that folder.

The periodic testing plan discusses the wherewithal (organization, documentation, testing equipment) for testing, how the tests are run, error correction, test acceptance, report formulation etc.

The testing instructions present, for each circuit, the preparations for testing, necessary changes in connections to enable circuit-specific testing, tripping instructions for the sources and instructions for record keeping.

### 5.4 Maintenance and modification

All maintenance operations for field and system equipment (calibration checkup, transmitter change, card replacement etc.) are regarded as maintenance. These do not require SIS compliant acceptance if the devices and limits remain unmodified. Comparable new devices of different brands require the SIS compliant acceptance.

Modification operations, on the other hand, include all changes in circuits within the domain of SIS (circuit additions, changes in cabling, cross-connections and applications). These must always be dealt with in accordance with the acceptance plan and inspection records must be kept of them.
It is the operation supervisor who has the power to give a permit for modifications. The supervisor also can decide which modifications are small, in which case they can be done independently, and which modifications require the use of the authorized assessment method.
The person responsible for the implementation of the modifications regarding SIS and for the competency of the persons involved in those modifications is the person in charge for SIS mentioned in Item 2. That person can decide whether to do the modification with the plant’s own resources or whether to ask help from the personnel of the equipment supplier or from other competent outside sources (In accordance with the Guide for modification procedures).

Tuning modifications for transmitters equipped with a so-called safety plate (a normal marking with a red background) must be done with consideration, and the modification must be entered in the SIS documentation.

Transmitters connected to SIS - if lockable either by their transmitter container or installation valve - must be kept locked.

The Guide for modification procedures can be found in the SIS documentation folder in its operation and maintenance instructions section. The instructions explain the procedures to be followed for modifications:
- Maintenance of the requirements definitions
- Contacts to authorities and/or assessors
- Maintenance of SIS safety definitions
- Maintenance of implementation plans
- Implementation design and planning, and documentation
- Modification acceptance
- Modification reports

### 5.5 Operation and maintenance journal

No separate SIS journal is kept. All SIS events – trippings, failures, faults, testing, modifications, etc. - are entered in a shift's event journal.

Shift managers and operators enter SIS related events due to faults, failures or trippings into the shift's event journal immediately after the fault, failure or tripping took place.

The operations supervisor must keep track of the events in the journal. If it is found that some fault or hazard situation repeats, measures must be taken to eliminate the problem. These measures can include personnel training, a change in the requirements definitions, a modification in the SIS safety definitions or implementation, replacement or addition of field equipment, etc.

If there is a need for a modification, the operations supervisor creates a change management form, of which a copy is delivered to the person in charge of SIS.

In all these cases the modification procedures of Item 5.4 should be complied with.

### 5.6 Maintenance instructions

The SIS logic solver does not normally require other maintenance apart from the periodic testing. Possible maintenance instructions are defined in the equipment supplier's instructions.

The maintenance instructions for field equipment that are related to SIS are kept in the documentation folders. Calibration and condition inspections take place during periodic testing.

## 6 EXCEPTIONAL SITUATIONS

In case of a failure in SIS (for example, a faulty card) processes cannot be run. No separate contingency bypasses have been built for testing or maintenance in case of a SIS failure. An exception to this, however, are the 2/3 measurement principles for analog measurements, where one transmitter can be removed, for example, for maintenance. When there is a SIS failure, the SIS related parts of the process are interrupted.

The maintenance personnel repair the faults that appear, in accordance with the operation and maintenance instructions. If deemed necessary, a representative of the equipment manufacturer is invited there.

Following a failure, testing or maintenance, the process startup is performed in accordance with the operation instructions as in the case of a normal startup.

**Recovery Boiler Ltd**
**SIS project**

**MODEL**

## GUIDE FOR SIS MODIFICATION PROCEDURES

## HISTORY

The first version was written on 15th January 2003.

## 1 TARGET OF THE INSTRUCTIONS

This recommendation applies to Safety Related Systems (SRS) for recovery boilers by Recovery Boilers Ltd.

## 2 GENERAL

All maintenance operations for field and system equipment (calibration checkup, transmitter change, card replacement etc.) are regarded as maintenance. These do not require SIS compliant testing if the devices and limits remain unchanged. Comparable new devices of different brands require the SIS compliant testing.

Modification operations, on the other hand, include all changes in circuits within the domain of SIS (circuit additions, changes in cabling, cross-connections, internal wiring and programs). These must always be dealt with in accordance with the testing plan and entered into testing records.

## 3 MAINTENANCE OF REQUIREMENT DEFINITIONS

The person responsible for the SIS requirement definitions, for their changes and for the maintenance, while the boiler mentioned above is in operation, is the person in charge for SIS. That person can give a permit for modifications and decide which modifications are small, in which case they can be done independently, and which modifications require the use of the authorized assessment method. For example, changes in tripping limits and in the user interface can be interpreted as small modifications. Modifications that are more significant include, for example, removals of safety inputs and safety additions.

## 4 MAINTENANCE OF IMPLEMENTATION PLANS

Before a modification is realized, it is designed and planned in the modification plans that are in the SIS modification folder. The person responsible for all the operation time maintenance of the SIS's implementation plans is the person in charge of SIS.

The modification should not noticeably change the overall reliability of SIS. Moreover, the modifications must be planned in accordance with the SIL principles such as:

- 2 channel structure, 1/2 or 2/3 tripping
- closed circuit principle
- occasional faults in SIS must not prevent the protection from operating when required
- protection must operate regardless process stations

When planning a modification, attention must be paid on that the alarms and protection control operations should enable the tracking and clarification of tripping signals and facilitate also fault detection.

## 5 IMPLEMENTATION CHANGES AND DOCUMENTATION

Only a person who is sufficiently knowledgeable in the relevant systems area is allowed to make changes in SIS software and wiring. The person in charge for SIS assumes the responsibility for the competence of the persons involved. It is recommended that the responsibility for the maintenance of the system's software is limited to 2-3 persons, each of whom takes the responsibility for the maintenance of program or other documentation.

Software modifications are kept in the folder for the management of the recovery boiler's configuration state modifications. The operations supervisor is provided with a copy of the modifications.

### 5.1 Application modifications

A password and a username are needed for signing in to the planning system.

The modifications in line with the implementation plans are prepared on the desktop to the modules from the file system.

The modified and checked up module is left on the desktop to wait for a suitable stoppage. In case it takes a longer time for a stoppage, a backup copy of the desktop should be made.

It must always be confirmed that a command gets through. The front indicator lights of a card confirm its startup.

Do not update the cards when the process is active, because updating momentarily resets the outputs and thus stops the related parts of the process.

### 5.2 Wiring modifications

The modifications in line with the implementation plans are drawn up for the diagrams of internal wiring circuits on the field and in SIS.

Wiring modifications/additions are realized according to the stoppage work list. To avoid short circuiting problems, connected channels are disconnected for the time the work takes.
Do not perform wiring modifications while the process is active, because possible connection problems during the modification work, when new connections are added, can cause the tripping of SIS for the process in question or the relevant parts of the process can get into an abnormal state

### 5.3 Field equipment modifications

Replacing a field device with a same type of a device is not a modification if the new device has the same calibration as the old one. On the other hand, to replace a field device with one of a different type, to add a new one or to change one's location is modification work, which must be planned and have approved by the person in charge of SIS or by the plant's operations supervisor or, if needed, by a competent authority.

Before a replacement with or addition of a new type of a device, it is necessary to ensure that the device's authorizations designate it as suitable for safety circuits.

When installing field devices, one must follow the installation methods and markings corresponding to the implementation plans presented in the SIS description.

## 6 MODIFICATION TESTING

Modifications/additions are tested in accordance with a testing plan drawn up, modification by modification, by the person in charge for SIS and approved by the plant's operations supervisor. To ensure testing that is independent of the implementation, in addition to the implementation planner, at least one person with a sufficient competence, e.g., the person in charge for SIS, must accompany the testing procedures.

The plan should present the personnel participating in the testing; how to test the operations of a module loaded after a change in the software or wiring modifications or changes in field devices; the acceptance criteria for the tests; and how to document the testing.

After the tests have been completed, the person in charge for SIS updates the related documents in different places in the SIS folder. When necessary, the modifications must be updated also to periodic testing documents and to operations and maintenance instructions.

## 7 REPORTING ON MODIFICATIONS

The tested modification/addition is reported to the person in charge of SIS, who gathers together all the documentation related to the modification and reports further on to the operation supervisor of the plant. The supervisor approves the modification as having been performed and tested, enters its details in the SIS operation and maintenance journal, and updates and distributes the bulletin in accordance with the instructions that he/she had devised.

If necessary, the plant’s operations supervisor reports to the authorities about the modification.

# APPENDIX 10

## MARKING RECOMMENDATION FOR SAFETY RELATED SYSTEMS

FINNISH RECOVERY BOILER COMMITTEE

# Finnish Recovery Boiler Committee (reg. assoc.)

# MARKING RECOMMENDATION FOR SAFETY RELATED SYSTEMS

19.10.2000

Report 9/2000
Rev. A

## 1 GENERAL

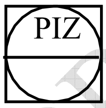
The members of the Finnish Recovery Boiler Committee have felt the need to standardize the marking of the circuits and devices in relation to safety related systems (SRS) for recovery boilers. This recommendation aims to standardize the markings of SIS circuits used in manufacturing and in planning and design.

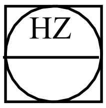
## 2 MARKING RECOMMENDATION FOR CIRCUITS OF SAFETY RELATED SYSTEMS (SRS)

### 2.1 PI diagram

Those circuits which have protection (safety) interlocks (e.g., a valve or something comparable that has been defined as needing interlocks or a measurement that gives locking limit information) are supplied with an additional letter, Z.

E.g: PIZ, HSZ, PICZ, etc.

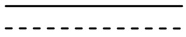




### 2.2 Interlock, control and circuit diagram

In interlock and control diagrams signals are marked by drawing a dashed line by the side of a normal line.

For example:



In cross-connection documents these wiring signals are marked with letter Z across the line.

For example:——————Z——————

The figures carry a legend: z line = red cross-connection wire

### 2.3 Wiring

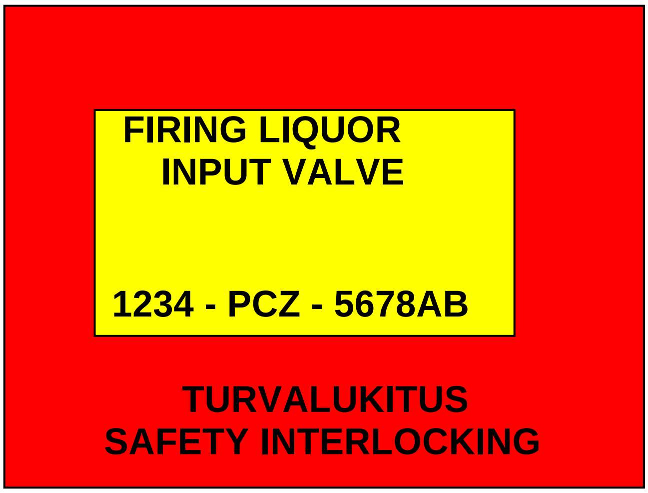
The cross-connection wiring for devices with safety interlocks is made with an orange wire.

## 2.4 Device plates and markings

The plates of the interlocked devices in field containers are of orange color. Those field containers which contain only circuits with interlocks are also equipped with an orange container plate.

Field devices connected with safety interlocks are equipped with normal field equipment plates which are fixed on base plates that are bigger in size and colored orange. An orange frame is thus shown around the normal plate, which has a text ‘Safety Interlocking’.

**Example:** Under the device plate (yellow) of the firing liquor input valve there is an orange safety interlocking plate installed.



FINNISH RECOVERY BOILER
COMMITTEE (REG. ASSOC.)REPORT
SERIES

1/99 Suomen Soodakattilayhdistys ry
Konemestaripäivä 1999, 20.-21.1.1999 Joensuu, esitelmät
16A0913-21, 00-A221-16A/E4

2/99 Suomen Soodakattilayhdistys ry
Soodakattila-alan yhteistoiminta. Vuosikertomus 1998.
16A0913-26, 00-A221-16A/E5

3/99 Suomen Soodakattilayhdistys ry
Vuosikokous 1999, 25.3.1999 Lappeenranta, Pöytäkirja
16A0913-31, 00-A221-16A/E6

4/99 Suomen Soodakattilayhdistys ry
KCL, Niemelä, K/ Jyväskylän yliopisto, Alén, R
Puun delignifioinnin eri vaiheissa muodostuvat liukoiset ja haihtuvat yhdisteet
Kirjallisuuskatsaus ja esiselvitys, 2.5.1999
16A0913-36, 00-A221-16A/E7

5/99 Suomen Soodakattilayhdistys ry
KCL, Sirén, K, Kaliumin ja kloorin poisto viherlipeää kiteyttämällä
15.4.1999
16A0913-38, 00-A221-16A/E8

6/99 Suomen Soodakattilayhdistys ry
Soodakattilapäivä 1999, 13.10.1999 Helsinki, esitelmät
16A0913-48, 00-A221-16A/E9

7/99 Suomen Soodakattilayhdistys ry
Karjunen Timo, Kaasuräjähdykset soodakattiloissa vesivuotojen aikana
27.10.1999
16A0913-52, 00-A221-16A/E10

8/99 Suomen Soodakattilayhdistys ry
Lehtinen. M, BLRBAC syyskokous; matkaraportti.
27.10.1999
16A0913-53, 00-A221-16A/E11

# FINNISH RECOVERY BOILER COMMITTEE (REG. ASSOC.)REPORT SERIES

1/2000 Suomen Soodakattilayhdistys ry
Konemestaripäivä 2000, 26.-27.1.2000
Imatran Valtionhotelli/Joutseno Pulp, esitelmät
16A0913-65, 00-A221-6A/E12

2/2000 Suomen Soodakattilayhdistys ry
Jaakko Pöyry Oy, Pekkanen Markku
Soodakattilassa poltettavat ainevirrat
19.1.2000
16A0913-66, 00-A221-16A/E13

3/2000 Suomen Soodakattilayhdistys ry
Jaakko Pöyry Oy, Jussila Pekka
Savukaasuanalysaattorikartoitus
23.3.2000
16A0913-68, 00-A221-16A/E14

4/2000 Suomen Soodakattilayhdistys ry
Soodakattila-alan yhteistoiminta. Vuosikertomus 1999
16A0913-73, 00-A221-16A/E15
20.3.2000

5/2000 Suomen Soodakattilayhdistys ry
VTT Energia, Paterson McKeough
Rikkiyhdisteiden vapautuminen mustalipeän haihdutuksessa
Kokeet yhdellä mustalipeällä.
16A0913-78, 00-A221-16A/E16
23.3.2000

6/2000 Suomen Soodakattilayhdistys ry
Lehtinen. M, BLRBAC kevätkokous; matkaraportti.
16A0913-82, 00-A221-16A/E17
25.4.2000

7/2000 Suomen Soodakattilayhdistys ry
Vuosikokous 2000, 30.3.Oulu, Pöytäkirja
16A0913-85, 00-A221-16A/E18

8/2000 Suomen Soodakattilayhdistys ry
Soodakattilapäivä 2000, 12.10.2000
Sokos Hotel Vantaa, esitelmät
16A0913-99, 00-A221-16A/E19

9/2000 Suomen Soodakattilayhdistys ry
Merkintäsuositus turvallisuuteen liittyvissä
järjestelmissä. 16A0913-103, 00-A221-16A/E20
19.10.2000

FINNISH RECOVERY BOILER COMMITTEE
(REG. ASSOC.)RECOMMENDATION

1 Suomen Soodakattilayhdistys ry

Hajukaasujen polttosuositus
Jaakko Pöyry Oy/Esa Vakkilainen
(16A0913-E0031)
30.5.2002

2 Suomen Soodakattilayhdistys ry

Soodakattilan turva-automaation suositus
Suomen Soodakattilayhdistys ry:n Automaatiotyöryhmä/Mauri Heikkinen
(16A0913-E0044)
15.1.2003
8.9.2008 rev. A

3 Suomen Soodakattilayhdistys ry

Soodakattilan tarkastus- ja peittaussuositus/Esa Ilves, Pekka Pohjanne, Jorma Kiimalainen
(16A0913-E0061)
15.12.2004

# LIITE IV

Ulrika Backman, VTT
Pienhiukkaset – alustava raportti
21.5.2010

TUTKIMUSRAPORTTI

VTT-R-XXXX-YY

# Metsäteollisuuden hiukkaspäästöt - draft

| | |
|---|---|
| Kirjoittajat: | Ulrika Backman |
| Luottamuksellisuus: | Luottamuksellinen |

| | |
|---|---|
| Raportin nimi | |
| Asiakkaan nimi, yhteyshenkilö ja yhteystiedot | Asiakkaan viite |
| Projektin nimi | Projektin numero/lyhytnimi |
| Raportin laatija(t) | Sivujen/liitesivujen lukumäärä<br>31/ |
| Avainsanat | Raportin numero<br>VTT-R- |
| Tiivistelmä | |
| Luottamuksellisuus | {luottamuksellinen, salainen tai julkinen} |

{Kirjoita kaupunki} 21.5.2010

| | | |
|---|---|---|
| Laatija | Tarkastaja | Hyväksyjä |
| {Nimenselvennys, asema} | {Nimenselvennys, asema} | {Nimenselvennys, asema} |

VTT:n yhteystiedot

Jakelu (asiakkaat ja VTT)

{Tilaaja, VTT ja muu jakelu. Luottamuksellisissa raporteissa mainittava yritys, henkilö ja kappalemäärä. Tarvittaessa kirjoita seuraavalle sivulle.}

## Sisällysluettelo

# 1 Johdanto

Hiukkaspäästöt ja etenkin pienhiukkaspäästöt ovat viime aikoina olleet paljon esillä hiukkasten mahdollisten aiheuttamien terveysvaikutusten ja ympäristövaikutusten takia. Metsäteollisuuden hiukkaspäästöt ovat vähentyneet 84 % tuotettua tonnia kohti vuodesta 1992 vuoteen 2008. Tänä päivänä metsäteollisuuden osuus Suomen hiukkaspäästöistä on selvästi alle 10 % [Metsäteollisuus 2009].

Metsäteollisuuden suurin ilmapäästöjen aiheuttaja on soodakattilat. Muita hiukkaspäästölähteitä metsäteollisuudessa ovat mm. voimalaitokset ja meesauunit. Apukattiloissa tuotetaan sähköä ja lämpöä sellutehtaan tarpeisiin polttamalla mm. puuta, kuorta, sahanpurua ja muita kiinteitä aineita mm. arinapolttona ja leijukerroskattiloissa. Yksittäisen prosessin hiukkaspäästöihin vaikuttaa monet asiat, mm. polttotekniikka, poltto-aine ja sen ominaisuudet sekä hiukkasten erotuslaitteet (sähkösuodatin, sykloni, letkusuodatin).

Nykypäivänä lainsäädäntö määrää päästöraja-arvoja yli 50 MW polttolaitoksille [Finlex 1017/2002]. Kiinteiden hiukkasten massapitoisuus saa olla 50 – 300 MW laitoksilla enintään 50 mg/Nm$^3$ ja yli 300 MW laitoksilla 30 mg/Nm$^3$ jos lupa on myönnetty 1.1.1994 jälkeen. Tämä asetus ei koske soodakattiloita ja meesauuneja. Sellutehtaiden ympäristöluvissa on määrätty soodakattiloille ja meesauuneille päästöraja-arvoja, joiden tavoitetaso nykyään on pääosin 50 mg/Nm$^3$ [www.ymparisto.fi, ympäristöluvat].

Hiukkaset ilmassa jaetaan usein eri kokoluokkiin. Halkaisijaltaan alle 10 µm:ä hienojakoisemmista hiukkasista käytetään termiä hengitettävät hiukkaset (PM 10, PM = particulate matter). Nykyään hiukkaset jaotellaan vielä tarkemmin, pieniin ja suuriin hiukkasiin kokorajan ollessa 2,5 µm. Pienhiukkasista puhuttaessa tarkoitetaan siis hiukkasia joiden halkaisija on alle 2,5 µm.

Tässä raportissa on kirjallisuuden avulla pyritty selvittämään metsäteollisuuden hiukkaspäästöjä (mm. päästömäärät, hiukkaskokojakaumat, kemiallinen koostumus) sekä hiukkasten haitallisuus verrattuna esim. pienpolttoon hiukkasiin ja dieselhiukkasiin. Tässä raportissa tarkastellaan vain suorat hiukkaspäästöt. Sekundäärihiukkasten muodostus $SO_2$ ja $NO_x$ muuntumisen kautta on rajattu pois. Yleisimmät päästömittauksissa käytetyt mittalaitteet on myös lyhyesti esitelty.

# 2 Mittausmenetelmät

Tässä kappaleessa esitellään lyhyesti ne mittausmenetelmät ja mittalaitteet jotka on käytetty kirjallisuudessa olevien tulosten aikaansaamiseksi.

## 2.1 Näytteenotto ja laimennus

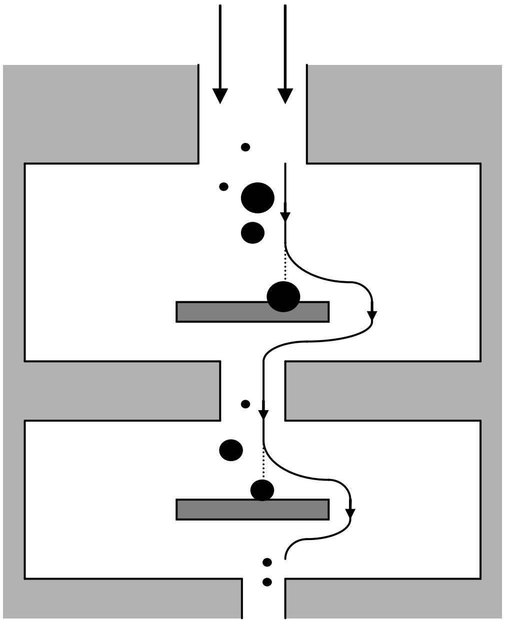
Hiukkasnäytteenotossa on tärkeätä varmistua mm. hiukkasnäytteen edustavuudesta ja isokineettisestä näytteenotosta. Isokineettinen näytteenotto tarkoittaa sitä että kaasun virtausnopeus on yhtä suuri suuttimessa kuin suuttimen kohdalla kanavassa. Näin voidaan varmistaa että hiukkaspitoisuuden ja jakauman arvot ovat oikein [Päästömittausten käsikirja, 2004].

Jos hiukkaspitoisuus on iso tai savukaasun lämpötila on korkea voidaan tarvittaessa hiukkasnäytettä laimentaa, jotta voidaan hiukkasia mitata mittalaitteilla. Laimennuksen avulla voidaan myös hallita kaasufaasissa olevien aineiden tiivistymistä. Laimennus tehdään erilaisilla laimentimilla, mistä tavallisimmat ovat huokoisen putken laimennin ja ejektorilaimennin. Usein jo ennen laimenninta kerätään isoimmat hiukkaset syklonin avulla, aerodynaaminen katkaisuraja D50 ollessa tyypillisesti 8-10 µm.

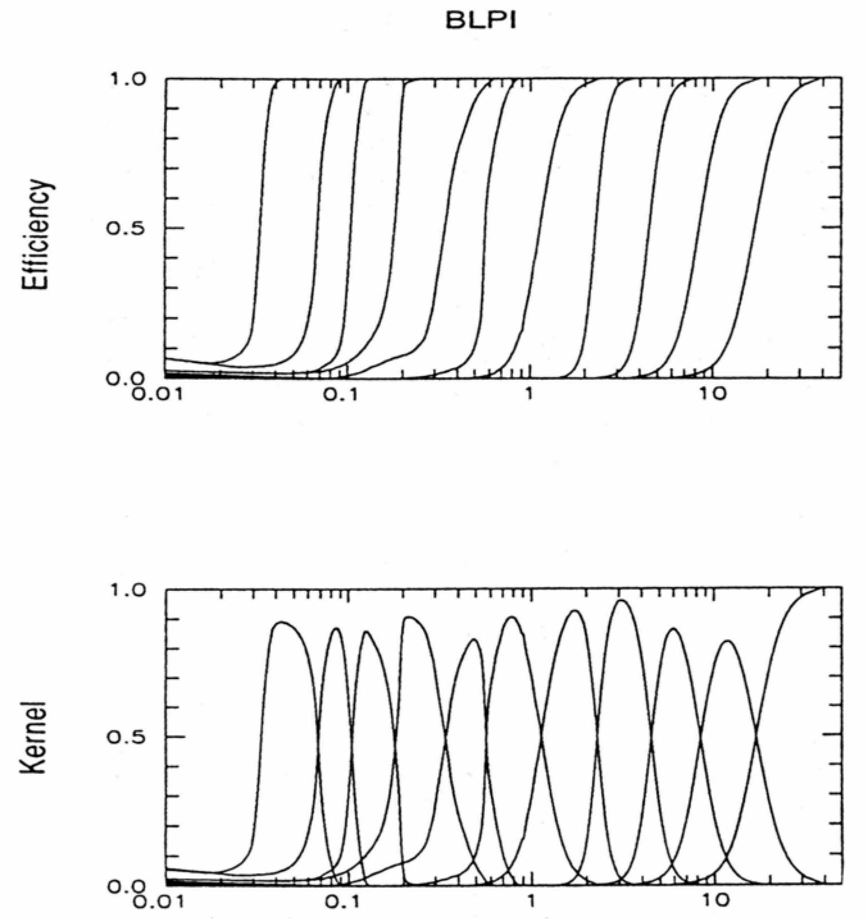
## 2.2 Massakokojakauma

Massakokojakaumaa voidaan mitata moniasteimpaktorilla. Näistä eniten käytetyt ovat Berner Low Pressure Impactor (BLPI) ja Dekati Low Pressure Impactor (DLPI).

Impaktorissa virtaus kulkee kapean suuttimen läpi nopeudella v. Suuttimen jälkeen virtaus kääntyy 90°. Halkaisijaa D50 suuremmat hiukkaset eivät seuraa virtausta vaan törmäävät keräysalustalle ja jäävät siihen kiinni. Impaktorin kaaviokuva on esitetty kuvassa 1. Käytännössä katkaisuraja D50 on hiukkaskoko, jonka keräystehokkuus on 0,5. Kuvassa 2 on esitetty BLPI:n keräystehokkuuskäyrät sen jokaiselle 11 asteelle. Kernel on teoreettinen hiukkaskokojakauma kullekin BLPI:n asteelle saatavista hiukkasista ja se on laskettu keräystehokkuuskäyristä. Lämpötilassa 140°C BLPI:n katkaisuraja pienimmällä asteella on 0,022 µm sekä suurimmalla 16,22 µm ja virtausnopeus sen läpi on 19 l/min (NTP). DLPI on 13 asteinen impaktori jonka mittausalue ylettyy 30 nm:stä 10 µm:iin. Virtaus DLPI:n läpi on 10 l/min [Dekati Ltd., 2010].



Kuva 1: Moniasteisen impaktorin toimintaperiaate



Kuva 2: BLPI:n keräystehokkuuskäyrät ja niistä laskettu teoreettinen kokojakauma kullekin BLPI:n asteelle [Kauppinen, 1991].

## 2.3 Massapitoisuus

Hiukkasten massapitoisuutta voidaan mitata suodatinkeräyksen avulla, laskemalla impaktorimittauksessa eri tasoille kerätyt massat sekä mahdollisen esisykloniin kerätty massa yhteen tai Tapered Element Oscillating Mircobalance (TEOM) mittalaitteella.

TEOM on jatkuvatoiminen hiukkasten massapitoisuusmittari. TEOMin toiminta perustuu värähtelevään elementtiin, jonka päässä on hiukkaset kerräävä suodatin. Näytevirtaus 3 l/min (NTP) kulkee suodattimen ja värähtelijän läpi. Kun suodattimen massa muuttuu, myös värähtelijän taajuus muuttuu. Värähtelytaajuuden muutoksesta voidaan laskea suodattimelle kertyneiden hiukkasten massa. TEOM mittaa värähtelijän taajuuden noin kahden sekunnin välein. Saatavan signaalin kohina on suuri, joten siihen on käytettävä pitkää keskiarvoistamista. Tämän takia kovin nopeita massapitoisuuden vaihteluita ei voida havaita.

## 2.4 Lukumääräkokojakauma

Aerosolihiukkasten lukumääräkokojakaumaa määritetään yleisesti Scanning Mobility Particle Sizer:llä, SMPS, sähköisellä alipaineimpaktorilla (Electrical Low Pressure Impactor, ELPI) sekä aerodynaamisella kokoluokittelijalla (Aerosol Particle Sizer, APS).

SMPS on mittausjärjestely joka koostuu sähköisestä liikkuvuusanalysaattorista (Differential Mobility Analyser, DMA) sekä kondensaatioydinlaskurista (Condensation Particle Counter, CPC). Ennen DMA:ta hiukkasvirtaus kulkee varaajan läpi, missä hiukkaset varataan. DMA:ssa hiukkaset luokitellaan kokoluokkiin jonka jälkeen niitä havaitaan ja lasketaan CPC:ssä. Riippuen käytössä olevista mittalaitteista ja järjestelyistä voidaan mitata hiukkasia 5 nm:stä 1 µm:iin. Mittaus kestää tyypillisesti 30 – 120 sekuntia.

Electric Low Pressure Impactor (ELPI) on moniasteinen alipaineimpaktori kuten BLPI. Erona on, että ennen impaktoria hiukkaset varataan neulavaraajalla ja kullakin asteella oleva varaus mitataan herkällä elektrometrillä jatkuvatoimisesti. Virtajakaumasta ELPI laskee hiukkasten lukumääräkokojakauman. Hiukkasten kokojakaumaa ja sen muutoksia voidaan monitorilta seurata reaaliaikaisesti. ELPI:ssä impaktoriasteita on 12, ja sen mittaama hiukkasten kokoalue on 30 nm - 10 µm. Joissakin mittauksissa käytettiin myös ELPI:ä jossa alimman impaktoriasteen tilalla oli suodatin. Suodatinasteella saadaan kerättyä 30 nm:ä pienemmätkin hiukkaset. ELPI:n vahvuutena on toiminta reaaliajassa laajalla hiukkaskokoalueella. Virtausnopeus ELPI:n läpi on 10 l/min (NTP) [Keskinen et al. 1992].

Aerodynaaminen kokoluokittelija (Aerosol Particle Spectrometer, APS) mittaa hiukkasten lentoaika kaasuvirtauksessa. Aerosolinäyte kiihdytetään suuttimessa, jolloin hiukkaset jäävät jälkeen inertiansa johdosta. Kaasuvirtauksen ja hiukkasten välinen nopeusero kasvaa koon ja tiheyden funktiona. Laitteessa käytetään kahta laseria mittaamaan etäisyyttä, jonka aerosolihiukkanen kulkee. APS havaitsee hiukkasia 0,5 µm:sta 10 µm:iin.

## 2.5 Kemiallinen koostumus

Kerättyjen hiukkasnäytteiden kemiallinen koostumus analysoidaan tyypillisesti joko Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS) tai Proton Induced X-ray Emission (PIXE) tekniikoiden avulla.

ICP-MS:ssä näyte pirskotetaan argon plasman keskelle, missä näytteen atomit irtoavat ja virittäytyvät korkeammille energiatiloille. Paluu perustiloille saa aikaiseksi säteilyä, joka on aineille tunnusomaista.

PIXE:ssä näytettä pommitetaan korkeaenergisillä protoneilla, jolloin alkuaineet virittyvät. Energiatilojen purkauksissa syntyvä Röntgen-säteily havaitaan energiadispersiivillä ilmaisimella (esim. Si(Li)). PIXEn kyky havaita kevyitä alkuaineita on huono ($Z<12$).

## 2.6 Morfologia

Hiukkasten morfologiaa voidaan analysoida joko Scanning Electron Microscopy (SEM) ja Transmission Electron Microscopy (TEM) - elektronimikroskooppien avulla.

# 3 Soodakattilan hiukkaspäästöt

Maailman sellusta noin 80 % valmistetaan sulfaattisellumentelmällä [IPPC, 2001]. Sulfaattisellun keitossa käytetään natriumhydroksidia ja natriumsulfidia keittokemikaaleina. Prosessissa syntyy jätelipeä, mustalipeä, jota poltetaan soodakattilassa. Mustalipeä koostuu rikistä ja natriumista eri yhdisteinä, sekä liuenneessa muodossa puusta irronneista orgaanisista yhdisteistä. Soodakattilassa mustalipeästä poltetaan orgaaninen puuaines, joka on suurimmaksi osaksi ligniiniä [Hupa ja Hyöty 1995, Uusitalo 2009]. Noin kolmasosan mustalipeän kuiva-aineesta koostuu epäorgaanisista kemikaaleista ja kaksi kolmasosaa liuenneista orgaanisista aineista [IPPC, 2001].

Soodakattilalla on kaksi tehtävää: ensinäkin sellunkeiton kemikaalit, rikki ja natrium vapautuvat mustalipeästä ja ne voidaan ottaa talteen ja regeneroida ja käyttää uudestaan. Näin saavutetaan huomattavia säästöjä, kun kemikaalien talteenotolla minimoidaan kalliiden kemikaalien häviöt polttoprosessissa. Toisaalta poltossa syntyvä lämpö otetaan talteen ja hyödynnetään prosessihöyrynä sekä sähkön tuotannossa. Mustalipeän energiasisältö on niin suuri että monet selluloosatehtaat kykenevät saavuttamaan energiaomavaraisuuden ja jopa syöttävät sähköä valtakunnanverkkoon [Hupa ja Hyöty 1995, Uusitalo 2009]. Koska mustalipeä on peräisin puusta, se pidetään biomassana ja näin ollen $CO_2$ neutraalina polttoaineena.

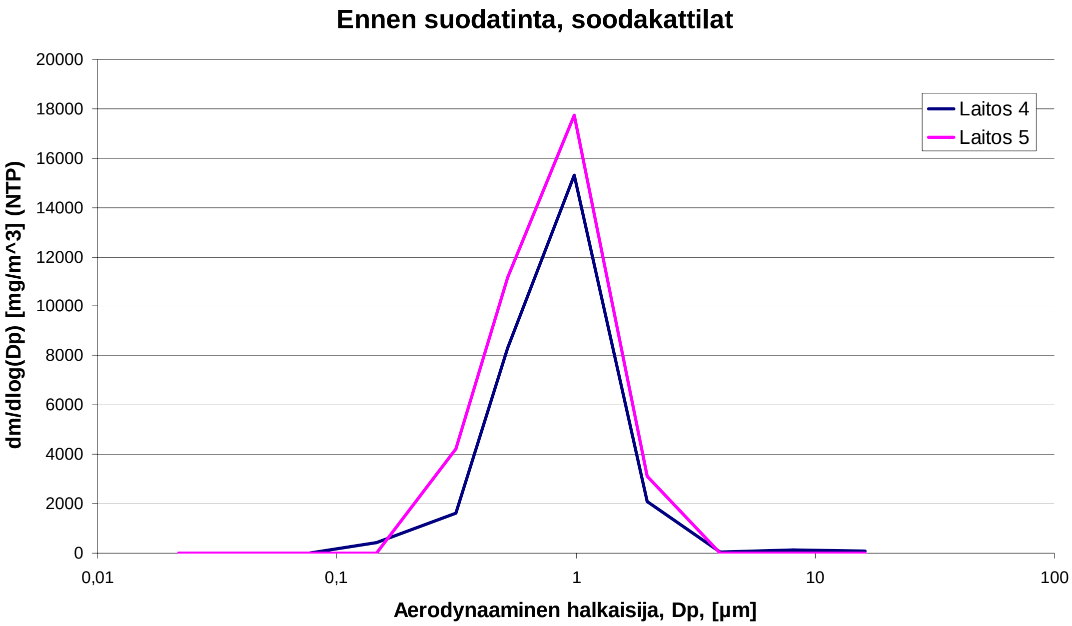
Kaikissa polttoprosesseissa syntyy päästöjä ilmaan, niin myös soodakattiloista. Soodakattilan päästöistä merkittävimmät ovat rikkidioksidi, typenoksidit, pienhiukkaset sekä haisevat rikkiyhdisteet. Soodakattilassa muodostuvat hiukkaset koostuvat kahdesta selvästi toisistaan eroavasta jakeesta. Toisaalta n.k. carry-over hiukkasista, jotka ovat tulipesästä karanneitten lipeäpisaroitten jäännöksiä sekä toisaalta hiukkasista jotka ovat muodostuneet tulipesästä höyrystyneestä ja myöhemmin tiivistyneestä materiaalista. Carry-over hiukkaset ovat tyypillisesti kooltaan kymmeniä tai satoja mikrometrejä. Pääosin ne koostuvat natriumkarbonaatista ($Na_2CO_3$), mutta hiukkasista löytyy usein myös $Na_2SO_4$ sekä $Na_2S$. Tiivistymisen kautta muodostuneet hiukkaset ovat huomattavasti pienempiä, kooltaan 0,5 – 1 µm. Niiden koostumus eroaa selvästi carry-over hiukkasista, pääosin nämä pienet hiukkaset koostuvat natriumsulfaatista ($Na_2SO_4$) sekä pienestä määrästä natriumkarbonaattia [Hupa ja Hyöty 1995]. Hiukkasista on havaittu myös kaliumia ja klooria [Lind et al. 2006].

Hiukkasten muodostumista soodakattilassa tunnetaan aika hyvin [mm. Mikkanen 2000]. Kokonaishiukkaspitoisuus soodakattilan ulostulossa, ennen sähkösuodatinta, on yleensä erittäin korkea, 14 – 32 g/Nm$^3$. Tästä massasta yli puolet on peräisin pienistä, alle 3 µm:n hiukkasista [Mikkanen, 2000]. Soodakattilasta mitatulla hiukkasmassajakaumalla on kaksi huippua, yksi huippu noin 0,7 – 1,2 µm:n kohdalla ja toinen pienempi huippu noin 5 µm:n kohdalla [Mikkanen et al. 1995, Mikkanen et al. 1996 ].

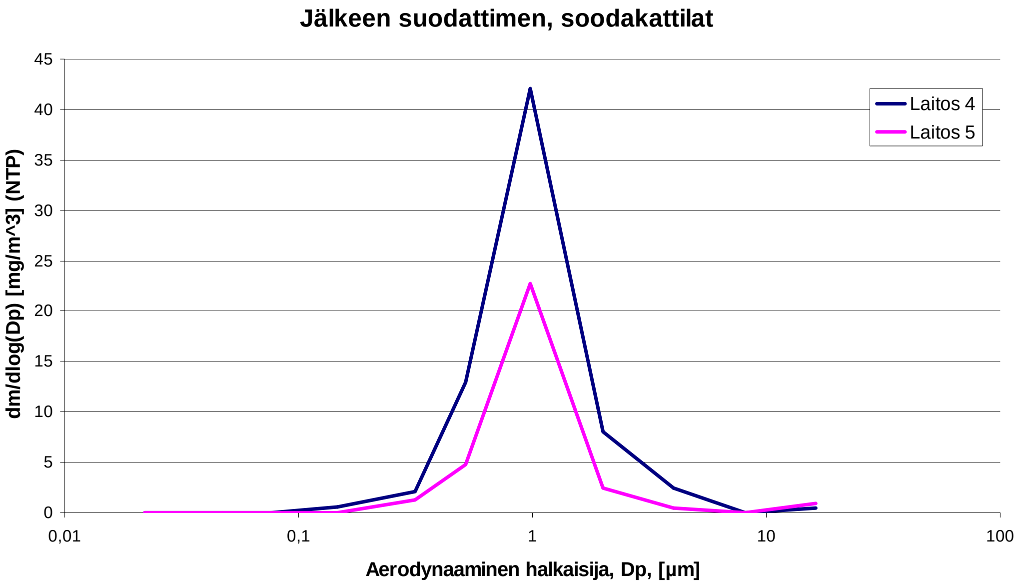
Suuren hiukkaspitoisuuden takia soodakattilat ovat yleensä varustettu sähkösuodattimilla, jolla kerätään talteen kalliita kemikaaleja sisältävää lentotuhkaa ja vähennetään hiukkaspäästöjä ilmaan. Suodattimien lisäksi myös pesurit vähentävät entisestään kiintoainepäästöjä. Soodakattilan päästöihin vaikuttaa mm. kattilan ikä, poltto-olosuhteet kuten lämpötila ja palamisilman määrä sekä mustalipeän kuiva-ainepitoisuus. Soodakattiloiden päästöt ovat pienentyneet viime vuosikymmeninä huomattavasti kehittyneen tekniikan ansiosta [Hupa ja Hyöty 1995, Uusitalo 2009].

Hiukkaspäästöistä suodattimien jälkeen on olemassa varsin vähän mittaustietoa. Yhteenveto kirjallisuudessa olevasta mittausdatasta löytyy Taulukosta 1. Kokonaishiukkasmassapitoisuus sähkösuodattimen jälkeen on raportoitu olevan 10 - 230 mg/Nm$^3$ [Moisio 1999, IPPC 2001, Hokkinen et al. 2004, Lind et al. 2006] ja massapitoisuus sähkösuodattimen ja pesurin jälkeen 80 mg/Nm$^3$ [Moisio 1999]. Massakokojakauma sähkösuodattimien jälkeen on yksihuippuinen ja huippu on noin 1 µm:n kohdalla [Moisio 1999, Hokkinen et al. 2004, Lind et al. 2006]. Kuvassa 3 on esitetty esimerkki soodakattilasta mitattu massakokojakauma. Mittauksissa on ollut käytössä sykloni, jonka katkaisuraja on ollut 4 µm. Kuvassa 4 on esimerkki soodakattilasta mitattu, suodattimien jälkeen, massakokojakauma.

Hiukkasten lukumääräpitoisuus ennen sähkösuodatinta oli 2.20* 10$^7$ #/cm$^3$ ja sähkösuodattimen jälkeen 7.61*10$^5$ #/cm$^3$ [Moisio 1999]. Moisio (1999) huomasi mittauksissaan että 59 % hiukkasten massasta ennen sähkösuodatinta on alle 2,5 µm hiukkasissa ja lukumäärästä peräti 99 %. Puhdistuslaitteiden jälkeen (sähkösuodatin ja pesuri) 66 - 94 % massasta on pienhiukkasissa, kun taas lukumäärästä 99 – 100 %.



Kuva 3: Hiukkasten massakokojakauma soodakattilassa ennen suodatinta. Syklonin katkaisuraja on 4 µm. [Hokkinen et al. 2004].



Kuva 4: Soodakattilasta, suodattimien jälkeen, mitattu massakokojakauma. [Hokkinen et al. 2004].

Taulukko 1: Yhteenveto kirjallisuudessa olevista soodakattiloiden päästömittauksista. ESP –sähkösuodatin

| | | **Massapitoisuus Ennen ESP/ muu jälkikäsittely [g/Nm$^3$]** | **Massapitoisuus Jälkeen ESP / muu jälkikäsittely [mg/Nm$^3$]** | **Lukumäärä-pitoisuus Ennen ESP [#/Ncm$^3$]** | **Lukumäärä-pitoisuus Jälkeen ESP [#/Ncm$^3$]** | **Kokojakauma käsittelyn jälkeen** | **Morfologia** | **Kemiallinen koostumus** |
|---|---|---|---|---|---|---|---|---|
| Moisio 1999 | Soodakattila ESP + gas scrubber | 12 | After ESP: 230<br>After scrubber: 80 | $2.20*10^7$ | $7.61*10^5$ | Huippu ~ 1 µm:n kohdalla | | |
| Hokkinen et al. 2004 | Soodakattila 250 MW ESP | 10-14 | 10-22 | | | Huippu ~ 1 µm:n kohdalla | | |
| Lind et al. 2006 | Soodakattila 1800 – 2000 t/d dry solid ESP | 11-24 | 12-40 | | | Huippu ~ 1 µm:n kohdalla | Yksittäisiä melkein pyöreitä sekä agglomeraatteja | natrium, sulfaatti, kalium, kloori |

# 4 Leijukerroskattilan hiukkaspäästöt

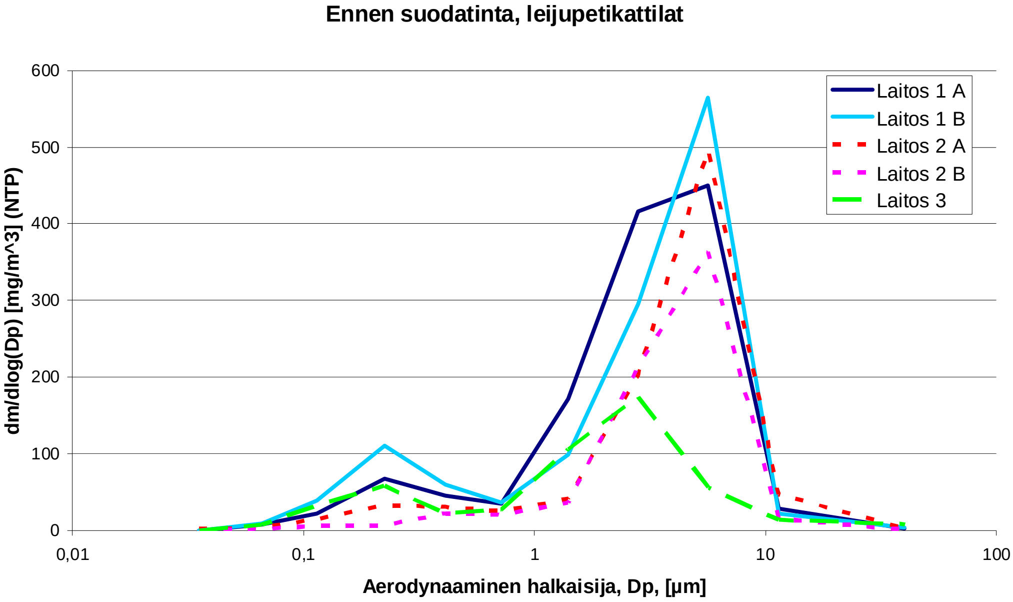
Leijukerroskattilassa tulipesän alaosasta syötetään ilmavirta, joka saa tulipesässä pidettävän hiekan, tuhkan ja polttoaineen leijumaan. Palaminen tapahtuu näin muodostuvassa pedissä. Polttoaineen jatkuva sekoittuminen tehostaa lämmön ja kaasujen siirtoa. Leijukerrostekniikka ei aseta polttoaineen laadulle mainittavia laatuvaatimuksia, joten on mahdollisuus käyttää myös kosteita ja matalan lämpöarvon omaavia polttoaineita, kuten kuori, hake, sahausjäte ja turve. Lisäksi seospolttoaineena voidaan käyttää muun muassa kierrätyspolttoainetta, yhdyskuntajätettä tai lietettä. Poltettava materiaali pitää kuitenkin murskata niin pieneksi, että leijutus onnistuu [Hyppänen ja Raiko 1995].

Leijukerrospoltto voidaan toteuttaa joko kuplivassa leijukerroksessa (BFB, kuplapeti) tai kiertoleijukerroksessa (CFB, kiertopeti). Kuplapedissä leijukerroshiukkaset pysysvät leijukerroksessa, kun taas kiertopedissä kiintoainehiukkaset kulkevat leijutuskaasun mukana pois leijutilasta ja ne on jatkuvuustilan aikaansaamiseksi palautettava takaisin. Leijukerroksen petilämpötila vaihtelee välillä 750 – 950 °C [Hyppänen ja Raiko 1995]. Khan et al. 2009 ovat koonneet hyvän yhteenvedon biomassan leijukerrospoltosta ja sen mahdollisuuksista ja haasteista.

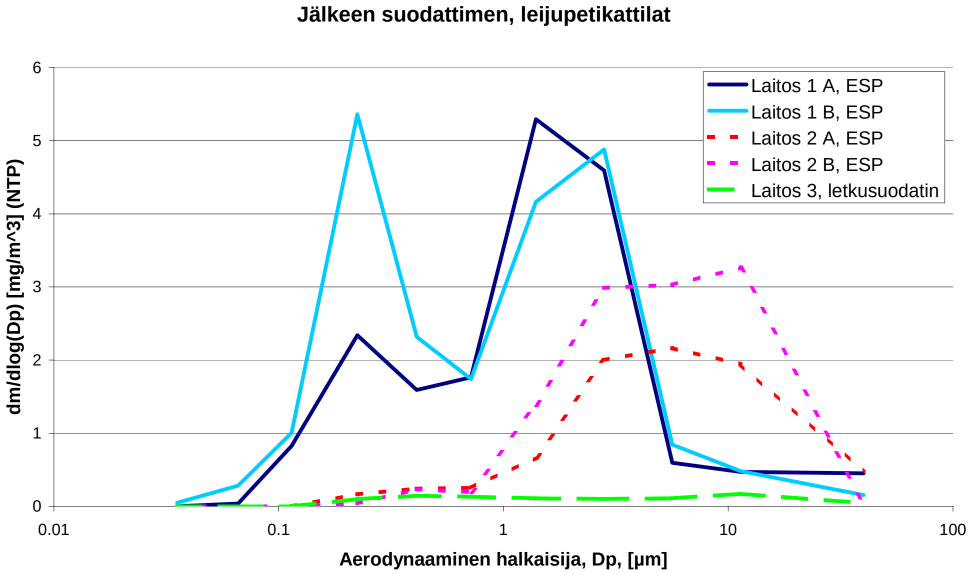
Hiukkasten muodostus leijukerrospoltossa on tutkittu ja tunnetaan suhteellisen hyvin. Yhteenveto kirjallisuudesta löytyvästä leijukerrospolton päästömittauksista löytyy Taulukosta 2. Hiukkasten massapitoisuus ennen suodattimia vaihtelevat hiilen poltossa 13700 – 18700 mg/Nm$^3$ [Lind et al. 1995], biomassan poltossa 260 – 6900 mg/Nm$^3$ ollen isoin puun ja turpeen sekapoltossa [Valmari et al. 1998, Valmari et al. 1999 a, Valmari et al. 1999 b, Maaskola 2002]. Erilaisten jätevirtojen poltossa (lietteet, puujäte, yhdyskuntajäte) massapitoisuus vaihtelee 650 - 8300 mg/Nm$^3$ välillä ennen suodattimia [Latva-Somppi et al. 1998, Moisio 1999, Hokkinen et al. 2004, Wilen et al. 2007, Lind et al. 2007].

Massapitoisuus suodattimien jälkeen (sähkösuodatin ja/tai letkusuodatin) vaihtelee 0,2 – 145 mg/Nm$^3$ välillä [Moisio 1999, Maaskola 2002, Hokkinen et al. 2004, Wilen et al. 2007, Lind et al. 2007, Ehrlich et al. 2007]. Päästömäärärään suodattimen jälkeen vaikuttaa kaikkein eniten suodatintyyppi, tässä pienimmät hiukkaspitoisuudet mitattiin laitoksessa missä on sekä sähkösuodatin että letkusuodatin käytössä.

Massakokojakaumassa on kaksi huippua, yksi noin 6 – 10 µm:n kohdalla ja toinen noin 300 nm:n kohdalla. Suuret hiukkaset ovat peräisin petimateriaalin pilkkoutumisesta ja jäännöstuhkahiukkasten muodostumisesta koksin sisällä tai pinnalla. Pienhiukkasmoodin hiukkaset ovat muodostuneet höyrystymisen ja tiivistymisen kautta [Lind 1999, Valmari 2000, Khan et al. 2009]. Massakokojakaumaa dominoi vahvasti suuret yli mikronin hiukkaset [Valmari et al. 1998, Maaskola 2002, Hokkinen et al. 2004]. Ehrlich et al. 2007 tekemissä mittauksissa 14,4 mg/Nm$^3$ kokonaishiukkasmassapäästöistä PM 10:ssä oli 97 %, PM 2,5:ssa 65,7 % ja PM 1:ssä 25,5 %. Muissa mittauksissa PM 1:sen osuus kokonaismassasta on ollut vielä pienempi [mm. Hokkinen et al. 2004, Lind et al. 2007, Wilen et al. 2007]. Kuvassa 5 on esitetty esimerkki massakokojakauma leijupetikattiloissa ennen suodatinta ja kuvassa 6 vastaavissa laitoksissa suodattimien (sähkösuodatin tai letkusuodatin) jälkeen. Pienhiukkasmoodin osa kokonaismassasta on pienempi hiilen poltossa kuin biomassan poltossa [Lind 1999].



Kuva 5: Hiukkasten massakokojakauma massakokojakauma leijupetikattiloilla ennen suodatinta. Syklonin katkaisuraja on 8µm laitoksilla 1 ja 2 sekä 4,5 µm laitoksella 3. [Hokkinen et al. 2004].



Kuva 6. Hiukkasten massakokojakauma leijupetikattiloilla suodattimen jälkeen (ESP: sähkösuodatin). Syklonin katkaisuraja on 2,5 µm laitoksella 3. [Hokkinen et al. 2004].

Hiukkaslukumäärää on mitattu vain yhdestä laitoksesta ja lukumäärä vaihteli ennen sähkösuodatinta $2,88*10^6$ - $6,5*10^6$ #/$cm^3$ välillä riippuen polttoaineen koostumuksesta. Sähkösuodattimen jälkeen pitoisuus oli $5,23*10^5$ - $8*10^5$ #/$cm^3$ [Moisio 1999].

Leijukerrospoltossa muodostuneet hiukkaset koostuvat agglomeroituneista 50 nm – 250 nm kokoisista hiukkasista [Lind et al. 2007]. Biomassan leijukerrospoltossa muodostuneet pienet hiukkaset koostuvat lähinnä kaliumista (K), kloorista (Cl), rikistä (S), natriumista (Na) ja kalsiumista (Ca) kun taas isot hiukkaset sisältävät kalsiumia (Ca), piitä (Si), kaliumia (K), rikkiä (S), natriumia (Na), alumiinia (Al), fosforia (P) ja rautaa (Fe) [Valmari et al. 1998, Jokiniemi et al. 2001]. Biomassan poltossa ei ole havaittu että raskasmetallit (Cd, Pb, Cu) rikastuisivat pienhiukkasiin [Lind et al. 1999] kun taas jätteenpoltossa Cd, Cu, Pb and Tl selvästi rikastuivat PM 1seen [Lind et al. 2007].

Taulukko 2: Yhteenveto kirjallisuudessa olevista leijupolttokattiloiden hiukkaspäästöistä. ESP –sähkösuodatin.

| | | **Massapitoisuus Ennen ESP/ muu jälkikäsittely [g/Nm$^3$]** | **Massapitoisuus Jälkeen ESP / muu jälkikäsittely [mg/Nm$^3$]** | **Lukumäärä-pitoisuus Ennen ESP [#/Ncm$^3$]** | **Lukumäärä-pitoisuus Jälkeen ESP [#/Ncm$^3$]** | **Kokojakauma käsittelyn jälkeen** | **Kemiallinen koostumus** |
|---|---|---|---|---|---|---|---|
| Moisio 1999 | CFB<br>19 MW<br>puukuori ja /tai liete,<br>ESP | 8 - 8,2 | 40 | 2,88 - 3,09 *10$^6$ | 5,23*10$^5$ | 2 huippua massajakauma: Pienempi 200 nm, isompi 2-3 µm | |
| Moisio 1999 | CFB<br>23 MW<br>Puukuori, puu<br>letkusuodatin | 1,3 | 145 | 6,5*10$^6$ | 8,8*10$^5$ | 2 huippua massajakauma: Pienempi 200 nm, isompi 2-3 µm | |
| Maaskola 2002 | CFB<br>295 MW<br>puu ja turve sekapoltto<br>ESP | 0,9 – 6,9 | 14 – 23 | | | Massa: Yksihuippuinen, huippu 2,5 – 5 µm välillä | |
| Hokkinen et al. 2004 | CFB<br>150 MW<br>kuorta, lietettä<br>ESP | 0,65 – 2,66<br>PM 1: 15-30 mg/Nm3 | 2,6 – 3,4<br>PM 1:0,12 – 0,18 | | | Massa: 2 huippua 200-300 nm (pieni) ja 5 – 10 µm | Al, SO4, Fe, Ca, Cl, K, Mn, Na, Zn |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Hokkinen et al. 2004 | BFB<br>60 MW<br>yhdyskuntajäte, turve, sahanpuru<br>ESP | 0,74 – 1,01<br>PM 1: 40 – 62 mg/Nm3 | 2,3 – 5,6<br>PM 1: 1,0 – 1,4 | | | Massa: 2 huippua 200-300 nm ja 2 – 4 µm | |
| Hokkinen et al. 2004 | BFB<br>90 MW<br>kuorta, turvetta, lietettä<br>letkusuodatin | 0,73<br>PM 1: 42 mg/Nm3 | 13<br>PM 1: 0,1 | | | | |
| Lind et al. 2007 | CFB<br>75 MW<br>Yhdyskuntajäte<br>ESP ja letkusuodatin | 4.6<br>PM 1: 250 – 310 mg/Nm3 | 0.5-0.7<br>PM 1: below 0.1 | | | 2 huippua: 400 nm ja 3 µm | PM 1: Na, K, Cl, SO4, Cu, Pb<br>Coarse mode: also Al and Fe |
| Wilen et al. 2007 | CFB<br>65 MW<br>Puu ja puujäte<br>ESP ja letkusuodatin | 2,4 – 4,3<br>PM 2: 140 - 220 mg/Nm3<br>PM 1: 22 – 44 mg/Nm3 | 0,2 – 0,4<br>PM2: 0,04<br>PM 1: 0,03 | | | | |

# 5 Arinapolton hiukkaspäästöt

Arinapolttolaitoksia on monen kokoluokan, aina omakotitalokattilasta isoihin yhdyskuntajätekattiloihin. Arinapolttoon sopii hyvinkin erilaisia polttoaineita, biopolttoaineet, hiili, turve, puun kuori, teollisuuden jätteet, yhdyskuntajätteet jne. joko erikseen tai yhdessä pääpolttoaineiden kanssa. Arinapoltolle on ominaista että suurin osa polttoaineen sisältämästä tuhkasta poistuu ns. tulipesätuhkana, eikä savukaasun mukana kuten pöly- ja leijupoltossa. Arinapoltossa polttoaine lämmitetään jolloin kosteus haihtuu, sen jälkeen seuraa pyrolyysi-vaihe ja haihtuvien palaminen ja lopuksi palaa jäännöshiili noin 1000 – 1100 °C lämpötilassa (Maskuniitty 1995). Yin et al. 2008 ovat koostaneet hyvän yhteenvetoartikkelin arinapoltosta, tekniikasta sekä etenkin biomassan poltosta, sen tutkimuksesta ja haasteista.

Hiukkasten muodostusmekanismeja biomassan arinapoltossa tunnetaan suhteellisen hyvin. Hiukkaset koostuvat kahdesta jakeesta, noin muutamasta mikrometristä 100 mikrometreihin kokoisista hiukkasista jotka ovat karanneet petistä sekä alle mikronin kokoisista hiukkasista jotka muodostuvat poltossa höyrystyvistä ja myöhemmin tiivistyneestä materiaalista. Pienten hiukkasten huippu on 50 nm – 300 nm välillä [Obernberger et al. 2001, Pagels et al. 2003, Yin et al. 2008,  Sippula et al. 2009,]. Jätteenpoltossa muodostuneet hiukkaset ovat 50 nm – 250 nm primaarihiukkasista koostuvia agglomeraatteja [Lind et al. 2007.]

Biomassan poltossa isot, yli mikronin, hiukkaset koostuvat ei-höyrystetystä tuhkasta ja sisältävät paljon kalsiumia (Ca), kaliumia (K) ja rikkiä (S). Alle mikronin kokoiset hiukkaset koostuvat pääosin kaliumista (K), rikistä (S) ja kloorista (Cl). Muita aineita ovat pienempiä määriä, etenkin raskasmetalleja kuten sinkki (Zn), kadmium (Cd), lyijy (Pb) ja kromi (Cr) [Pagels et al. 2003, Wierzbicka et al. 2005]. Jätteenpoltossa muodostuneet pienet hiukkaset koostuivat natriumista (Na), kaliumista (K), kloorista (Cl), sulfaatista ($SO_4$) ja lyijystä (Pb). Hiukkasissa oli myös pieniä määriä raskasmetalleja, mutta kuitenkin selvästi alle EU:n jätedirektiivin asettamat raja-arvot [Lind et al. 2007]. Hiukkasten tarkempi koostumus riippuu polttoaineesta, kuormasta sekä hiukkaskoosta. Poltettaessa polttoaineita joilla on korkea tuhkapitoisuus (esim. hakkuujätettä) muodostuu hiukkasia jotka sisältävät enemmän raskasmetalleja kun matalamman tuhkapitoisuuden polttoaineista. Isommalla kattilan kuormalla metallien pitoisuus pienhiukkasissa on isompi kuin alhaisemmalla kuormalla [Wierzbicka et al. 2005].

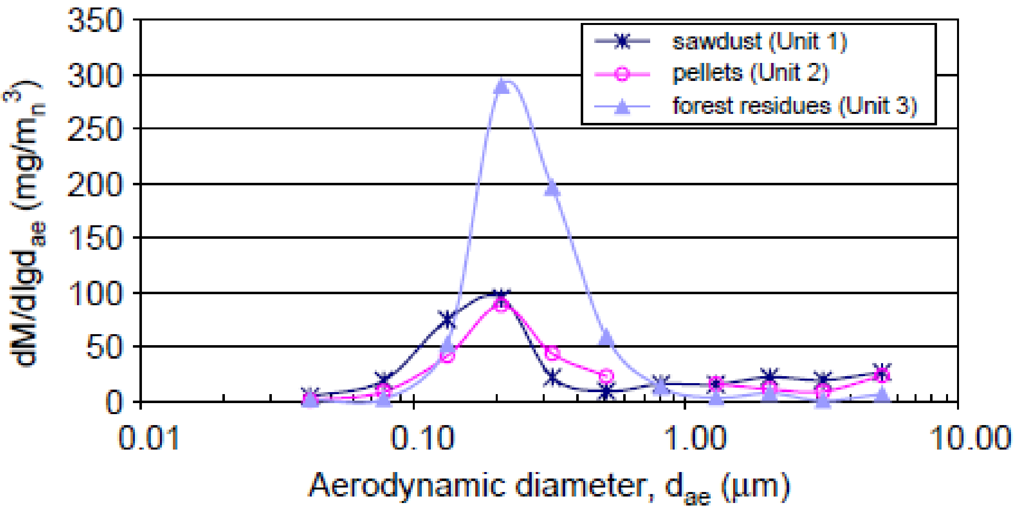
Hiukkasten massapitoisuus arinakattoiloissa ennen jälkikäsittely vaihtelevat runsaasti. Eroja syntyy itse kattilan rakenteen lisäksi myös polttoaineen laadun vaihteluista, syötön epäsäännöllisyydestä jne. Monissa etenkin pienissä arinapolttolaitoksissa jälkikäsittely puuttuu kokonaan. Alle 6 MW:n laitoksissa multisykloni on yleisin jälkikäsittely, sitä isommat laitokset ovat myös varustettu sähkösuodattimilla [Wierzbicka et al. 2005]. Näissä tuloksissa on esitetty vain mittaustuloksia missä on jatkuva poltto, joten kaikki panospoltto on rajattu pois.

Hiukkasten massapitoisuus ennen jälkikäsittelyä, joka monista pienemmistä arinapolttokattiloista kokonaan puuttuu, vaihteli erilaisten puuperäisten polttoaineiden osalta 20 - 160 mg/Nm$^3$ välillä [Obernberger et al. 2001, Strand et al. 2002, Jöller et al. 2005, Strand 2007], oljen poltossa 300 – 480 mg/Nm$^3$ (PM 1) välillä [Christensen et al. 1996]. Jätteenpoltossa kokonaishiukkaspitoisuus ennen puhdistimia oli 1200 - 1700 mg/Nm$^3$ josta PM1:stä oli 1100 - 1400 mg/Nm$^3$ [Lind et al. 2007].

Jälkikäsittelyn jälkeen mitatut massapitoisuudet vaihtelevat riippuen jälkikäsittelystä ja käytetystä polttoaineesta. Taulukosta 3 löytyy yhteenveto kirjallisuudessa olevista mittaustuloksista. Pölynerottimena arinakattiloissa on yleensä käytetty multisykloni. Multisykloneilla varustetuista arinapolttolaitoksista kokonaishiukkasmassa syklonin jälkeen vaihteli 34 - 240 mg/Nm$^3$ välillä [Johansson et al. 2003, Wierzbicka et al. 2005] riippuen polttoaineesta. Tästä PM 5 oli 51 - 120 mg/Nm$^3$ [Wierzbicka et al. 2005] ja PM 1 100 - 145 mg/Nm$^3$ [Pagels et al. 2003]. Kun multisyklonin perään lisää sähkösuodattimen päästöt vähenevät 135 mg/Nm$^3$:sta 16 mg/Nm$^3$:iin kosteaa metsäjätettä poltettaessa. Lauhduttimen jälkeen päästötaso on vielä matalampi, 8,2 mg/Nm$^3$ [Strand et al. 2002]. Jätteenpoltossa hiukkaserottimien (sähkösuodatin ja letkusuodatin) jälkeen kokonaismassapitoisuus oli enää 0,3 mg/Nm$^3$ mistä PM 1 oli alle 0,1 mg/Nm$^3$ [Lind et al. 2007].

Saksassa tehdyissä laajoissa mittauksissa hiukkasten massapitoisuus vaihteli 7 ja 251 mg/Nm$^3$ välillä riippuen mm. arinakattilan tehosta, poltto-aineesta ja hiukkaspuhdistintekniikasta. Tästä PM 10 oli 73,5 – 100 % ja PM 2,5 31,4 – 99,5 % ja PM 1 oli 13,8 – 95,6 % massasta [Ehrlich et al. 2007].

Massakokojakaumaa hallitsee yleensä pienhiukkaset [Johansson et al. 2003, Jöller et al. 2005, Wierzbicka et al. 2005]. Kuvassa 6 on esitetty esimerkki arinapoltosta mitatusta massakokojakaumasta multisyklonin jälkeen. Isommilla kuormilla myös isompien hiukkasten massa kasvaa, kun taas vaikutus pienhiukkasiin on pieni [Pagels et al. 2003].



Kuva 6: Esimerkki arinapoltossa syntyvästä massakokojakaumasta [Wierzbicka et al. 2005].

Hiukkasten lukumääräpitoisuus ennen hiukkaspuhdistimia on luokkaa $10^7$ #/$cm^3$ ja käsittelyn jälkeen (multisykloni, sähkösuodatin, lauhdutin) $2*10^6$ #/$cm^3$ [Strand et al. 2002]. Muut ovat raportoineet käsittelyn jälkeen $0,5*10^7$ - $1*10^8$ #/$cm^3$ riippuen onko mitattu kokonaishiukkaslukumäärää vai alle jonkun tietyn kokoiset hiukkaset [Johansson et al. 2003, Lillieblad et al. 2004, Wierzbicka et al. 2005, Strand 2007]. Pienhiukkaset hallitsevat myös lukumääräkokojakaumaa [Johansson et al. 2003, Wierzbicka et al. 2005]. Kattilan tehon lisäys kasvatti kokonaishiukkaslukumäärää, mutta pienhiukkasten lukumäärään vaikutus oli pieni [Lillieblad et al. 2004].

Hiukkasten pitoisuutta on yritetty myös muilla kuin suodattimilla vähentää. Lisäämällä rikkiä hiukkaspitoisuus väheni ja hiukkaset olivat isompia, mutta hiukkasissa oleva rikin määrä kasvoi merkittävästi [Strand 2007]. Hiukkaspäästöt voidaan pienentää optimoimalla polttoprosessia, mm. tarpeeksi viipymäaikaa kuumassa lämpötilassa, tehokkaalla sekoittamisella sekä polttoaineen laadulla [Johansson et al. 2003, Yin et al. 2008].

Taulukko 3: Yhteenveto kirjallisuudessa olevista arinapolttokattiloiden hiukkaspäästöistä. Mukana ovat vain sellaiset laitokset missä jälkikäsittelyä on.

| | | **Massapitoisuus Ennen ESP/ muu jälkikäsittely [mg/Nm$^3$]** | **Massapitoisuus Jälkeen ESP / muu jälkikäsittely [mg/Nm$^3$]** | **Lukumäärä-pitoisuus Ennen ESP [#/Ncm$^3$]** | **Lukumäärä-pitoisuus Jälkeen ESP [#/Ncm$^3$]** | **Kokojakauma** | **Kemiallinen koostumus** |
|---|---|---|---|---|---|---|---|
| Strand et al. 2002 | Arina<br>6 MW<br>Kostea metsätähde multicyclone +ESP+ flue gas condenser | 134<br>57 % in fine mode | After ESP: 15.8<br>After ESP + condenser: 8.2 | < 0,6 µm: 4,42*$10^7$<br>0,8-6 µm: 8,69*$10^3$ | After ESP<br>< 0,6 µm: 1,79*$10^6$<br>0,8-6 µm: 3.34*$10^2$<br>After ESP + condenser:<br><0,6 µm: 1.72*$10^6$<br>0,8-6 µm: 2.45*$10^2$ | 2 huippua 0.2 ja 2 µm | Fine fraction less than 1 micron: K, S, Cl and Zn<br>Coarse 1-6.8 microns: Ca, Fe Mn |
| Pagels et al. 2003 | Arina<br>Kostea metsätähde<br>1 MW<br>Multi-sykloni | | PM 10: 122-218<br>PM 1: 100-145 | | 17-550 nm: 4,7 – 6,8 *$10^6$<br>1-10 µm: 150 - 6100 | 2 huippua: 200 – 300 nm ja 3 µm | Fine fraction: K, S, Cl<br>Coarse fraction: Ca, K, S |
| Pagels et al. 2003 | Arina<br>Kostea metsätähde<br>6 MW | | PM 10: 157<br>PM 1: 79 | | 17-550 nm: 4.4*$10^7$<br>1-10 µm: | 2 huippua: 200 – 300 nm ja 2 µm | Fine fraction: K, S, Cl<br>Coarse fraction: Ca, K, S |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | Multi-cyclone + ESP | | | | 4800 #/cm3 | | |
| Johansson et al. 2003 | Arina<br>1,75 ja 2 MW<br>Pelletteja ja brikettejä<br>multisykloni | | 34 – 240 | | 0,5-6,5*$10^7$ | Huippu 80-200 m | |
| Lillieblad et al. 2004 | Arina<br>Kuivaa puulastua ja sahanpurua<br>1 MW<br>multisykloni | | 50-75 | | ~1 *$10^8$ | 2 huippua: 100 – 200 nm ja 2 – 3 µm | |
| Wierzbicka et al 2005 | Arina<br>metsätähde, pellets, sawdust<br>1-1.5 MW<br>multisykloni | | 101-153<br>PM 5: 51-120 | | PM5: 6.3-7.7*$10^7$ | 2 huippua: 200 – 300 nm ja 3 – 4 µm | PM 1: Na, K, Cl, SO4, Cu, Pb<br>Coarse mode: also Al and Fe |
| Strand 2007 | Arina<br>märkä sahapuru<br>7 MW<br>multisykloni | PM1: 45-55<br>S-lisäys: 58 – 96 | | | 20-470 nm<br>4-4.5*$10^7$<br>S-lisäys: 3-3.6*$10^7$ | 2 huippua: 200 – 300 nm ja 2 µm | |
| Wilen et al 2007 | Arina<br>10MW, sahanpurua, kuorta, rakennusjätettä | 2200-3800<br>PM2: 210-460<br>PM1: 140-340 | 0,1<br>PM2: 0,03<br>PM1: 0,04 | | | 2 huippua: 500 nm ja 5 µm | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | sykloni + ESP | | | | | | |
| Lind et al. 2007 | Arina<br>18 MW<br>Yhdyskuntajätettä<br>ESP + letkusuodatin | 1200 – 1700<br>PM 1: 1000-1400 | 0.3<br>PM 1: alle 0.1 | | | 1 huippu: 600 nm | |

# 6 Meesauunin hiukkaspäästöt

Meesa on kiinteässä olomuodossa olevaa kalsiumkarbonaattia ($CaCO_3$), joka syntyy keitto- eli valkolipeän valmistuksessa ja joka erotetaan valkolipeästä suodattamalla. Kaustisointiprosessissa syntyvää meesa pelkistetään takaisin kalkiksi lämmittämällä meesaa pitkässä pyörivässä meesauunissa 1000 - 1300 °C lämpötilassa [Uusitalo 2009].

Suurimmat päästöt ilmaan meesauunista ovat rikkidioksidi, typpioksideja, pelkistyneitä haisevia rikkiyhdisteitä sekä hiukkasia. Hiukkaset koostuvat kalkkipölystä sekä kondensoituneesta natriumista [IPPC, 2001].

Meesauunien hiukkaspäästöistä löytyy vain vähän mittausdataa. Botnia Rauman meesauunista kokonaispölypäästöt 2007 tehdyissä mittauksissa olivat 6 mg/Nm$^3$, mistä PM 10 oli 4 mg/Nm$^3$. Laitoksella oli käytössä sähkösuodatin ja venturipesuri [Talaslahti 2010]. Pietarsaaressa UPM:n tehtaalla kokonaispöly oli 2004 tehdyissä mittauksissa 16 mg/Nm$^3$, mistä PM10 oli 3 mg/Nm$^3$ [Nordbäck 2010]. Sähkösuodattimien uusimisen jälkeen massapitoisuudet on raportoitu olevan 2 – 8 mg/Nm$^3$, mistä PM 10 raportoitiin olevan alle 0,33 mg/Nm$^3$ [Poulsen ja Lund 2006]. Mutta myös isompia massapitoisuuksia on raportoitu, sähkösuodattimien jälkeen 20 - 150 mg/Nm$^3$ ja märkäpesurien jälkeen 200 – 600 mg/Nm$^3$ [IPPC, 2001].

# 7 Hiukkaspäästöjen haitallisuus

On tunnettu jo vuosikymmeniä että ilmassa olevat saastehiukkaset lisäävät kuolleisuutta ja aiheuttavat terveyshaittoja, mm. keuhko ja sydänoireita sekä syöpää. Suurin osa ulkoilman pienhiukkasista on peräisin erilaisista polttoprosesseista.

Yli 10 mikronin hiukkaset jäävät pääasiassa ylähengitysteiden limakalvoille, kun taas sitä pienemmät hengitettävät hiukkaset eli PM 10-hiukkaset kulkeutuva syvemmälle. Alle 2,5 µm:n pienhiukkaset pääsevät tunkeutumaan aina keuhkorakkuloihin saakka.

Terveyshaitat on todettu olevan sidoksissa PM10, PM 2,5 sekä sulfaattihiukkasiin, ja näistä kaikkein eniten PM 2,5:een. Haitat ilmenevät sekä lyhyt että pitkäaikaisissa altistuksessa ja pitoisuus-vaste funktio on lineaarinen ilman selkeätä kynnysarvoa. Hiukkasten aiheuttamien terveysvaikutusten tarkkaa syytä ei vielä tiedetä, mutta erilaisia mekanismejä on ehdotettu, mm. oxidatiivinen stressi, tulehdus, haitallisia muutoksia sydämen autonomisiin tomintoihin sekä systeeminen translokaatio [Pope ja Dockery 2006].

Tärkeimmät ominaisuudet hiukkasissa jotka vaikuttavat terveysvaikutuksiin ovat hiukkasten koko ja pinta-ala, sekä kemiallinen koostumus (etenkin orgaaniset aineet ja metallit) [Donaldson et al. 2005]. Eri polttoprosesseista peräisin olevilla hiukkasilla on löydetty vasteita solu ja eläinkokeissa, esim. puun poltosta peräisin olevat hiukkaset on havaittu aiheuttavan DNA vaurioita ja tulehdusvasteita [Karlsson et al. 2006, Kocbach Bolling et al. 2009, Jalava et al. 2010] dieselhiukkasilla on vaikutuksia mm. tulehdusvasteisiin keuhkosoluissa [Sydbom et al. 2001] sekä poltto-öljyn ja hiilen sekapoltosta syntyneillä hiukkasilla vaikutuksia keuhkosolujen metabolismiin [Okeson et al. 2003].

Tutkimuksissa on havaittu että puun poltosta peräisin olevat hiukkaset ovat pahempia kuin ajoneuvoista peräisin olevat, kun on kyseessä keuhkosyövän kehittymisestä [Høgh Danielsen et al. 2009]. Toisissa tutkimuksissa taas tulehdusaktiivisuus oli pienempi puun poltosta peräisin olevilla hiukkasilla kuin kadulta kerätyillä hiukkasilla [Karlsson et al. 2006].

Useimmissa tutkimuksissa ei ole otettu huomioon poltto-olosuhteet jotka vaikuttavat hiukkasten kokoon, kemialliseen koostumukseen ja näin ollen myös vasteeseen. Myös koko-luokittelua on harvemmin tehty. Tähän on alettu kiinnittää huomiota vasta viime aikoina.

Hiilen pölypoltosta peräisin olevilla ultrapienillä hiukkasilla (< 100 nm) on havaittu suuresti kasvanut todennäköisyys aiheuttaa keuhkotulehdusta ja makrofagien kuolemaa kuin pienillä (PM 2,5) sekä isommilla (> PM 2,5) hiukkasilla. Todennäköisin syy tähän kasvaneeseen riskiin on hiukkasten iso pinta-ala, koska niihin ei ollut rikastunut myrkyllisiä metalleja [Gilmour et al. 2004].

Jalava et al. 2010 tutkivat miten erilaiset poltto-olosuhteet vaikuttavat hiukkasten aiheuttamaan vasteeseen. He havaitsivat että puun pienpoltossa huonon polton hiukkaset aiheuttavat solukuolemaa ja DNA-vaurioita ihmisen keuhkoepteelisolujen viljelmissä matalampina annoksina kuin tavanomaisen polton hiukkaset. Toisaalta Karlsson et al. 2006 ei huomanneet eri poltto-olosuhteista peräisin olevilla hiukkasilla juurikaan eroja genotoksisuudessa.

# 8 Yhteenveto

Tässä raportissa on tarkasteltu metsäteollisuuden hiukkaspäästöt ja niiden haitallisuus kirjallisuuden avulla. Eri polttotekniikoilla muodostuvien hiukkasten muodostumismekanismeja tunnetaan suhteellisen hyvin. Ennen jälkikäsittelyä hiukkasten massapitoisuus on suurin soodakattiloissa, pitoisuudet ovat myös korkeat leijupoltossa kun taas arinapoltossa massapitoisuus on huomattavasti alhaisempi. Sähkösuodatin tai muu jälkikäsittely vähentää tehokkaasti päästöjä jopa alle 1 mg/Nm$^3$ tasolle. Usein hiukkaserotuslaitteistojen erotustehokkuus kokonaismassasta on yli 95 % ja jopa yli 99 %, mutta 0,1 – 1,0 µm hiukkasilla sähkösuodattimen erotustehokkuus on huonompi, vain noin 90 %.

Hiukkasten massakokojakaumat eri polttotekniikoista eroaa toisistaan. Soodakattiloiden hiukkasten massakokojakaumassa on yksi huippu noin 1 µm kohdalla, kun taas niin leijupoltossa kun arinapoltossa syntyy kaksihuippuinen massakokojakauma. Leijupoltossa isot yli mikronin hiukkaset dominoivat massakokojakaumaa, kun arinapoltossa pienet alle mikronin hiukkaset dominoivat jakaumaa.

Lukumääräpitoisuuksia ja lukumääräkokojakaumia on mitattu huomattavasti vähemmän, koska perinteisesti päästötasot on määritelty massan avulla.

Meesauunien päästöistä on niukasti tietoa, päästötasoa tiedetään mutta esim. kokojakaumaa ei ole tiedossa.

Polttoperäisillä hiukkasilla on todettu olevan terveysvaikutuksia, mutta niiden tarkkaa syytä ei tiedetä. Osittain tulokset ovat myös ristiriitaisia. Soodakattiloiden ja meesauunien hiukkasten terveysvaikutuksista ei ole tietoa lainkaan. Voidaan olettaa soodakattilan hiukkasten aiheuttavan terveysvaikutuksia koska muilla polttoperäisillä hiukkasilla on todettu terveysvaikutuksia ja sen lisäksi soodakattiloista peräisin olevat hiukkaset sisältävät raskasmetalleja.

# Lähdeviitteet

Christensen K.A., Livbjerg H. (1996) A field study of submicron particles from the combustion of straw. Aerosol Science and Technology, 25, pp. 185 – 199.

Dekati Ltd. (2010). www.dekati.com

Donaldson K., Tran L., Jimenez L.A., Duffin R., Newby D.E., Mills N., MacNee W., Stone V. (2005) Combustion-derived nanoparticles: A review of their toxicology following inhalation exposure. Particle and Fibre Toxicology, 2.

Ehrlich C., Noll G., Kalkoff W.-D., Baumback G., Dreiseidler A. (2007) PM 10, PM 2.5 and PM 1.0 – Emissions from industrial plants – Results from measurment programmes in Germany. Atmospheric Environment, 41, pp. 6236 – 6254.

www.finlex.fi - Finlex 1017/2002. [viitattu 18.5.2010]

Gilmour M.I., O'Connor A., Dick C.A.J., Miller C.A., Linak W.P. (2004) Differential pulmonary inflammation and in vitro cytotoxicity of size-fractionated fly ash particles from pulverized coal combustion. Journal of the Air & Waste Managment Association, 54, pp. 286 – 295.

Hokkinen J., Jokiniemi J., Aurela M., Hillamo R. (2004) Energiatuotannon ja prosessiteollisuuden pienhiukkas- ja raskasmetallipäästöjen karakterisointi. VTT Tiedotteita 2258.

Hupa M. ja Hyöty P. (1995) Mustalipeän poltto ja soodakattila, kirjassa Poltto ja palaminen, luku 17. International Flame Research Foundation, Suomen kansallinen osaston. ISBN 951-666-448-2.

Hyyppänen T. ja Raiko R. (1995) Leijupoltto, kirjassa Poltto ja palaminen, luku 16. International Flame Research Foundation, Suomen kansallinen osaston. ISBN 951-666-448-2.

Høgh Danielsen P., Loft S. Kocbach A., Schwarze P.E:, Møller P. (2009) Oxidative damage to DANN and repair induced by Norwegian wood smoke particles in human A549 and THP-1 cell lines. Mutation Reseach/Genetic Toxicology and Environmental Mutagenesis, 674, pp. 116 – 122.

IPPC (2001) Integrated Pollution Prevenation and Control. Reference document on best available techniques in the pulp and paper industry.

European Commission. Verkkojulkaisu, saatavilla: ftp://ftp.jrc.es/pub/eippcb/doc/ppm_bref_1201.pdf

Jalava P.I., Salonen R.O., Nuutinen K., Pennanen A.S., Happo M.S., Tissari J., Frey A., Hillamo R., Jokiniemi J., Hirvonen M-R. (2010) Effect of combustion condition on cytotoxic and inflammatory activity of residential wood combustion particles. Atmospheric Environment, 44, 1691 – 1698.

Johansson L.S., Tullin C., Leckner B., Sjövall P. (2003) Particle emsission from biomass combustion in small combustors. Biomass and Bioenergy, 25, pp. 435 – 446.

Jokiniemi J.K., Lind T., Hokkinen J., Kurkela J., Kauppinen E.I. (2001) Modelling and experimental results on aerosol formation, deposition and emissiosn in fluidized bed combustion of biomass. In Aerosols from Biomass Combustion Ed. Thomas Nussbaumer. ISBN 3-908705-00-2.

Jöller M., Brunner T., Obernberger I. (2005) Modeling of aerosol formationd during biomass combustion in grate furnaces and comparison with measurements. Energy & Fuels, 19, pp. 311 – 323.

Karlsson H.L., Ljungman A.G., Lindbom J. Möller L. (2006) Comparison of genotoxic and inflammatory effect of particles generated by wood combustion, a road simulator and collected from street and subway. Toxicology Letters, 165, pp. 203 – 211.

Kauppinen E.I. (1991) On the determination of continuous submicron liquid aerosol size distribution with low pressure impactors. Aerosol Science and Technology, 16, pp. 171 – 197.

Keskinen J., Pietarinen K., Lehtimäki M. (1992) Electrical low pressure impactor. Journal of Aerosol Science, 23 pp. 353 – 360.

Khan A.A., de Jong W., Jansens P.J., Spliethoff H. (2009) Biomass combustion in fluidized bed boilers: Potential problems and remedies. Fuel Processing Technology, 90, pp. 21 – 50.

Kocbach Bølling A., Pagels J., Yttri K.E., Barregard L., Sallsten G., Schwarze P.E. Boman C. (2009) Health effects of residential wood smoke particles: the importance of combustion conditions and physicochemical particle properties. Particle and Fibre Toxicology, 6:29.

Latva-Somppi J., Moisio M., Kauppinen E.I., Valmari T., Ahonen P., Tapper U., Keskinen J. (1998) Ash formation during fluidized-bed incineration of paper mill waste sludge. Journal of Aerosol Science, 29, pp. 461 – 480.

Lillieblad L., Szpila A., Strand M., Pagels J., Rupar-Gadd K., Gudmundsson A., Swietlicki E., Bohgard M., Sanati M. (2004) Boiler operation influence on the emissions of submicrometer-sized particles and polycyclic aromatic hydrocarbons from biomass-fired grate boilers. Energy & Fuels, 18, pp. 410 – 417.

Lind T., Kauppinen E.I., Kurkela J.,Maenhaut W., Shsh A., Huggins F. (1995) Mineral, Sorbent and Sulfur interactions in Real-Scale CFBC. Proceedings of the 13th International Conference in Fluidised Bed Combustion. Heinschel Key J. (Ed.). ASME, pp. 1129 – 1136.

Lind T., Valmari T., Kauppien E.I., Sfiris G., Nilsson K., Maenhaut W. (1999) Volatilization of the heavy metals during circulating fluidized bed combustion of forest residue. Environmental Science and Technology, 33, pp. 496 – 502.

Lind T. (1999) Ash formation in circulating fluidised bed combustion of coal and solid biomass. Ph.D. Thesis. VTT Publications 378.

Lind T., Hokkinen J., Jokiniemi J.K., Hillamo R., Makkonen U., Raukola A., Rintanen J. Saviharju K. (2006) Electrostatic precipitator performance and trace element emissions from two kraft recovery boilers. Environmental science & technology, 40, pp. 584-589.

Lind T., Hokkinen J., Jokiniemi J. (2007) Fine particle and trace element emissions from waste combustion – Comparison of fluidized bed and grate firing. Fuel Processing Technology 88 (2007) pp. 737 – 746.

Maaskola T. (2002) Puun ja turpeen sekapolton vaikutus leijukerroskattilan hiukkaspäästöihin. Diplomityö, Lappeenrannan teknillinen korkeakoulu.

Maskuniitty H. (1995) Arinapoltto, kirjassa Poltto ja palaminen, luku 15. International Flame Research Foundation, Suomen kansallinen osaston. ISBN 951-666-448-2.

Metsäteollisuus r.y. (2009). Metsäteollisuuden ympäristötilastot vuodelta 2008. Helsinki

Mikkanen P., Kauppinen E.I., Jokiniemi J.K., Sinquefield S.A., Frederick W.J. (1995) Bimodal fume particle size distributions from recovery boiler and laboratory scale black liquor combustion. TAPPI Journal 77, pp. 81-84.

Mikkanen P., Kauppinen E.I., Pyykönen J., Jokiniemi J.K., Mäkinen M. (1996) Alkali salt ash formation during black liquor combustion at kraft recovery boilers. Teoksessa Applications of Advanced Technology to Asah-Related Problems in Boilers. Edited by L. Baxter ja D. DeSollar.

Mikkanen P. (2000) Fly ash particle formation in kraft recovery boilers. Ph.D. Thesis. VTT Publications 421.

Moisio M. (1999). Real time size distribution measurement of combustion aerosols. Ph. D. Thesis. Tampere University of Technology, Publications 279.

Nordbäck K. (2010) Sähköposti 27.4.2010.

Obernberger I., Brunner T. Jöller M. (2001) Characterisation and formation of aerosols and fly-ashes from fixed-bed biomass combustion. In Aerosols from Biomass Combustion Ed. Thomas Nussbaumer. ISBN 3-908705-00-2.

Okeson C.D., Riley M.R., Fernandez, A., Wendt J.O.L. (2003) Impact of the composition of combustion generated fine particles on epithelial cell toxicity: influences of metals on metabolism. Chemosphere, 51, pp. 1121 – 1128.

Pagels J., Strand M., Rissler J., Szpila A., Gudmundsson A., Bohgard M., Lillieblad L., Sanati M., Swietlicki E. (2003) Characteristics of aerosol particles formed during grate combustion of moist forest residue. Journal of Aerosol Science, 34, pp. 1043 – 1059.

Pope C.A., Dockery D.W. (2006) Health effect of fine particulate air pollution: Lines that connect. Journal of the Air & Waste Management Association, 56, pp. 709 – 742.

Poulsen K.S., Lund C.R. (2006) Reduction of fine particulate emissions from ESPs. Presentation at ICESP X conference in Cairns, Australia.

Päästömittausten käsikirja, osa 1 (2004). Ilmansuojeluyhdistys ja VTT. Saatavilla www.isy.fi.

Sippula O., Hokkinen J., Puusistinen H., Yli-Pirilä P. Jokiniemi J. (2009) Particle emissions from small wood-fired district heating units. Energy & Fuels, 23, pp. 2974 – 2982.

Sydbom A., Blomberg A., Parnia S., Stenfors N., Sandström T., Dahlén S-E. (2001) Health effects of diesel exhaust emissions. European Respiratory Journal 17, pp. 733 – 746.

Strand M., Pagels J., Szpila A., Gudmundsson A., Swietlicki E., Bohgard M., Sanati M. (2002) Fly ash penetration through electrostatic precipitator and flue gas condenser in a 6 MW biomass fired boiler. Energy & Fuels, 16, pp. 1499 – 1506.

Strand M. (2007) Particulate and CO emissions from a moving-grate boiler fired with sulphur-doped woody fuel. Energy & Fuels, 21, pp. 3653 – 3659.

Talaslahti O. (2010) Sähköposti 27.4.2010.

Uusitalo A. (2009) Soodakattiloiden päästöt ilmaan. Energiatekniikan kandidaatintyö ja seminaari, Lappeenrannan teknillinen yliopisto

Valmari T., Kauppinen E.I., Kurkela J., Jokiniemi J.K., Sfiris G., Revitzer H. (1998) Fly ash formation and deposition during fluidized bed combustion of willow. Journal of Aerosol Science 29, pp. 445 – 459.

Valmari T., Lind T.M., Kauppinen E.I., Sfiris G., Nilsson K., Maenhaut W. (1999a) A field study on ash behaviour during circulating fluidized bed combustion of biomass. 1. Ash Formation. Energy and Fuels, 13, pp. 379 – 389.

Valmari T., Lind T.M., Kauppinen E.I., Sfiris G., Nilsson K., Maenhaut W. (1999b) A field study on ash behaviour during circulating fluidized bed combustion of biomass. 2. Ash deposition and alkali vapour condensation. Energy and Fuels, 13, pp. 390 – 395.

Valmari T. (2000) Potassium behaviour during combustion of wood in circulating fluidised bed power plants. Ph.D. Thesis. VTT Publications 414.

Wierzbicka A., Lillieblad L., Pagels J., Strand M., Gudmundsson A., Gharibi A., Swietlicki E., Sanati M., Bohgard M. (2005) Particle emissions from district heating units operating on three commonly used biofuels. Atmospheric Environment, 39, pp. 139 – 150.

Wilen C., Moilanen A., Hokkinen J., Jokiniemi J. (2007) Fine particle emissions of waste incineration. VTT Project report, prepared for IEA bioenergy agreement – Task 36

Yin C., Rosendahl L.A., Kaer S.K. (2008) Grate-firing of biomass for heat and power production. Progress in Energy and Combustion Science, 34, pp. 725 – 754.

www.ymparisto.fi – ympäristöluvat. [viitattu 18.5.2010]

# LIITE V

Ulrika Backman, VTT
Pienhiukkaset – esitys
YTR 25.5.2010

# Metsäteollisuuden hiukkaspäästöt

Ulrika Backman, VTT

# Johdanto

- Kirjallisuuden avulla selvitetty metsäteollisuuden hiukkaspäästöjä
- Päästölähteet:
  - Soodakattilat
  - Leijukerrospoltto
  - Arinapoltto
  - Meesauunit
- Päästöt:
  - Massapitoisuus
  - Lukumääräpitoisuus
  - Kokojakaumat
  - Kemiallinen koostumus
  - Haitallisuus
- Vain suoria päästöjä, ei sekundäärisiä hiukkasia $SO_2$ ja $NO_x$ muuntumisen kautta

# Johdanto

- Metsäteollisuuden hiukkaspäästöt ovat vähentyneet 84 % tuotettua tonnia kohti vuodesta 1992 vuoteen 2008.
- Tänä päivänä metsäteollisuuden osuus Suomen hiukkaspäästöistä on alle 10 %.
- Lainsäädäntö määrää päästöraja-arvoja yli 50 MW polttolaitoksille
    - Ei koske soodakattiloita ja meesauuneja
    - 50 mg/Nm$^3$ jos laitos 50 – 300 MW
    - 30 mg/Nm$^3$ jos laitos yli 300 MW
- Ympäristöluvissa soodakattiloille ja meesauuneille usein raja-arvona 50 mg/Nm$^3$.

# Mittalaitteet

- Massapitoisuus
  - Suodatinkeräys
  - TEOM
  - BLPI + sykloni
- Massakokojakauma
  - BLPI: 11 astetta 22 nm – 16 µm
  - DLPI: 13 astetta 30 nm – 10 µm
- Lukumääräpitoisuus
  - CPC: 5 nm –
  - ELPI: 30 nm – 10 µm

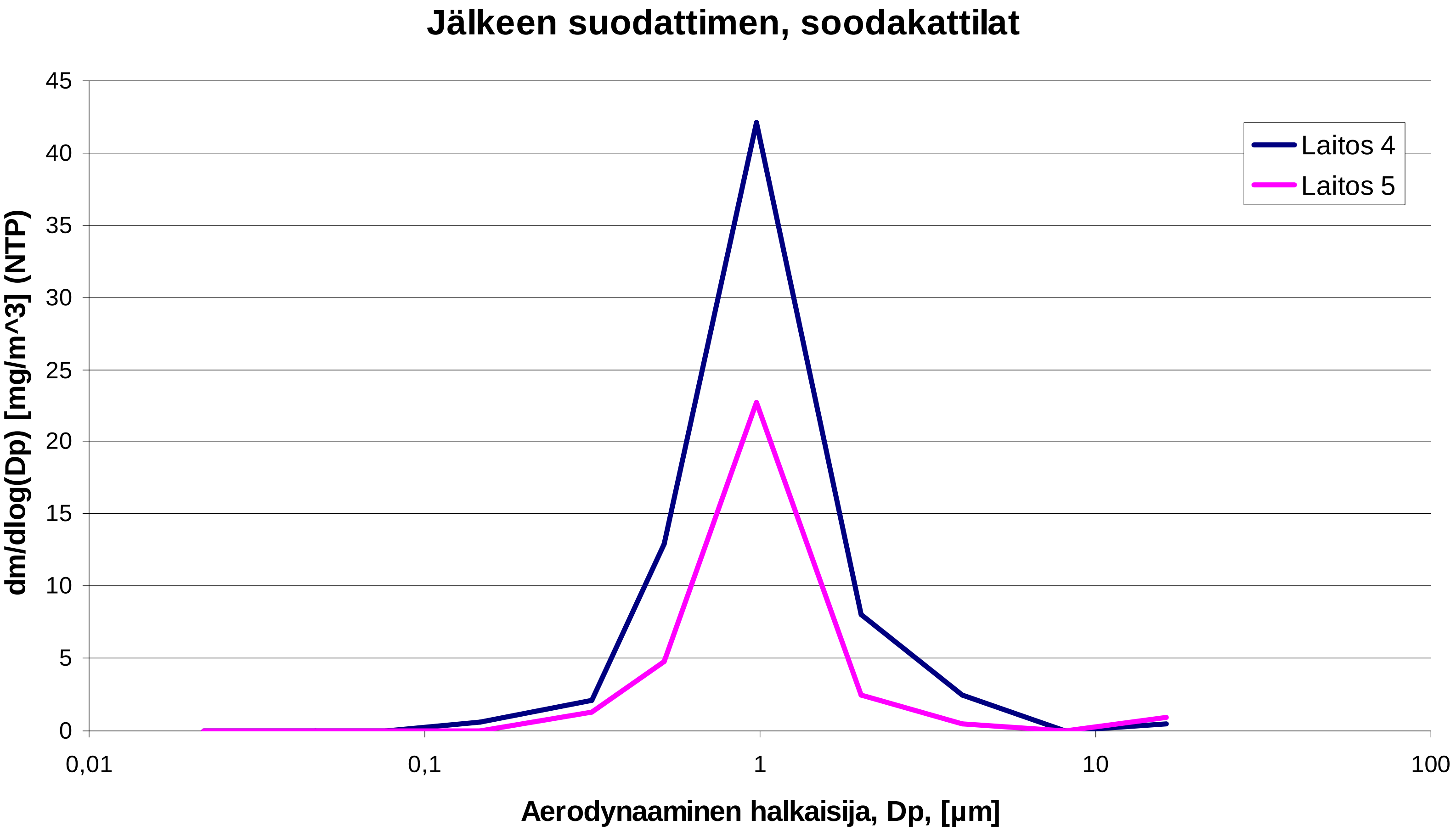
# Mittalaitteet

- Lukumääräkokojakauma
  - SMPS: 5 nm – 1 µm
  - ELPI: 30 nm – 10 µm
  - APS: 0,5 µm – 10 µm
- Kemiallinen koostumus
  - ICP-MS
  - PIXE
- Morfologia
  - SEM
  - TEM

# Soodakattilat

- Hiukkasten muodostuminen kattilassa tunnetaan hyvin
- Vähän mittausdataa saatavilla suodattimien jälkeen
- Massapitoisuus
    - Ennen suodatinta: 14 – 32 g/Nm$^3$
    - Sähkösuodattimen jälkeen: 10 – 230 mg/Nm$^3$
    - Sähkösuodattimen ja pesurin jälkeen: 80 mg/Nm$^3$
- Lukumääräpitoisuus
    - Ennen suodatinta: $10^7$ #/cm$^3$
    - Suodattimen jälkeen: $10^5$ #/cm$^3$
- Kemiallinen koostumus:
    - $Na_2SO_4$ pääosin
    - $NaCO_3$
    - K ja Cl

# Soodakattilasta mitattu massakokojakauma



Hokkinen et al. 2004

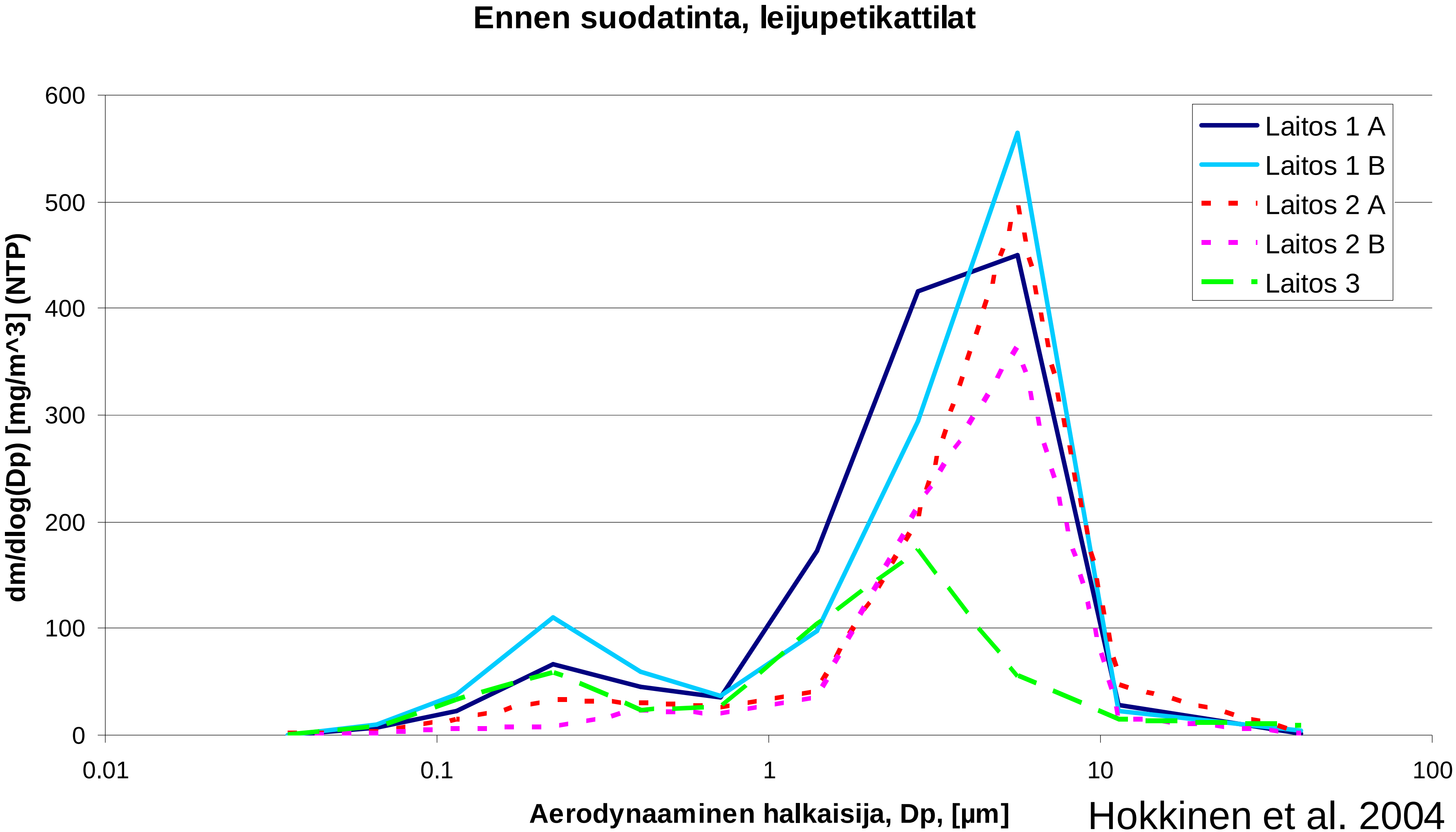
# Soodakattilat

- Ennen suodatinta
  - Massasta 59 % PM 2,5
  - Lukumäärästä 99 % PM 2,5
- Jälkeen suodattimen
  - Massasta 66 – 94 % PM 2,5
  - Lukumäärästä 99 – 100 % PM 2,5
- Hiukkaset yksittäisiä melkein pyöreitä sekä niistä koostuvia agglomeraatteja

# Leijukerroskattilat

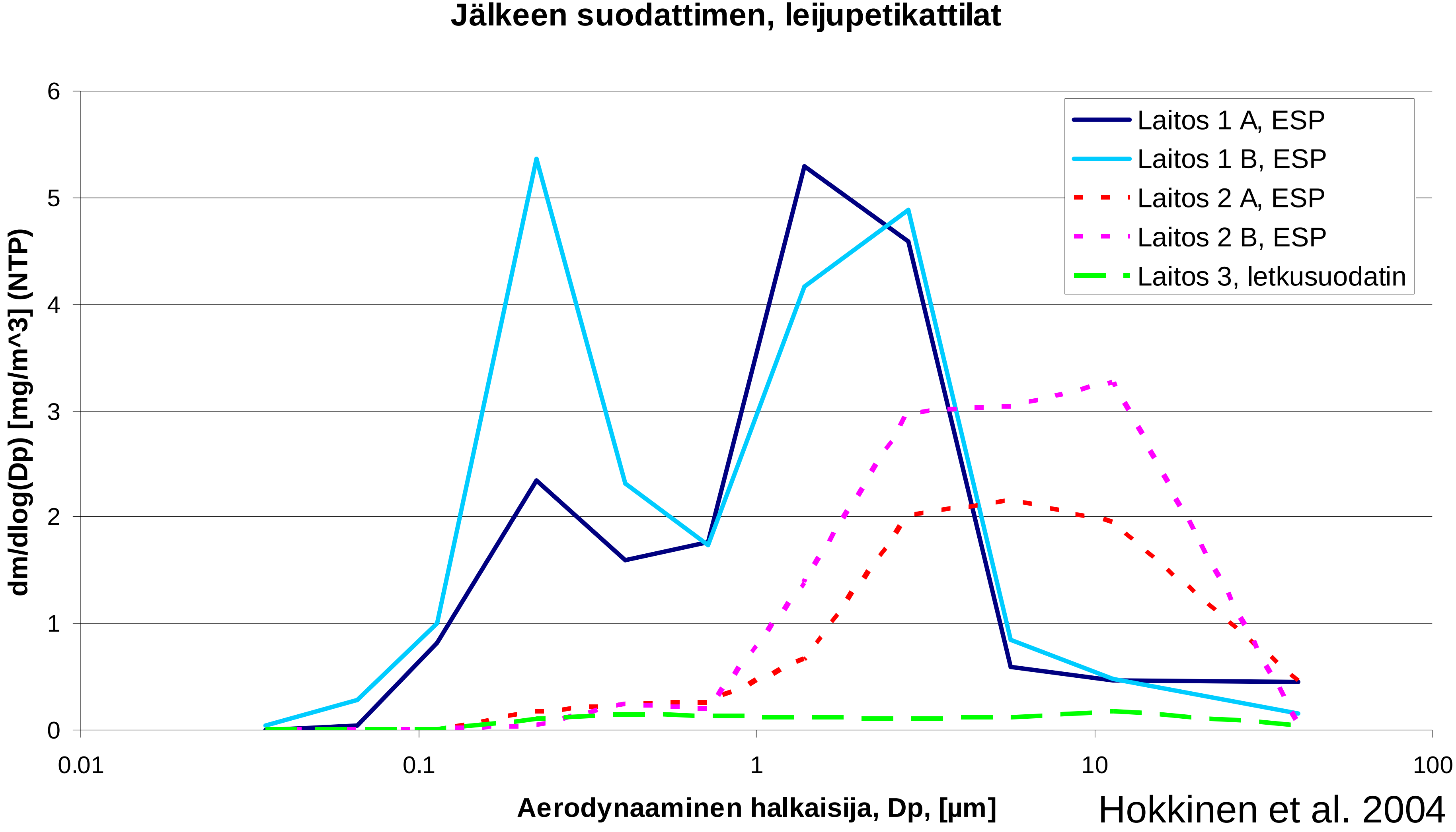
- Mittausdataa löytyy aika hyvin eri polttoaineille
- Massapitoisuus
  - Ennen suodatinta: 13 – 19 g/Nm$^3$ (hiili), 0,26 – 6,9 g/Nm$^3$ (biomassaa), 0,65 – 8,3 g/Nm$^3$ (jäte)
  - Suodattimen jälkeen: 0,2 – 145 mg/Nm$^3$
- Lukumääräpitoisuus
  - Ennen suodatinta: 10$^6$ #/cm$^3$
  - Suodattimen jälkeen: 10$^5$ #/cm$^3$

# Leijukerroskattilasta mitattu massakokojakauma



Hokkinen et al. 2004

# Leijukerroskattilasta mitattu massakokojakauma



Hokkinen et al. 2004

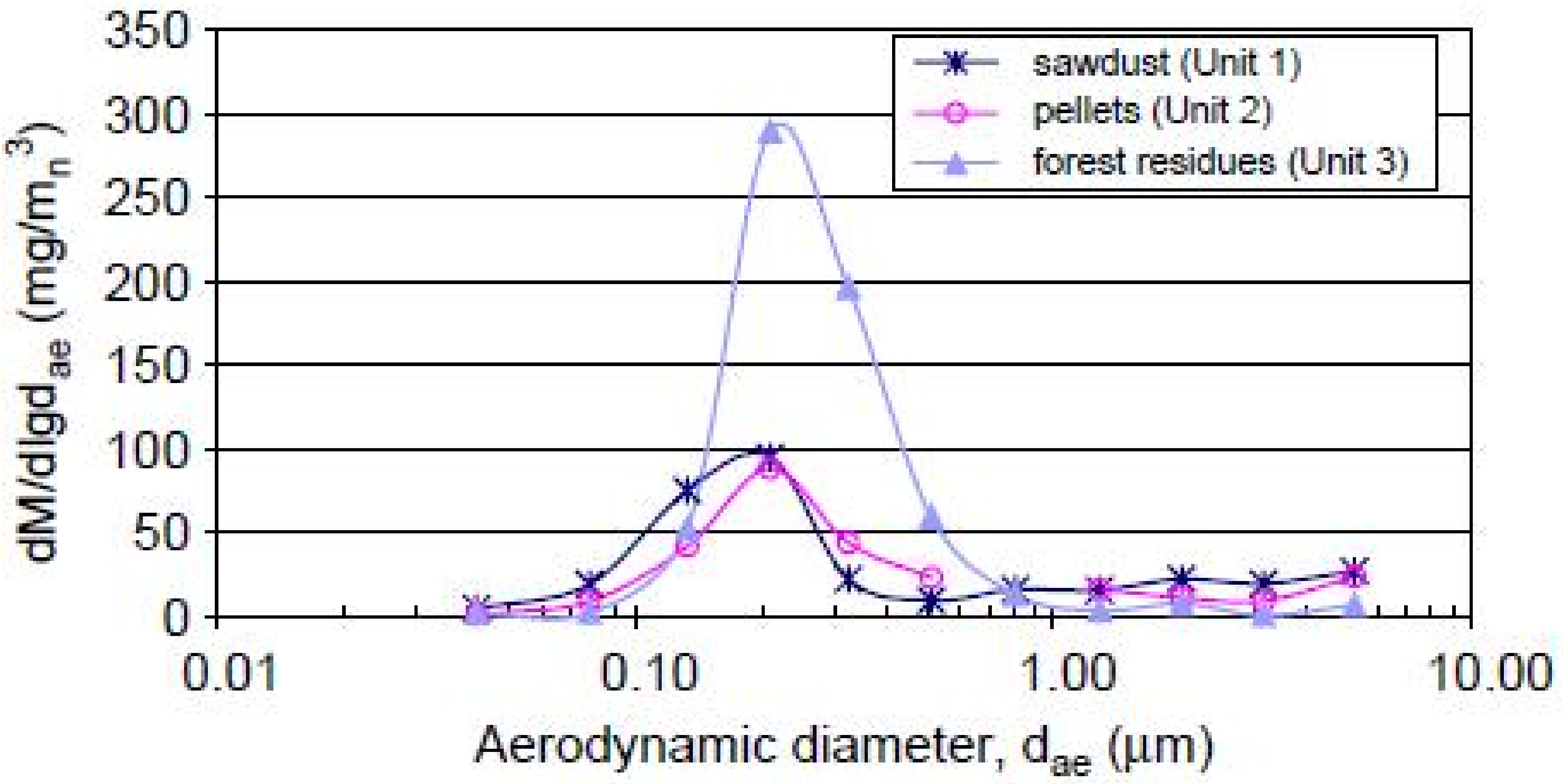
# Leijukerroskattilat

- PM 1:sen osuus hiukkasmassasta on tyypillisesti alle 5 %, mutta joskus voi olla peräti 25 %
- Kemiallinen koostumus biomassan poltossa
    - Pienet: K, Cl, S, Na ja  Ca
    - Isot: Ca, Si, K, S, Na, Al, P ja Fe
- Hiukkaset agglomeraatteja, primaarikoko 50 nm – 250 nm

# Arinakattilat

- Mittausdataa löytyy aika hyvin
- Jälkikäsittely vaihtelee: puuttuu kokonaan, multisykloni, sähkösuodatin
- Massapitoisuus
    - Ennen suodatinta: 20 – 160 mg/Nm$^3$ (puuperäistä), 1200 - 1700 mg/Nm$^3$ (jäte)
    - Multisyklonin jälkeen: 34 – 240 mg/Nm$^3$
    - Multisykloni ja ESP: 16 mg/Nm$^3$ + lauhdutin: 8,2 mg/Nm$^3$
    - ESP + letkusuodatin (jätepoltto): 0,3 mg/Nm$^3$
- Lukumääräpitoisuus
    - Ennen suodatinta: $10^7$ #/cm$^3$
    - Käsittelyn jälkeen: $10^6$ #/cm$^3$

# Arinakattilasta mitattu massakokojakauma multisyklonin jälkeen



Wierzbicka et al. 2005

# Arinakattilat

- Massakokojakaumaa hallitsee pienet hiukkaset
  - PM 2,5: 31 – 100 % massasta
  - PM 1: 14 - 96 % massasta
- Pienet hiukkaset hallitsevat myös lukumääräkokojakaumaa
- Kemiallinen koostumus biomassan poltossa
  - Pienet: K, S, Cl ja pienempiä määriä Zn, Cd, Pb, Cr
  - Isot: Ca, K, S
- Hiukkaset agglomeraatteja, primaarikoko 50 nm – 250 nm

# Meesauuni

- Vain vähän dataa saatavilla
- Massapitoisuus
  - Käsittelyn jälkeen: 6 - 16 mg/Nm$^3$ mistä PM 10 19 – 70 %
  - Isompiakin raportoitu: ESP:n jälkeen 20 – 150 mg/Nm$^3$ ja märkäpesurin jälkeen 200 – 600 mg/Nm$^3$
- Kemiallinen koostumus
  - Kalkkipöly ja natrium

# Hiukkaspäästöjen haitallisuus

- Suurin osa ulkoilma hiukkasista peräisin polttoprosesseista
- On tunnettu jo vuosikymmeniä että ulkoilman hiukkaset aiheuttavat terveyshaittoja mm. keuhko ja sydänoireita ja syöpää
- Syitä ei tarkkaan tiedetä
- Tärkeimmät hiukkasten ominaisuudet: koko, pinta-ala, kemia
- Puun poltosta peräisin olevat hiukkaset aiheuttaneet mm. DNA vaurioita ja tulehdusvasteita
- Dieselhiukkasilla mm. tulehdusvasteita keuhkosoluissa
- Puun poltosta peräisin pahempia kuin ajoneuvoista peräisin olevat kun kyseessä keuhkosyövän kehittymisestä
- Toisaalta tulehdusaktiivisuus pienempi puun polton hiukkasilla kuin kaduilta kerätyillä hiukkasilla

# Hiukkaspäästöjen haitallisuus

- Usein ei olla kiinnitetty huomiota poltto-olosuhteisiin jotka merkittävästi vaikuttavat hiukkasten ominaisuuksiin, eikä kokoluokittelua ole tehty
- Hiilen pölypoltosta peräisin olevat PM 0,1 hiukkaset suuresti kasvanut todennäköisyys aiheuttaa keuhkotulehdusta ja makrofagien kuolemaa verrattuna PM 2,5 ja isommilla
- Huonon puun pienpolton hiukkaset aiheuttivat solukuolemaa ja DNA-vaurioita keuhkosoluissa matalampina annoksina kuin tavanomaisen polton hiukkaset.
- Genotoksisuudessa ei havaittu merkittävää eroa poltto-olosuhteissa

# Yhteenveto

- Eri polttotekniikoille syntyvien hiukkasten muodostumismekanismit tunnetaan
- Ennen jälkikäsittelyä massapitoisuus on suurin soodakattilassa, myös korkeat pitoisuudet leijukerrospoltossa. Arinapoltossa selkeästi alhaisemmat
- Sähkösuodatin ja muut käsittelyt vähentävät tehokkaasti hiukkaspitoisuutta jopa alle 0,1 mg/Nm$^3$
- Erotustehokkuus yli 95 % massasta, huonoiten sähkösuodatin toimii 0,1 – 1 µm hiukkasilla

# Yhteenveto

- Massakokojakaumassa on eroja eri polttotekniikoilla
    - Soodakattilasta 1 huippu (1 µm)
    - Leijukerros 2 huippua, isot dominoi
    - Arinapoltossa 2 huippua, pienet dominoi
- Lukumääräpitoisuuksia mitattu vähän, koska päästöraja-arvot massaperusteisiä
- Meesauuneista erittäin vähän mittausdataa
- Polttoperäisillä hiukkasilla terveysvaikutuksia, mutta tarkkaa syytä ei tiedetä
- Voidaan olettaa että myös soodakattiloista peräisin olevilla hiukkasilla on terveysvaikutuksia

# VTT luo teknologiasta liiketoimintaa

# LIITE VI

Nikolai DeMartini, Åbo Akademi
NH3 Formation and Recovery in a Kraft Pulp Mill – presentation
YTR 25.5.2010

# N in Kraft Pulp Mills & Kymi Campaign

Nikolai DeMartini
Åbo Akademi University

# $NH_3$ Project

- Objective: identify the streams in a pulp mill from which $NH_3$ can be stripped and collected for use elsewhere in the mill.
- Tasks
  - One mill balance – pulp mill and chemical recovery cycle (mill with a WL oxidation system & biosludge addition) (~50 samples)
  - Laboratory tests for stripping of $NH_3$ from white liquor at 3 temperatures

# Content

- Review on N in Kraft Pulp Mills
  - 3 Mill balance in EU for N + some data from Finnish Recovery Boiler balances
  - Key factors in N balances
- Conclusions
- Kymi mill campaign

# Nitrogen in a Pulp Mill

1. Pulping
2. Evaporation
3. Black Liquor Combustion
4. Recausticizing
5. Total $NH_3$ and NO emissions
6. Biosludge

# Nitrogen forms in the Pulp Mill

- Organic
  - Proteins and protein fragments, amino acids, volatile organic compounds

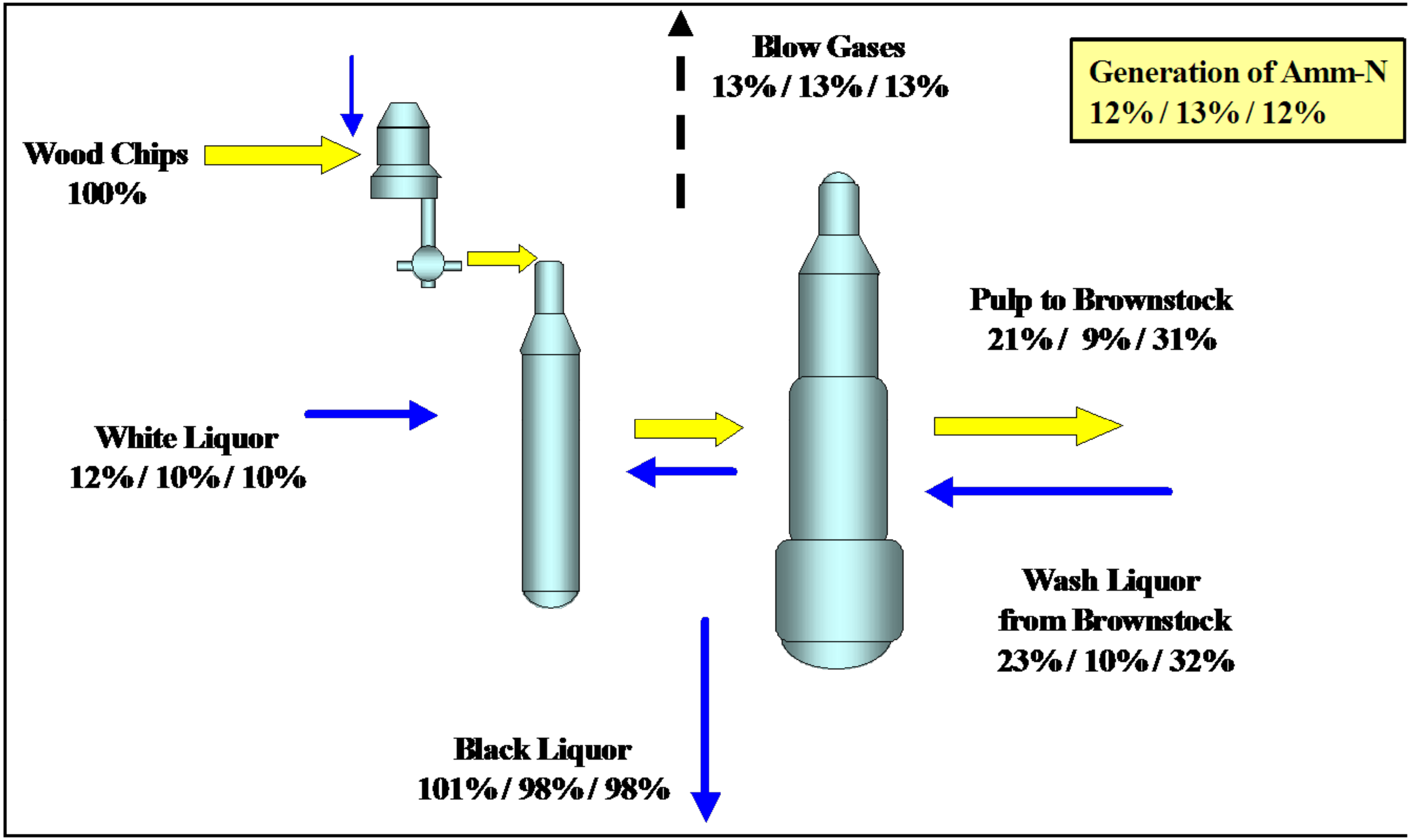
- Inorganic
  - $NH_3$, NO
  - Cyanate $^{-}O\text{-}C\equiv N$ & $O=C=N^{-}$

# Three European Kraft Pulp Mills

| Mill | Production (Adt/d) | Wood Pulped | N content of wood (mg N/kg d.s.) |
|---|---|---|---|
| A | 1000 | 80% Spruce + 20% Pine | 1,1 |
| B | 900 | Eucalyptus | 0,7 |
| C | 1200 | 80% Birch + 20% Aspen | 1,2 |
|  | 110 | Sawdust | 1,7 |

*None of the mills had biosludge addition to BL at time of campaigns

# Nitrogen in Pulping (3 mills) – EU Rempulp



**Blow Gases**
13% / 13% / 13%

**Generation of Amm-N**
12% / 13% / 12%

**Wood Chips**
100%

**Pulp to Brownstock**
21% /  9% / 31%

**White Liquor**
12% / 10% / 10%

**Wash Liquor from Brownstock**
23% / 10% / 32%

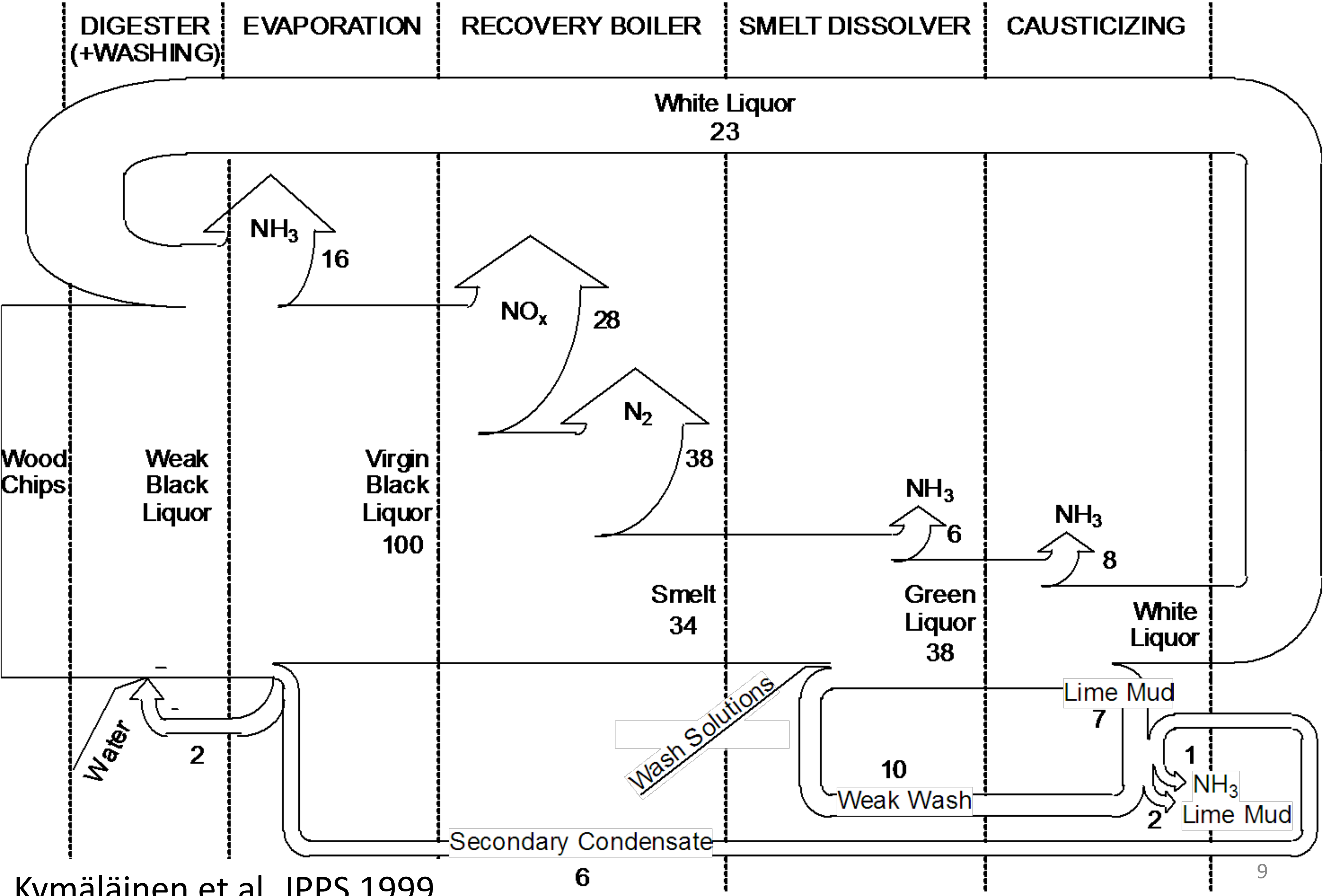
**Black Liquor**
101% / 98% / 98%

DeMartini et al. ICRC 2004

# Summary N in Pulping

- $\text{Flow}_{\text{N,wood}} = \text{Flow}_{\text{N,BL}}$
- $\text{Flow}_{\text{N,pulp}}$ ~0 (very low)
- ~10% of wood N is recycled back to the digester with the white liquor
- $\text{Flow}_{\text{N,WL}}$ ~$\text{Flow}_{\text{N,blow gases}}$
- 10-15% of the N in wood forms $NH_3$ during pulping

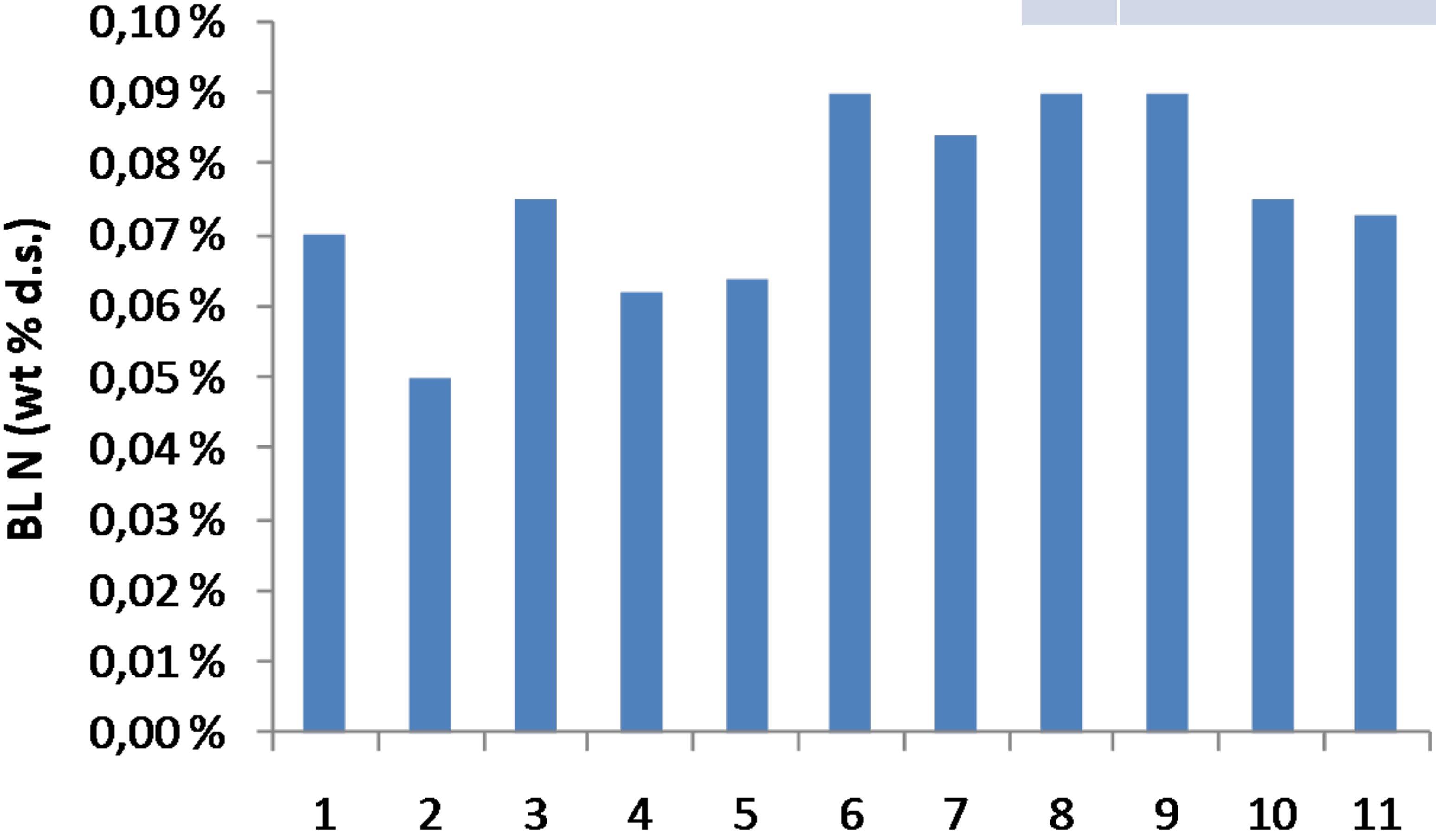
# N in the Chemical Recovery Cycle



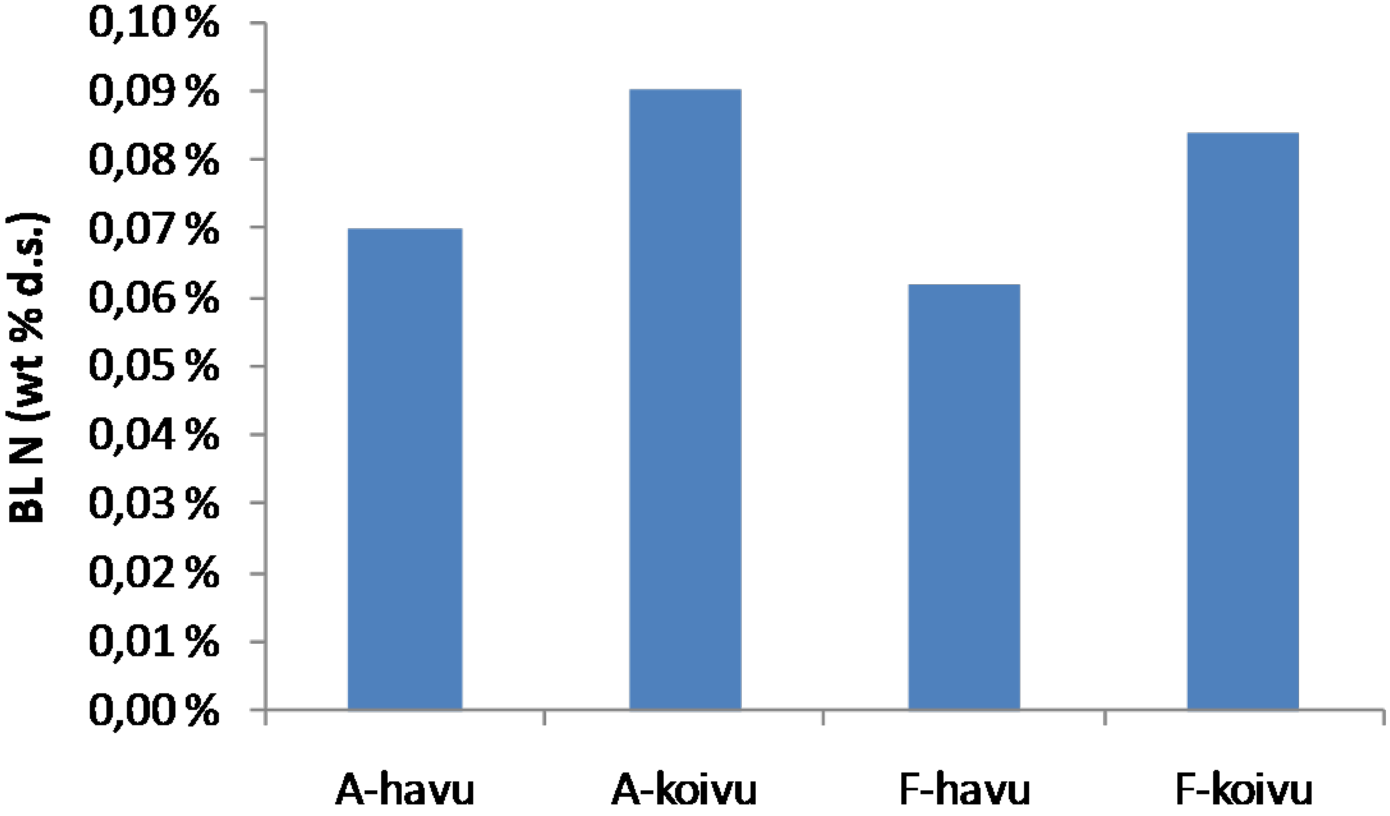
Kymäläinen et al. JPPS 1999

# BL Nitrogen Content

| BL | Wood Pulped |
|---|---|
| 1-5 | havu |
| 6-7 | koivu |
| 8-9 | koivu, haapa, sahanpuru |
| 10 | havu, koivu |
| 11 | havu, koivu, eukalyptus |

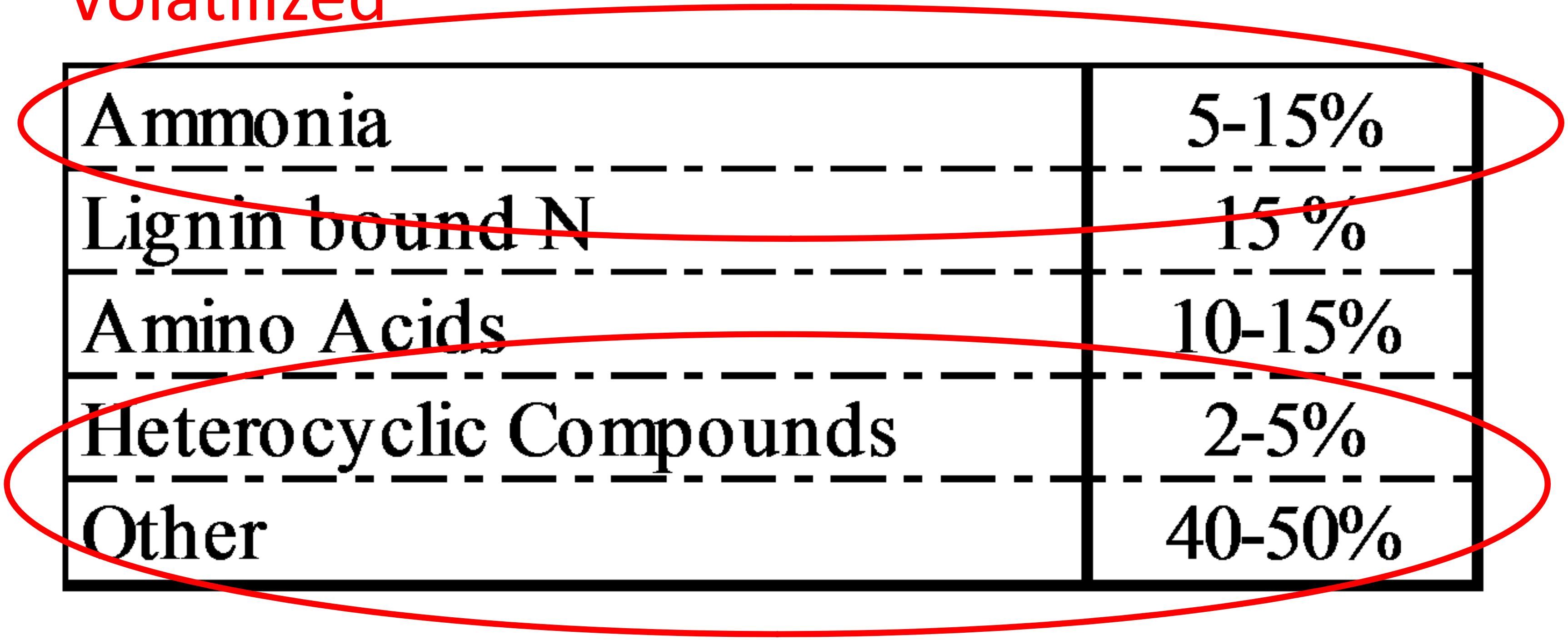


# BL-N Content (havu vs koivu)



# N in Weak BL

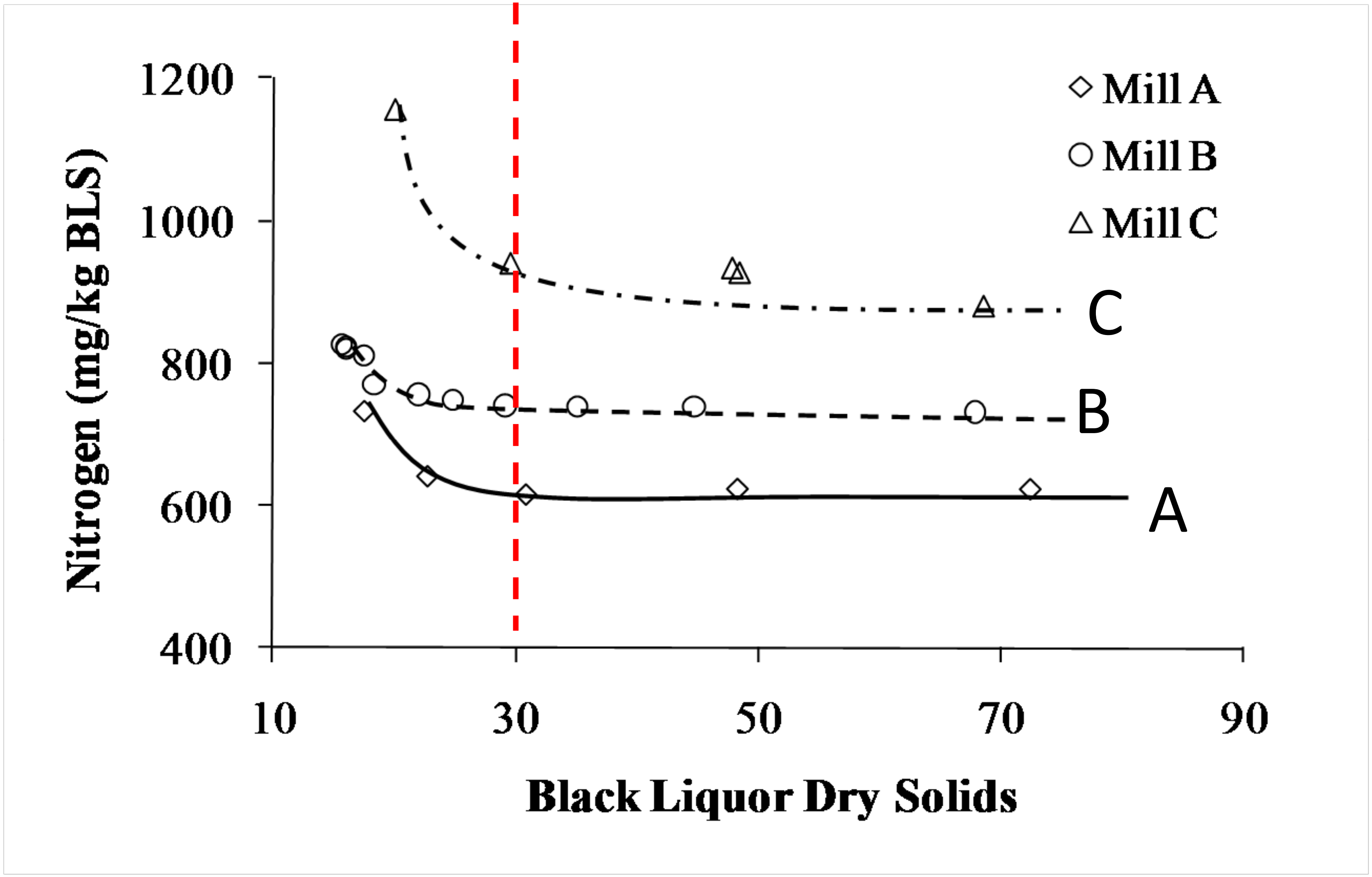
Volatilized



| | |
|---|---|
| Ammonia | 5-15% |
| Lignin bound N | 15 % |
| Amino Acids | 10-15% |
| Heterocyclic Compounds | 2-5% |
| Other | 40-50% |

Small % volatilized

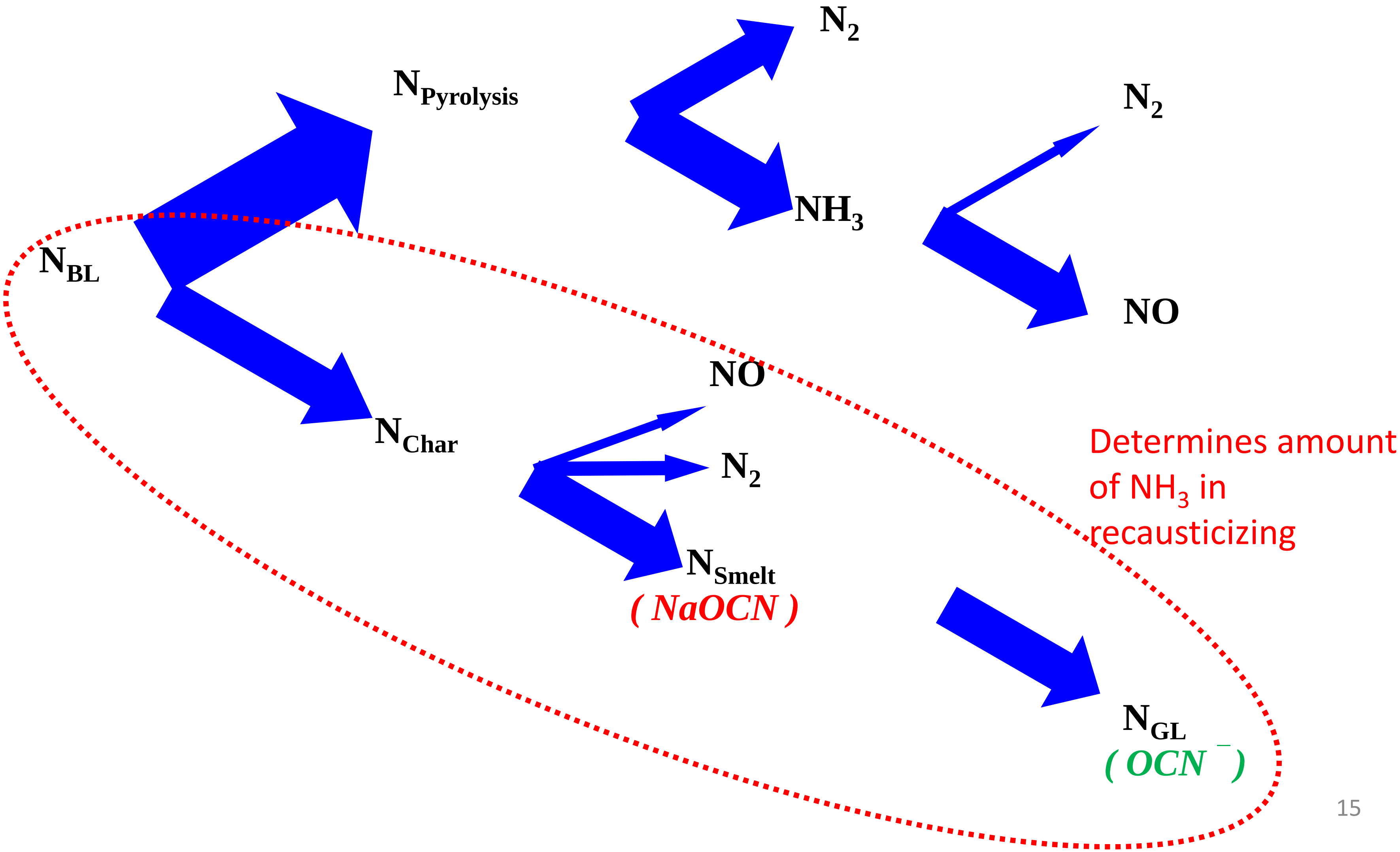
# Mill Balance: Evaporation



# N in Evaporation

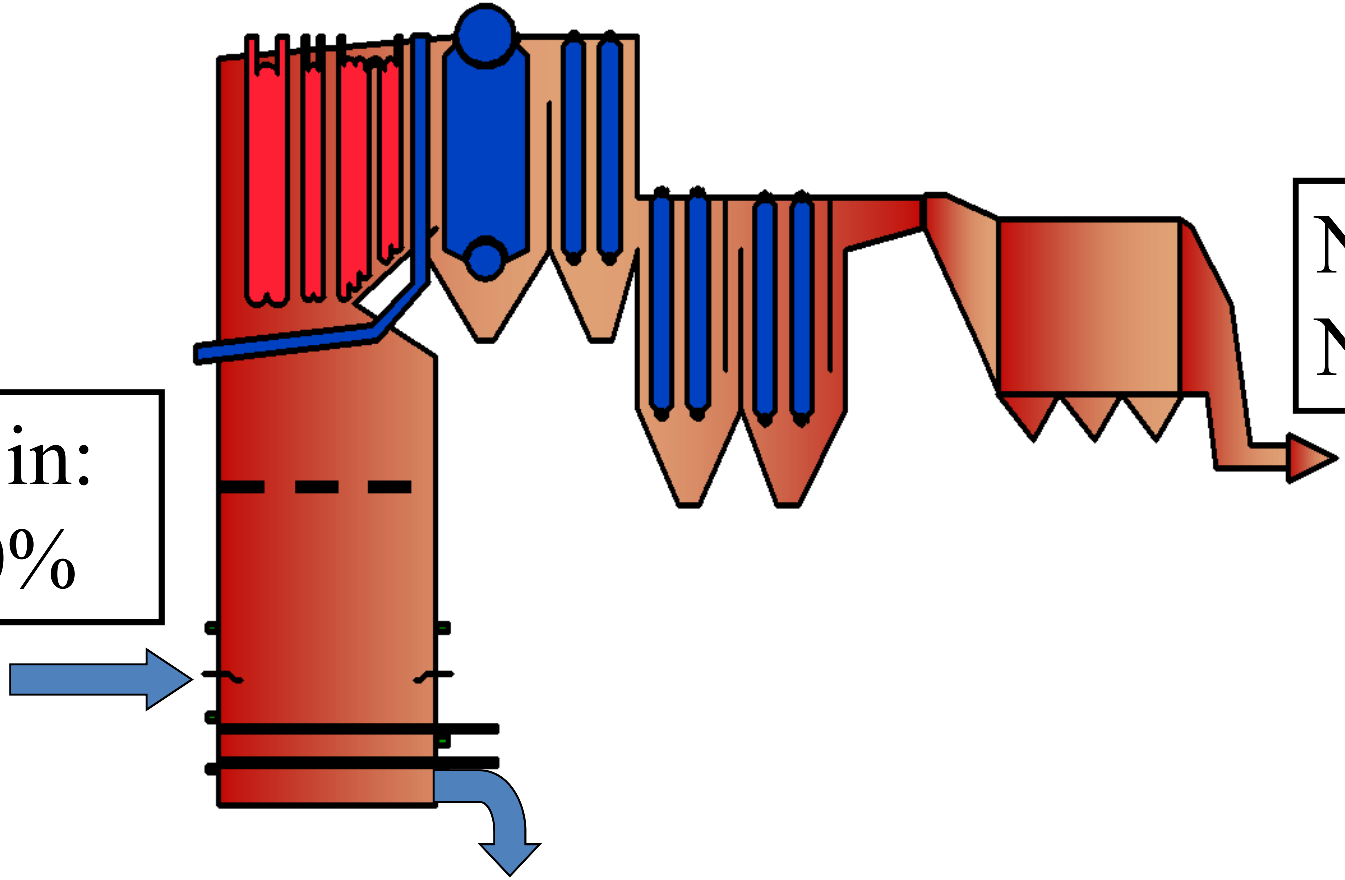
- 10-20% of total N is volatilized
- Up to 10% more ammonia formed during evaporation (seen in laboratory tests + appears at least partially consistent with mill balances)
- Volatile N is released by 30% d.s.

# N Distribution in BL Combustion



Determines amount of $NH_3$ in recausticizing

# Mill Balance: RB Mill C



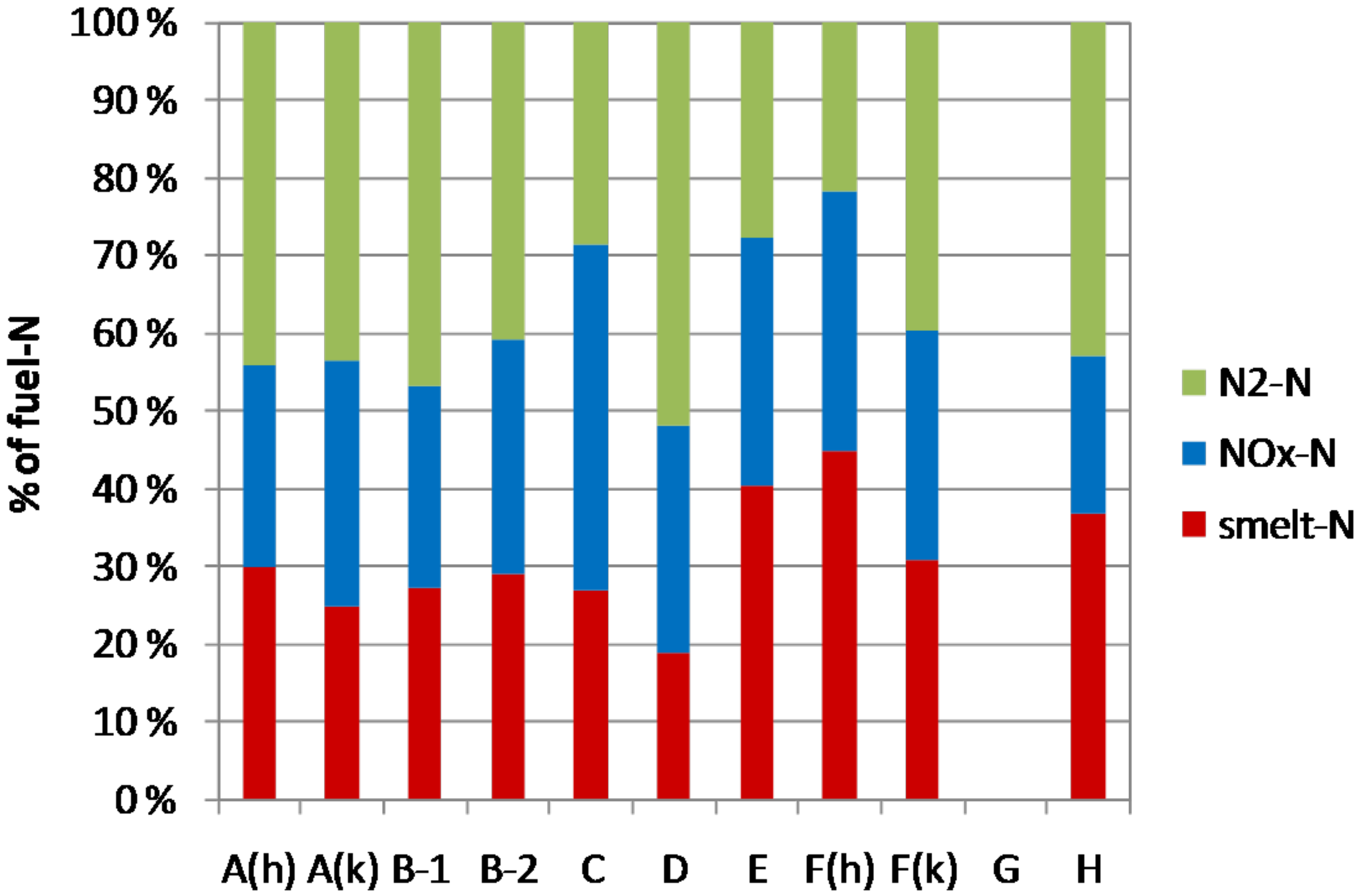
BL in: 100%

NO: 24%

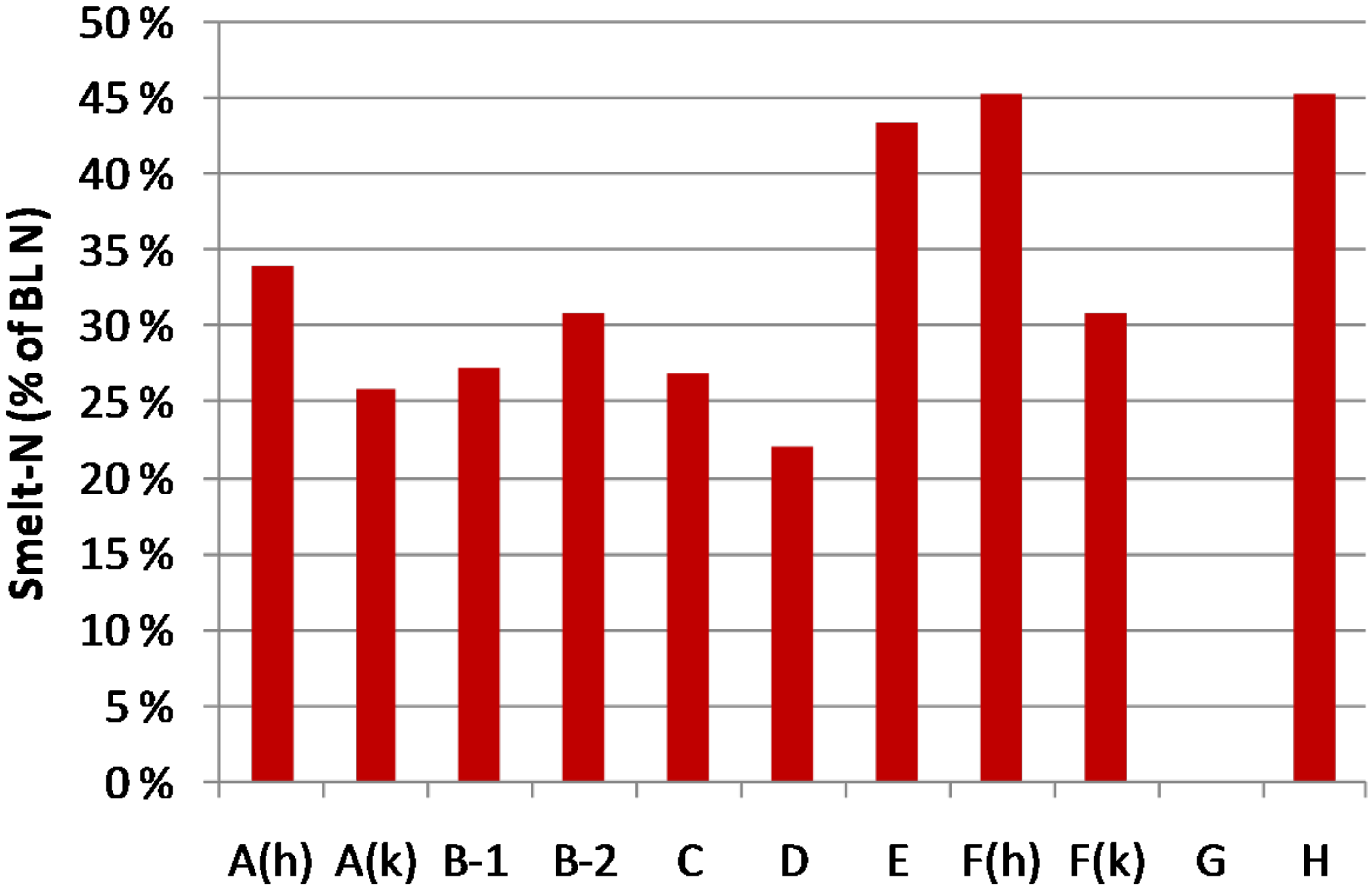
$N_2$: 45%

Smelt: 31%

# RB Fuel N Distribution



# Smelt N (% of BL-N)



# Nitrogen – Recovery Boiler

- Good rule of thumb ~30% N in smelt
- Smelt N balance best made using balance around dissolving tank
- Cyanate concentration in smelt varies with spout
- Cyanate decomposition in smelt sampling?
- Source of $NH_3$ in dissolving tank vent gases?

# Ammonia Formation in Green & White Liquors

$$OCNH + H_3O^+ \rightarrow NH_4^+ + CO_2 \tag*{/1/}$$

$$OCNH + H_2O \rightarrow NH_3 + CO_2 \tag*{/2/}$$

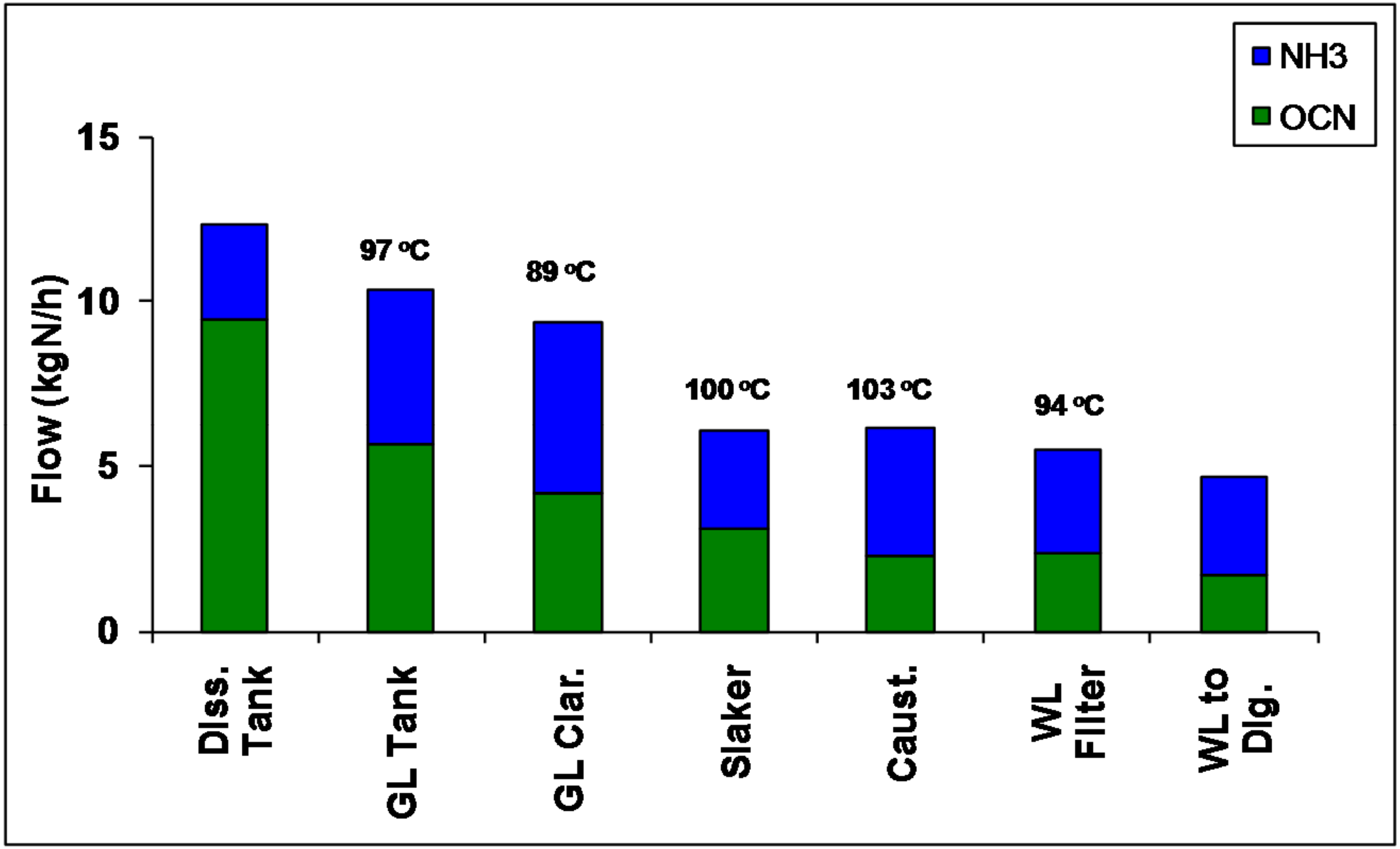
$$OCN^- + 2H_2O \rightarrow NH_3 + HCO_3^- \tag*{/3/}$$

$$OCNH + OH^- \rightarrow NH_2 - COO^- + H_2O \rightarrow NH_3 + HCO_3^- \tag*{/4/}$$

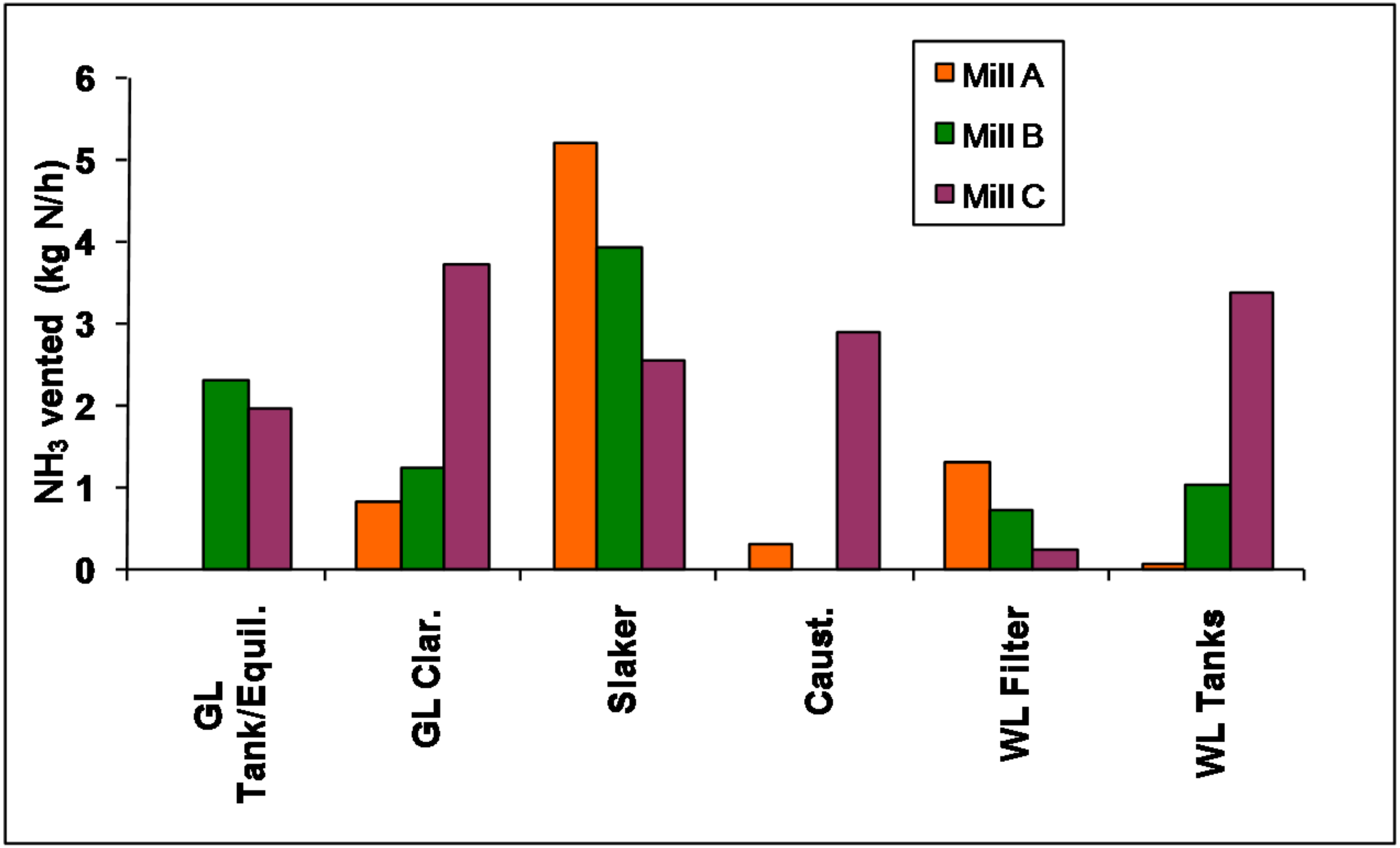
Relevant to Recausticizing

/4/ thought to be the most likely; it is catalyzed by bicarbonate among other anions

# Mill Balance: Recausticizing Mill C



# $NH_3$ Vented in Recausticizing



# Modeling of $NH_3$ Formation in GL & WL

$$\frac{d[NH_3]}{dt} = -\frac{d[OCN^-]}{dt} = \left(k_3 + k_{HCO_3^-}[HCO_3^-]\right)[OCN^-] = \left(k_3 + k_{HCO_3^-}\left(\underbrace{\frac{K_{H_2O}}{K_{HCO_3^-}}\frac{[CO_3^{2-}]}{[OH^-]}\frac{f_{CO_3^{2-}}}{f_{OH^-}f_{HCO_3^-}}}_{[HCO_3^-]}\right)\right)[OCN^-]$$

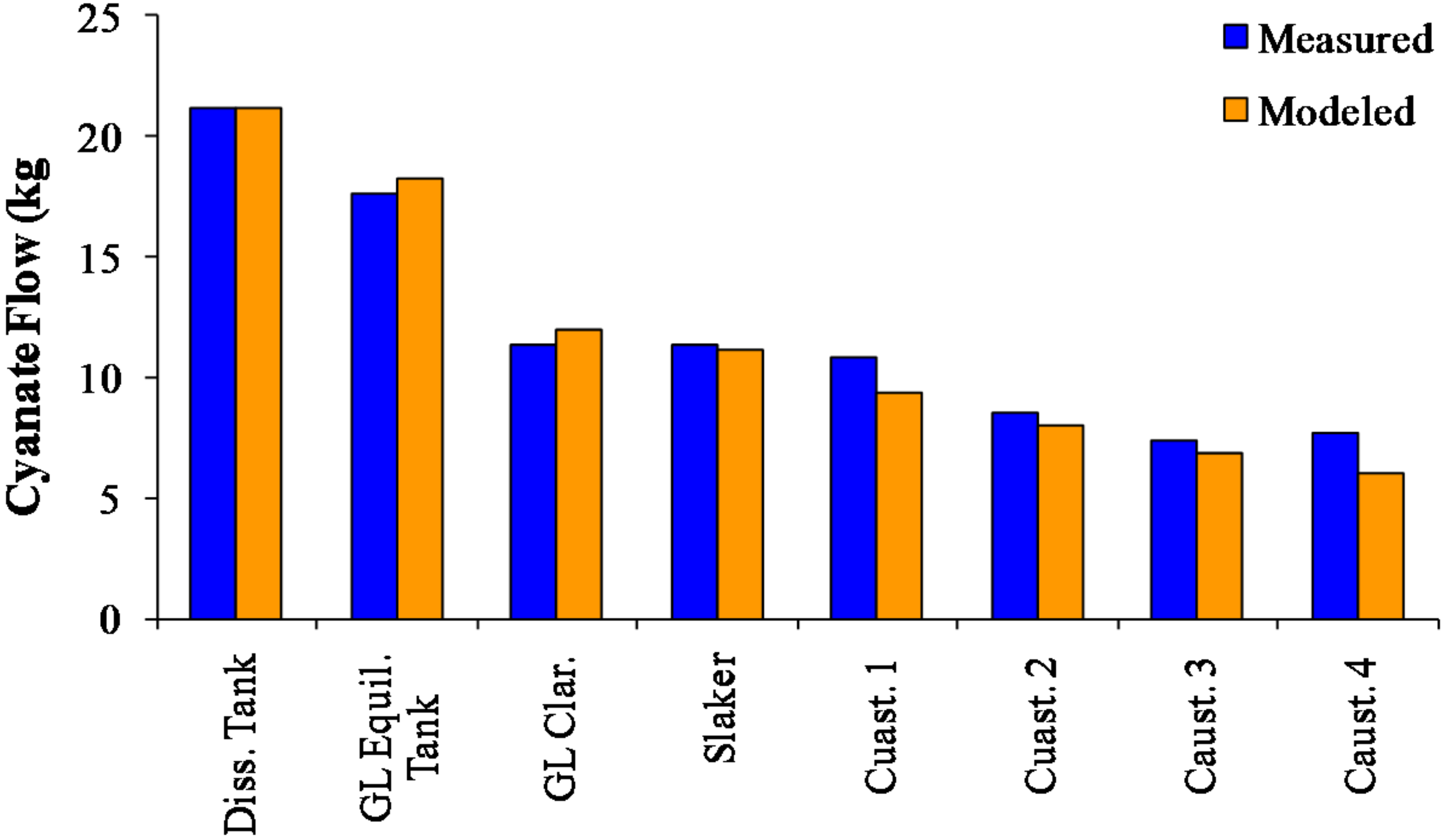
$$k_3 = 7.96\times10^{10}e^{\frac{-11600}{T}}$$

Ea = 96 KJ/mol

$$k_{HCO_3^-} = 4.55\times10^{9}e^{\frac{-8725}{T}}$$

Ea = 73 KJ/mol

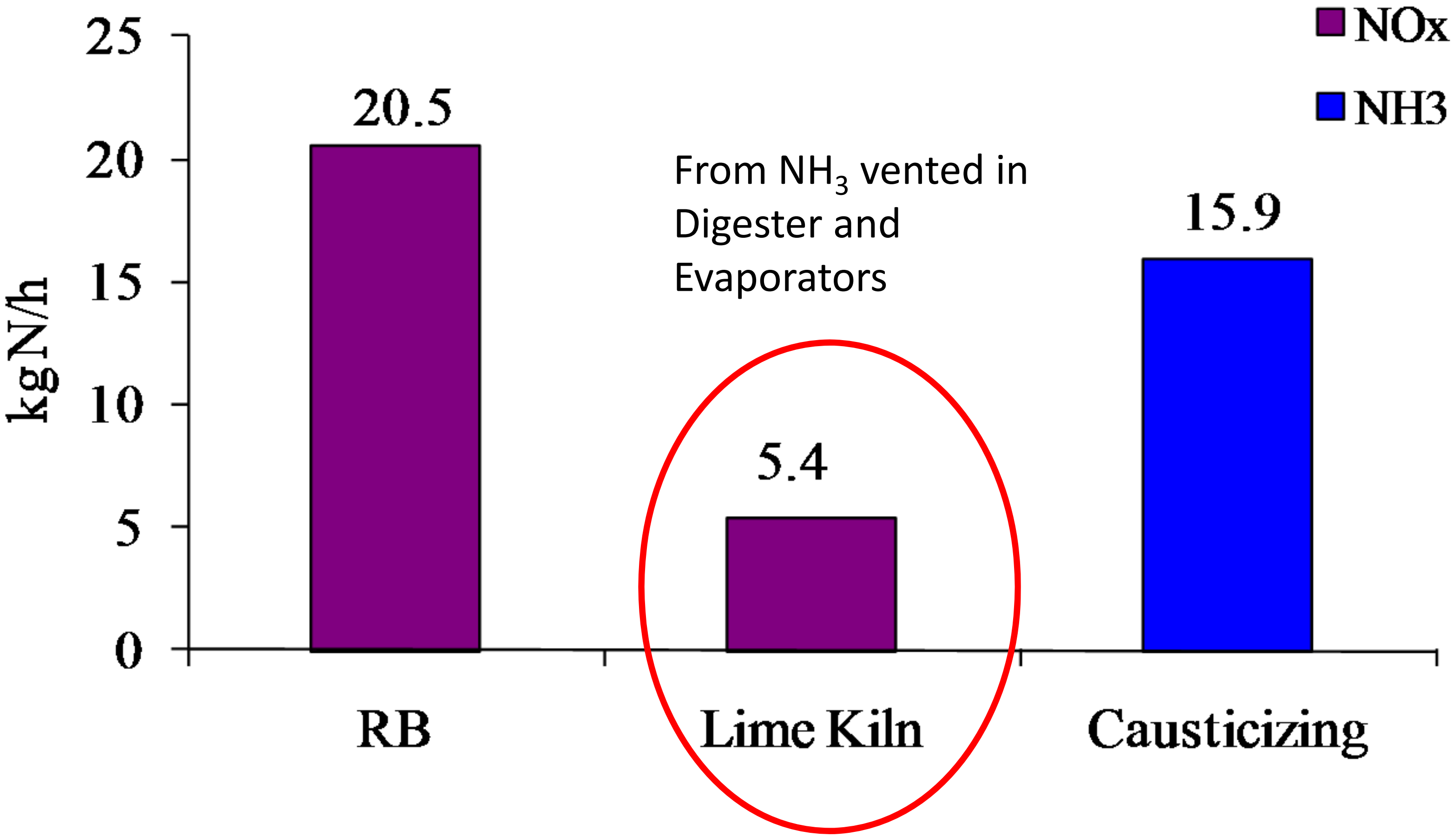
# Modeling of Cyanate Decomposition – Mill C



# $NH_3$ Formation and Release in Recausticizing

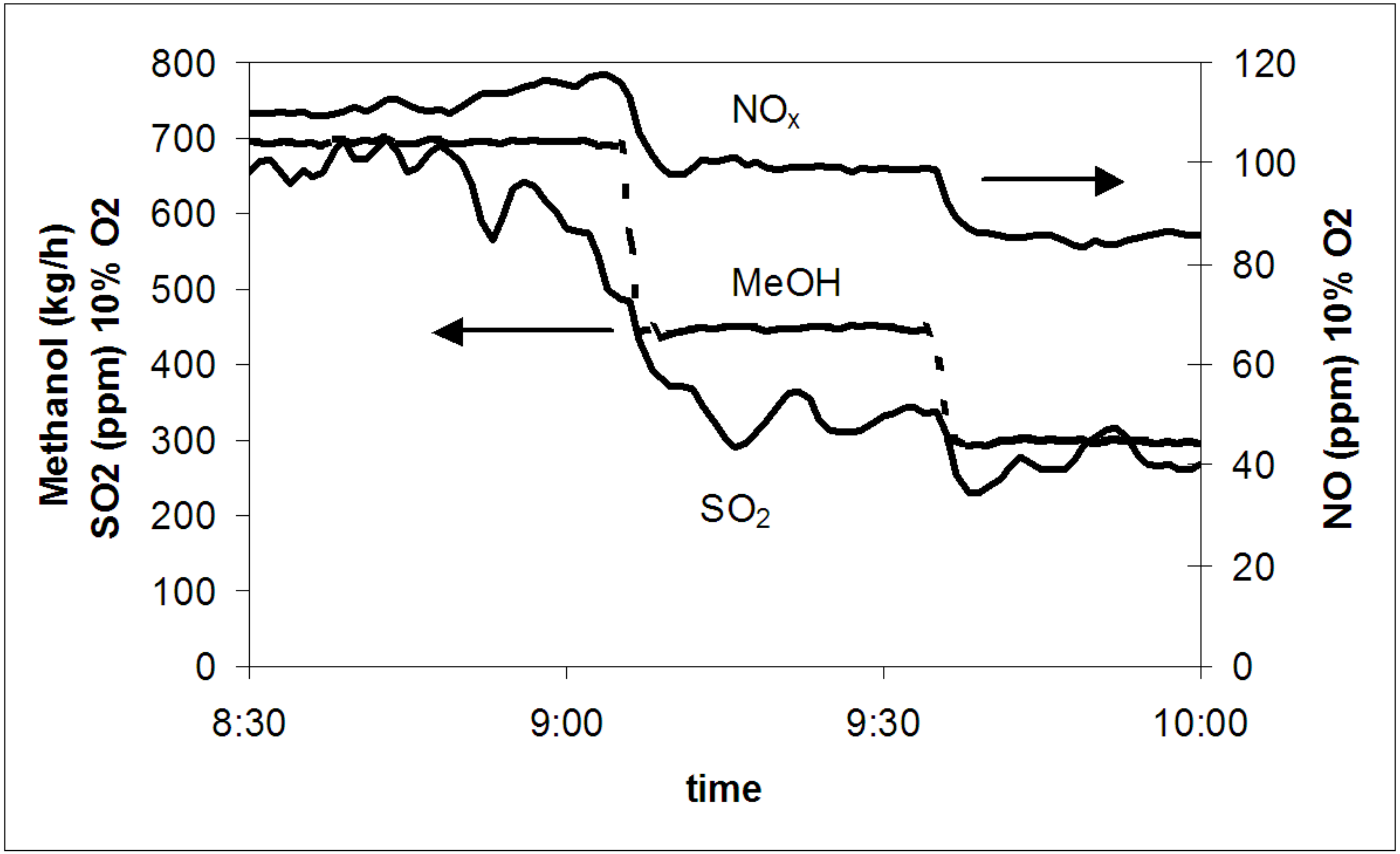
- $NH_3$ formation is slow and it is formed throughout recausticizing
- $NH_3$ release depends on concentration and venting conditions
- Can be scrubbed from vent gases with acidic solution

# Total N Emmisions – Mill C



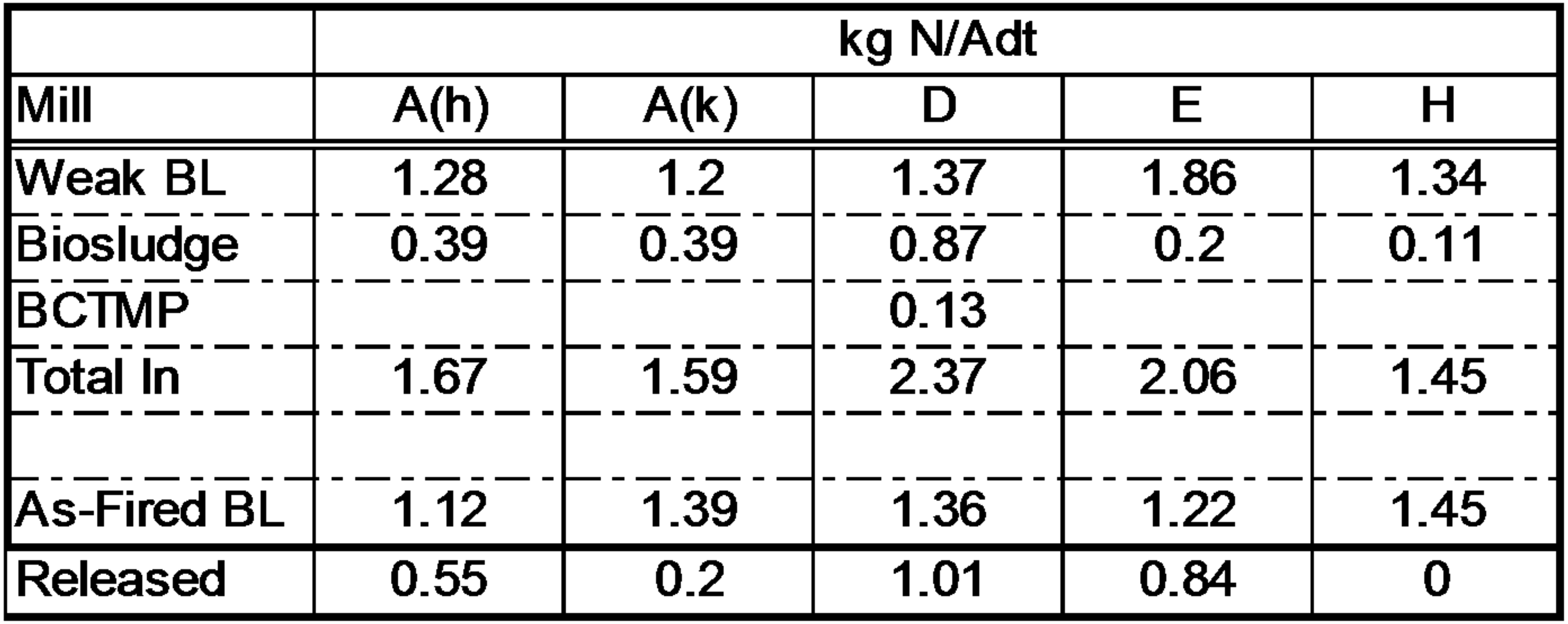
From $NH_3$ vented in Digester and Evaporators

# Impact of MeOH on Lime Kiln Nox – B1



DeMartini et al. ICRC 2004

# Biosludge Addition - Finland



| | kg N/Adt | | | | |
|---|---|---|---|---|---|
| Mill | A(h) | A(k) | D | E | H |
| Weak BL | 1.28 | 1.2 | 1.37 | 1.86 | 1.34 |
| Biosludge | 0.39 | 0.39 | 0.87 | 0.2 | 0.11 |
| BCTMP | | | 0.13 | | |
| Total In | 1.67 | 1.59 | 2.37 | 2.06 | 1.45 |
| | | | | | |
| As-Fired BL | 1.12 | 1.39 | 1.36 | 1.22 | 1.45 |
| Released | 0.55 | 0.2 | 1.01 | 0.84 | 0 |

# Biosludge N

- Potentially significant source of N
- Biosludge $NH_3$ appears to be small amount of total-N
- As $NH_4^+$ in neutral solutions
- As $NH_3$ in alkaline solutions
- Does not significantly increase NO in RB

# Biosludge N

- Appears biosludge N is released in concentrators in many cases
- Released as $NH_3$, other?
- $NH_3$ formation in concentrators?
- This has not been confirmed by mass balance around concentrators (need condensate samples) or laboratory work

# Summary

- Pulping
  - Rapid and complete (>95%) dissolution of wood N during cooking
  - ~10% of wood N forms $NH_3$ during cooking

- Evaporation
  - Volatile N compounds (95%+ is $NH_3$) released by 30% BLS
  - up to ~10% of additional $NH_3$ can be produced during evaporation observed

# Summary

- BL Combustion
  - ~30% of black liquor N exits with the smelt

- Recausticizing
  - $NH_3$ formation from cyanate slow
  - N vented as $NH_3$ can be ~75% of recovery boiler NO-N
  - $NH_3$ fed to digester with WL ~10% of total N entering the digester

# Summary

- MeOH and NCG combustion
  - $NH_3$ in MeOH and NCG can have a significant impact on NO emissions
  - $NH_3$ stripping from MeOH?
- Biosludge
  - Fate of biosludge N?
  - N in clean condensates?
- Overall
  - ~40% of wood N recoverable at $NH_3$?
  - Biosludge N as NH3?

# $NH_3$ Project

- Objective: identify the streams in a pulp mill from which $NH_3$ can be stripped and collected for use elsewhere in the mill.
- Tasks
  - One mill balance – pulp mill and chemical recovery cycle (mill with a WL oxidation system & biosludge addition) (~50 samples)
  - Laboratory tests for stripping of $NH_3$ from white liquor at 3 temperatures

# Sample Campaign - Kymi

- Contact: Toni Orava, Production Engineer
- Am obtaining P&I diagrams now to identify sampling points
- Dates
  - 9.6 ND to visit mill and make first identification of sample points
  - Mill shutdown 28.6.-3.7.2010
  - August – finalize sampling points
  - Week 45 sampling campaign (Emmissions testing for stack gases happening this week)

Thank You!

Questions?

# LIITE VII

ATR/Pöyry
TAJ:n määräaikaistestaukset – tarjous
9.3.2010

PÖYRY

**Pöyry Finland Oy**
PL 4 (Jaakonkatu 3)
FI-01621 Vantaa, Finland
Kotipaikka Vantaa
Y-tunnus 0625905-6
Puh. +358 10 3311
Faksi +358 10 33 21818

# TARJOUS

**Päiväys 9.3.2010**

**Viite 16FEC0708**
Sivu 1 (2)
Yhteyshlö Mauri Heikkinen
Puh. 010 33 22476
mauri.heikkinen@poyry.com

Suomen Soodakattilayhdistys ry
Olli Ahava / UPM-Kymmene
Markus Nieminen / Pöyry Finland Oy

## TAJ:N MÄÄRÄAIKAISTESTAUKSET

Viitaten käytyihin keskusteluihin tarjoamme soodakattilan TAJ:n määräaikaistestausten selvitystä, jolla saataisiin koottua parhaat hyväksyttävät testausmenetelmät TAJ:ään liittyville kenttälaitteille.

## 1 TYÖN KOHDE

Työn kohteena on soodakattilan TAJ:n määräaikaistestausselvitykset, joilla saataisiin koottua parhaat hyväksyttävät testausmenetelmät TAJ:ään liittyville kenttälaitteille.

## 2 TEHTÄVÄT

Työ käsittää seuraavaa:

- Valita erityistarkasteluun kolme tehdasta, joissa on poikkeuksellisen pitkä määräaikaistestausväli TAJ:n laitteille. Osa tehtaista voisi olla eri toimialalla toimivia (esim. öljynjalostus tai voimalaitos). Valituilta tehtailta selvitettäisiin esim. seuraavia asioita.
    - Mikä on tehtaalla käytössä oleva TAJ:n määräaikaistestausten suorittamisen väli?
    - Miten ko. määräaikaistestausväli on määritelty ja hyväksytty?
    - Tehdäänkö TAJ:n määräaikaistestaukset tasaisesti määrätyn ajan välein?
        - Onko kaikilla suojilla sama testausväli?
    - Vaaditaanko käynnin aikana joitakin erityistoimenpiteitä, joilla pitkää testausväliä voidaan turvallisuusmielessä perustella?
    - Onko kunnonvalvontaa tai laitteiden diagnostiikka hyödynnetty testauksissa ja testausvälin pituuden määrittelyssä?
    - Onko TAJ:n määräaikaistestauksissa löytynyt vikoja?
    - Tarvitaanko määräaikaistestauksissa ulkopuolista työvoimaa vai selvitäänkö omalla henkilökunnalla.
    - Miten määräaikaistestausten tekoa voisi tehostaa ja määräaikaistestausten väliä pidentää?
- Työssä selvitetään lisäksi:
    - Mitä standardit EN61508 ja EN61511 määrittävät määräaikaistestauksista
    - Mitä painelaitesäädökset ja standardit määrittelevät painelaitteiden varolaitteiden määräaikaistestauksista. (TAJ on soodakattilan varolaite).

- o Voiko kunnonvalvonnalla ja laitteiden omalla diagnostiikalla pidentää määräaikaistestausten väliä?
- o Vaikuttaako turvalaitteen jatkuva käyttö perusautomaation osana testaustarpeen pituuteen?
- o Valvonta- ja arviointilaitosten (Tukes, Inspecta) kanta mahdollisista eri tavoista pidentää määräaikaistestausten pituutta.

- Tarkastella teoreettisesti eheystasojen ja rakennearkkitehtuurien kautta mahdollisuutta pidentää testausväliä.
- Yhteenvedon laadinta.

## 3 ORGANISAATIO

Työn koordinoija ja tekijä on Mauri Heikkinen.

## 4 AIKATAULU

Olemme valmiit aloittamaan työn keväällä 2010 ja saattamaan loppuun vuoden 2010 loppuun mennessä.

## 5 KAUPALLISET EHDOT

Tarjoamme työn kiinteään hintaan 15 000 EUR. Hinta ei sisällä alv:tä.

Hinta sisältää matkakustannukset selvitykseen valittuihin tehdaslaitoksiin.

Laskutamme työn, kun se on tehty, 15 päivää netto.

Tarjouksemme on voimassa 30.03.2010 saakka.

## 6 MUUT EHDOT

Muutoin ovat voimassa Pöyry Finland Oy:n General Terms and Conditions for Professional Services (liite I).

Toivomme tarjouksen vastaavan toivomuksianne. Tarjoukseen liittyen yhdyshenkilönä toimii Mauri Heikkinen.

Ystävällisin terveisin

Pöyry Finland Oy

Mika Rahikka
Osastonjohtaja
Automaatio- ja IT osasto

LIITE I General Terms and Conditions for Professional Services

LIITE I

---

# GENERAL TERMS AND CONDITIONS FOR PROFESSIONAL SERVICES

# GENERAL TERMS AND CONDITIONS FOR PROFESSIONAL SERVICES

**1. APPLICABILITY.** These General Terms and Conditions for Professional Services ("Conditions") shall apply to all professional services rendered by **Pöyry Finland Oy** ("Consultant") to a customer ("Client") unless otherwise agreed in a contract between the Client and Consultant.

**2. DEFINITIONS**

By "Services" is meant professional services in the nature of studies; preliminary engineering; engineering; project design; monitoring, owner's engineer services; management and supervision services; and other related services provided by the Consultant to the Client.

By "Contract" is meant, concerning the provision of the Services, (a) the agreement document duly signed by the parties, or if such document does not exist, (b) the Consultant's written offer accepted by the Client without changes, or (c) the Client's purchase order accepted by the Consultant without changes; each together with these Conditions, which form an integral part of the Contract. Any changes to the Contract shall be made in writing and signed by both parties.

**3. SCOPE OF SERVICES**. The parties agree on the scope of Services in sufficient detail in the Contract and its attachments.

**4. COMPENSATION TO CONSULTANT**. In consideration of the performance of the Services, the Client shall compensate the Consultant in accordance with the payment terms of the Contract. If not otherwise agreed in the Contract, the Consultant charges a fee based on the time consumed for the Services plus direct expenses. The fee is calculated in accordance with the current fee rates of the Consultant applicable to the type of services provided and is payable monthly net against invoice within 21 days from the date of the invoice in the currency prescribed. The interest on overdue payments is the reference rate of interest confirmed by the Central Bank of the domicile of the Consultant plus ten (10) percentage points. If any part of the invoice is disputed by the Client, the Client shall give the Consultant prompt notice with reasons and shall pay the undisputed part of the invoice without delay. All prices and payments to the Consultant are exclusive of any taxes (other than the Consultant's income tax in its domicile), withholdings, duties, bank charges and similar dues. Value added tax (VAT), sales tax and other equivalent tax, if applicable, is not included in the prices and will be marked separately in the invoice and paid by the Client.

**5. CLIENT'S GENERAL OBLIGATIONS.** The Client shall promptly provide the Consultant with all basic data and other data and information, and all reviews and approvals required by the Consultant in order to complete the Services in accordance with the Contract.

**6. DELIVERY TIME**. The Consultant shall perform the Services within the time schedule defined in the Contract except if the performance is delayed by reasons not attributable to the Consultant.

**7. PROFESSIONAL STANDARD**. The Consultant shall perform the Services in accordance with the standards of skill, care and diligence generally practiced by members of the engineering profession currently operating in the same region under similar conditions. If, during the one (1) year period following completion or termination of the Consultant's Services, whichever is earlier, it is shown that the Consultant has failed to meet this standard, and the Client has promptly notified the Consultant in writing of such failure, the Consultant shall perform such corrective services within the original scope of Services as may be necessary to make its Services conform to such standard. This obligation shall be the Consultant's sole obligation and the Client's exclusive remedy in respect of the quality of the Services.

The Consultant makes no warranties (express or implied) and assumes no liability for cost estimations made by the Consultant; or for modification, operation, availability or performance of the Client's or other end-user's facilities.

**8. CONSTRUCTION REVIEW**. Construction review and monitoring services provided by the Consultant do not give rise to any warranty or guarantee whatsoever. Construction contractors retained by the Client shall be fully responsible for the quality of their own work and for adhering to the plans and specifications. The Client shall be solely responsible for the supervision and management of the work forces of the constructors, including the means, methods, techniques, sequences or safety procedures employed by them to complete the work.

**9. DEFECTS IN SERVICES**. The Client shall promptly report to the Consultant any alleged defects in the Services in order that the Consultant may take prompt measures to remedy the same.

**10. DELAYS IN SERVICES**. If the parties have agreed in the Contract on certain completion milestones or on a final completion date for the Services, and the Consultant is in delay of such date(s) for reasons solely attributable to the Consultant, the Client is entitled to liquidated damages for delay. The amount of the liquidated damages for delay is 0.5 % of the fee for the particular phase or partial assignment delayed per each full week of delay. The total aggregate amount of the liquidated damages for delay is limited to five percent (5 %) of the total fee for the Services rendered by the Consultant under the Contract. This obligation shall be the Consultant's sole obligation and the Client's exclusive remedy in respect of the delay of the Services.

**11. CHANGES**. Any agreed upon schedule, completion date, price and/or maximum cost shall be equitably adjusted to reflect (1) the addition to, modification of or deletion from Services; (2) the discovery of any subsurface or other conditions which differ from (a) those shown in or reasonably inferable from Contract, (b) those ordinarily encountered and generally recognised as inherent in work of the type contemplated herein; (3) change in the applicable law or in the interpretation thereof, which increases the cost of or time required for performing Services; (4) delay or suspension of, or interference with the Services by the Client or by any other entity; (5) a modification to or delay in providing design criteria, decisions or other information needed by the Consultant; or (6) any increase in the Consultant's costs or in the time required for completion of the Services due to a Force Majeure event as defined in section 23 hereof, or any other cause beyond the Consultant's reasonable control. If the Client requires changes to be made by the Consultant to the content of the Services; or the use of methods, materials and constructions objected to by the Consultant in writing, the Consultant shall have no liability for damages, losses or delays arising out of such causes.

**12. COMPLETION**. When the Consultant deems it has completed the Services, it shall so notify the Client in writing. Within ten (10) days thereafter, the Client shall advise the Consultant in writing of any defects in Services for which he considers the Consultant to be responsible under the Contract. As soon as any such defects are corrected, or as soon as the ten (10) day period for such notice has expired if the Client has not advised the Consultant of any such defects within the period, the Client shall accept the Services in writing or they shall be deemed accepted.

**13. INDEPENDENT CONSULTANT**. The Consultant shall, for all purposes, be deemed to be an independent consultant and nothing in the Contract shall be construed to make the Consultant the agent, employee or servant of the Client. The Consultant shall have control over and be responsible for the means and methods for performing the Services.

**14. ASSIGNMENT AND SUB-CONTRACTING.** Neither party shall, without the prior written consent of the other, assign or subcontract any of its rights or obligations under the Contract, except that the Consultant may have parts of the Services performed by its affiliated entities. In the event any part of the Services is performed by the Consultant's affiliated entities or other subconsultants of the Consultant, the Consultant's responsibility for the Services remains unchanged and the Client shall look solely to the Consultant as if all the Services were performed by the Consultant alone.

**15. INTELLECTUAL PROPERTY RIGHTS.** The intellectual property rights to all drawings, specifications, database and other material supplied by the Consultant to the Client pursuant to the Contract shall rest with the Consultant. The Client agrees to use the information contained therein solely for the agreed purpose and for no other purpose. The Client agrees not to disclose the same to others for purposes other than for which it is intended, without the prior written consent of the Consultant. The Consultant is not responsible for any unauthorised use of the same.

**16. PUBLIC LIABILITY.** Each party shall indemnify, defend and hold the other party harmless from all claims, liabilities and causes of action for bodily injury to and/or death of any person and/or loss of, damage to and/or destruction of third-party property, if and to the extent caused by the negligent acts or omissions of the indemnifying party.

**17. PROFESSIONAL LIABILITY.** The Consultant shall be liable to the Client for errors, omissions and professional negligence of the Consultant in performing the Services in accordance with the Contract, which have caused the Client documented direct damage.

**18. LIMITATION OF LIABILITY.** Notwithstanding anything contained in the Contract, the Consultant's total aggregate liability under or in relation to the Contract (including any breach thereof) or the Services shall in no case exceed (a) the amount of the total fee (exclusive of direct expenses) paid to the Consultant for the Services if the total value of the Contract is less than 500 000 euros; or (b) 500 000 euros plus ten percent (10%) of such part of the total fee (exclusive of direct expenses) paid to Consultant that exceeds 500 000 euros if the total value of the Contract is 500 000 euros or more. The Consultant shall have no liability for any minor individual damage of less than 5 000 euros.

In no event shall the Consultant have any liability under or in relation to the Contract (including any breach thereof) or Services for any indirect or consequential damages of any nature whatsoever such as but not limited to damages arising out of or pertaining to loss of use of property, loss of profits or other revenue, interest, loss of product, increased expenses or business interruption, however the same may be caused. Furthermore, the Consultant has no liability for damages which are caused by reasons or circumstances not attributable to the Consultant or which are beyond the reasonable control of the Consultant.

**19. LIABILITY PERIOD.** The liability of the Consultant under or in relation to the Contract or Services shall in all cases expire after one (1) year has elapsed from the date of acceptance of the Services or the date when the Services are deemed accepted as set out in section 12 (Completion) hereof. All claims to the Consultant shall be presented immediately upon detection, however before the expiry of the liability period.

**20. INSURANCES.** To cover its professional liability with respect to the Services performed under the Contract, the Consultant shall maintain professional indemnity insurance for engineering undertakings. The Consultant's liability for damages caused by errors, omissions or other professional negligence is limited to the maximum liability defined in section 18 hereof however only to the extent and amount the liability is covered by the professional liability insurance. To cover its public liability, the Consultant shall maintain general liability insurance covering bodily injury and third-party property damage with a limit of not less than 500 000 euros annual aggregate.

**21. REMEDIES.** All of the parties' rights, liabilities, responsibilities and remedies arising out of and relating to the Contract (including any breach thereof) shall be exclusively those expressly set forth in the Contract or provided by the applicable mandatory law.

**22. SUSPENSION AND TERMINATION.** The Client may suspend or terminate the Contract at its convenience upon thirty (30) days' prior written notice to the Consultant. The Consultant may suspend or terminate the Contract if payments are thirty (30) days or more overdue, or the Client or other project participants have delayed or neglected to fulfil their obligations thus preventing the proper execution of the Services by the Consultant and such default has not been corrected within thirty (30) days of the written notice to the Client, or the Client has requested to deviate from applicable laws and regulations, professional standards as described in section 7 hereof or the working ethics of the Consultant. In addition, either party may terminate the Contract upon written notice to the other in the event the other party becomes insolvent or bankrupt, or is the debtor in any receivership or bankruptcy proceeding or effects a general assignment for the benefit of its creditors, or in the event the other party commits a substantial breach of the Contract and fails to correct or take reasonable steps to correct the breach within ten (10) days after receipt of written notice from the other party thereof. Upon any suspension or termination of the Contract, the Client shall pay the Consultant the costs incurred and fees earned until the effective date of termination, and neither party shall have any further liability to the other.

**23. FORCE MAJEURE.** No delay in or failure of performance by either party, other than payment of money, shall constitute default hereunder if and to the extent such delay or failure is caused by any occurrence beyond the reasonable control of the party otherwise required to perform and which by the exercise of reasonable diligence by said party could not have been prevented.

**24. CONFIDENTIALITY.** During the term of the Contract and two (2) years thereafter, the Consultant shall not disclose, orally or in writing, to any third party without the Client's prior written consent any information regarding the Client's business, industrial plants or any aspects of the project. Notwithstanding the foregoing, the Consultant shall be entitled to describe the Services and/or the project by title and generally as to scope, type and size, and state the name of the Client in qualifications, promotional and experience materials after the information of the project can be made public. These materials shall not reveal details of the project that contain proprietary technology or trade secrets, but may include such information that is published or otherwise in the public domain.

**25. VALIDITY.** In the event that any part of Contract is held to be void or unenforceable, the parties agree to negotiate in good faith to reach an equitable provision which shall affect the intent of the parties as set forth in the Contract.

**26. GOVERNING LAW.** The Contract shall be governed by and interpreted in accordance with the laws of Finland excluding provisions thereof that refer to the laws of another jurisdiction.

**27. SETTLEMENT OF DISPUTES.** All disputes arising out of or in connection with the Contract shall be finally settled by arbitration in accordance with the Arbitration Rules of the Finnish Central Chamber of Commerce. The arbitration procedure shall be conducted in the English language in Helsinki, Finland

**28. NOTICES.** All notices pertaining to the Contract must be in writing and shall be sufficient if sent by telefax or mail to the official addresses of the parties.

# LIITE VIII

## ATR/Botnia Mill Service
## TAJ:n määräaikaistestaukset – tarjous
## 30.4.2010

BMS
BOTNIA MILL SERVICE

30.4.2010

**Olli Ahava**
**UPM-Kymmene Oyj**
Pietarsaari

## TLJ:N MÄÄRÄAIKAISTESTAUKSET

Viitaten sähköpostiviestiin 14.4.2010 keskusteluun 28.4.2010 tarjoamme suunnittelupalvelua seuraavasti:

### Miehitys ja osaamisalueet

| | |
|---|---|
| Eero Hakkarainen | projektipäällikkö, TLJ-asiantuntija |

### Tehtävämäärittely

Selvitys TLJ:n määräaikaistestausten suorittamisesta laite- ja järjestelmätoimittajien antamien määräaikaistestaus väliaikojen ja testausmenetelmien mukaisesti.
Selvitys sisältää Tukesin ja valtuutetun tarkastuslaitoksen mahdolliset kannanotot TLJ-lähteiden ja -kohteiden sekä TLJ-järjestelmän eri pituisiin määräaikaistestausväleihin sekä lähteiden ja kohteiden määräaikaistestausmenetelmiin.

Mahdollisesti tehtävät kyselyt soodakattilayhdistyksen jäseniltä päätetään erikseen

### Aikataulu

Työn aloitus erikseen sovittavan aikataulun mukaisesti.

### Hinnat

Kokonaishinta on **8 250 €,** ALV 0%

Mahdolliset lisätyöt 58,50 €/h, ALV 0%

Matkakustannukset eivät sisälly hintoihin

## Maksuehdot

100 %, kun selvitystyö on valmis

Maksu laskua vastaan 30 pv netto, viivästymiskorko on korkolain mukaan.

Muut ehdot KSE 1995 mukaan.

Tarjouksemme on voimassa 31.5.2010 saakka.

Yhteyshenkilömme sopimusteknisissä ja kaupallisissa asioissa on Eero Hakkarainen 050 - 404 2786

Toivomme tarjouksemme vastaavan tarpeitanne ja johtavan tilaukseen.

Ystävällisin terveisin

OY BOTNIA MILL SERVICE AB

Eero Hakkarainen

# LIITE IX

## Esa Vakkilainen, LUT
## SKYREC - välitulistuksen kannattavuus

Open your mind. LUT.

Lappeenranta University of Technology

Open your mind. LUT.
Lappeenranta University of Technology

# Välitulistuksen teoriaa

Esa Vakkilainen
esa.vakkilainen@lut.fi

# Miksi välitulistus ei kannattanut?

- Soodakattilayhdistyksen välitulistusprojektissa tutkittiin erilaisia tulevaisuuden soodakattilavaihtoehtoja
- Välitulistusvaihtoehto Case E ei tuottanut sähköä paljoakaan enempää kuin Paras perinteinen Case C

# Tutkitut tapaukset

A. luonnonkierto 82 %, 490 $^oC$, 9.0 MPa (Joutseno)

B. luonnonkierto 85 %, 505 $^oC$, 10.2 MPa (Kymi)

C. luonnonkierto 85 %, 515 $^oC$, 12.0 MPa (Yonago)

**Tulevaisuuden kattila tapaus**

D. avustettu kierto 85 %, 540 $^oC$, 16.0 MPa (SoTu)

**Välitulistus kattilat**

E. luonnonkierto 85 %, 515/515 $^oC$, 12.0/3.0 MPa (SkyRec)

F. läpivirtaus 85 %, 540/540 $^oC$, 26.0/5.4 MPa (Skyrec+)

| Case | | A | B | C | D | | |
|---|---|---|---|---|---|---|---|
| Capacity | tds/d | 5500 | 5500 | 5500 | 5500 | 5500 | 5500 |
| capacity (virgin) | tds/d | 5005 | 5005 | 5005 | 5005 | 5005 | 5005 |
| Dry solids | % | 82.0 | 85.0 | 85.0 | 85.0 | 85.0 | 85.0 |
| ds (virgin) | % | 80.6 | 83.8 | 83.8 | 83.8 | 83.8 | 83.8 |
| recycle ash | % | 9.0 | 9.0 | 9.0 | 9.0 | 9.0 | 9.0 |
| HHV | MJ/kgds | 13.00 | 13.00 | 13.00 | 13.00 | 13.00 | 13.00 |
| LHV | MJ/kgds | 12.28 | 12.28 | 12.28 | 12.28 | 12.28 | 12.28 |
| O2 in dry flue gas | % | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 |
| Primary air percentage | % | 23.0 | 22.0 | 22.0 | 22.0 | 22.0 | 22.0 |
| Primary air temperature | °C | 150.0 | 190.0 | 190.0 | 190.0 | 190.0 | 190.0 |
| Secondary air percentage | % | 50.0 | 54.0 | 54.0 | 54.0 | 54.0 | 54.0 |
| Secondary air temperature | °C | 120.0 | 190.0 | 190.0 | 190.0 | 190.0 | 190.0 |
| Tertiary air percentage | % | 27.0 | 12.0 | 12.0 | 12.0 | 12.0 | 12.0 |
| Tertiary air temperature | °C | 30.0 | 190.0 | 190.0 | 190.0 | 190.0 | 190.0 |
| Quartenary air percentage | % | 0.0 | 12.0 | 12.0 | 12.0 | 12.0 | 12.0 |
| Quartenary air temperature | °C | 30.0 | 190.0 | 190.0 | 190.0 | 190.0 | 190.0 |
| Total air temperature | °C | 102.6 | 190.0 | 190.0 | 190.0 | 190.0 | 190.0 |
| Reduction | % | 95.00 | 96.00 | 96.00 | 96.00 | 96.00 | 96.00 |
| Main steam pressure RB | bar(a) | 91.0 | 102.0 | 120.0 | 160.0 | 105.0 | 260.0 |
| Main steam temperature RB | °C | 490.0 | 505.0 | 515.0 | 540.0 | 505.0 | 540.0 |
| Main steam pressure PB | bar(a) | 91.0 | 102.0 | 102.0 | 102.0 | 102.0 | 102.0 |
| Main steam temperature PB | °C | 490.0 | 505.0 | 505.0 | 505.0 | 505.0 | 505.0 |
| Feedwater pressure | bar(a) | 110.0 | 121.0 | 146.0 | 182.0 | 290.0 | 290.0 |
| Feedwater temperature | °C | 120.0 | 148.0 | 148.0 | 148.0 | 148.0 | 148.0 |
| | | 511.3 | 630.9 | 632.5 | 634.8 | 641.8 | 641.8 |
| Reheater inlet pressure | bar(a) | | | | | 36 | 56 |
| Reheater inlet temperature | °C | | | | | 348 | 337 |
| Reheater outlet pressure | bar(a) | | | | | 34 | 54 |
| Reheater outlet temperature | °C | | | | | 400 | 460 |
| HP FWpreheater inlet temperatur | °C | 200 | 200 | 200 | 200 | 200 | 200 |
| HP FWpreheater outlet temperatu | °C | 200 | 200 | 220 | 220 | 220 | 220 |
| Flue gas temperature (eco out) | °C | 155 | 197 | 197 | 197 | 197 | 197 |
| Flue gas temperature (to stack) | °C | | 155 | 155 | 155 | 155 | 155 |
| Sootblowing | kg/s | 6.0 | 6.0 | 6.0 | 6.0 | 8.0 | 8.0 |

# Sähkön tuotanto (voimakattila mukana)

| **Tapaus** | | **A** | **B** | **C** | **D** | **E** | **F** |
|---|---|---|---|---|---|---|---|
| Kapasitetti | tds/d | 5500 | 5500 | 5500 | 5500 | 5500 | 5500 |
| Kuiva-aine | % | 82.0 | 85.0 | 85.0 | 85.0 | 85.0 | 85.0 |
| HP höyry | bar(a) | 94.0 | 104.0 | 124.0 | 164.0 | 124.0 | 264.0 |
| HP höyry | °C | 490.0 | 505.0 | 515.0 | 540.0 | 515.0 | 540.0 |
| Höyryvirtaus (SK) | kg/s | 215.0 | 226.4 | 232.5 | 232.0 | 224.0 | 218.5 |
| | % | 0.0 | 5.3 | 8.1 | 7.9 | 4.1 | 1.6 |
| Sellutehdas käyttö | MW | 87.6 | 88.1 | 88.9 | 90.2 | 88.2 | 93.2 |
| Tehtaan käyttö | MW | 95.5 | 96.1 | 96.9 | 98.2 | 96.2 | 101.2 |
| Sähkön tuotanto | MW | 234.4 | 239.5 | 249.8 | 262.9 | 250.1 | 263.4 |
| Sähkö myyntiin | MW | 138.9 | 143.3 | 153.0 | 164.7 | 153.8 | 162.2 |
| Hyötysuhde | % | 23.2 | 23.1 | 24.1 | 25.4 | 24.1 | 25.4 |
| | | | | | | | |
| Lisäsähkö | MW | 0.0 | 4.4 | 14.0 | 25.8 | 14.9 | 23.2 |
| | % | 0.0 | 3.2 | 10.1 | 18.5 | 10.7 | 16.7 |

# Sähkön tuotanto (ei voimakattilaa)

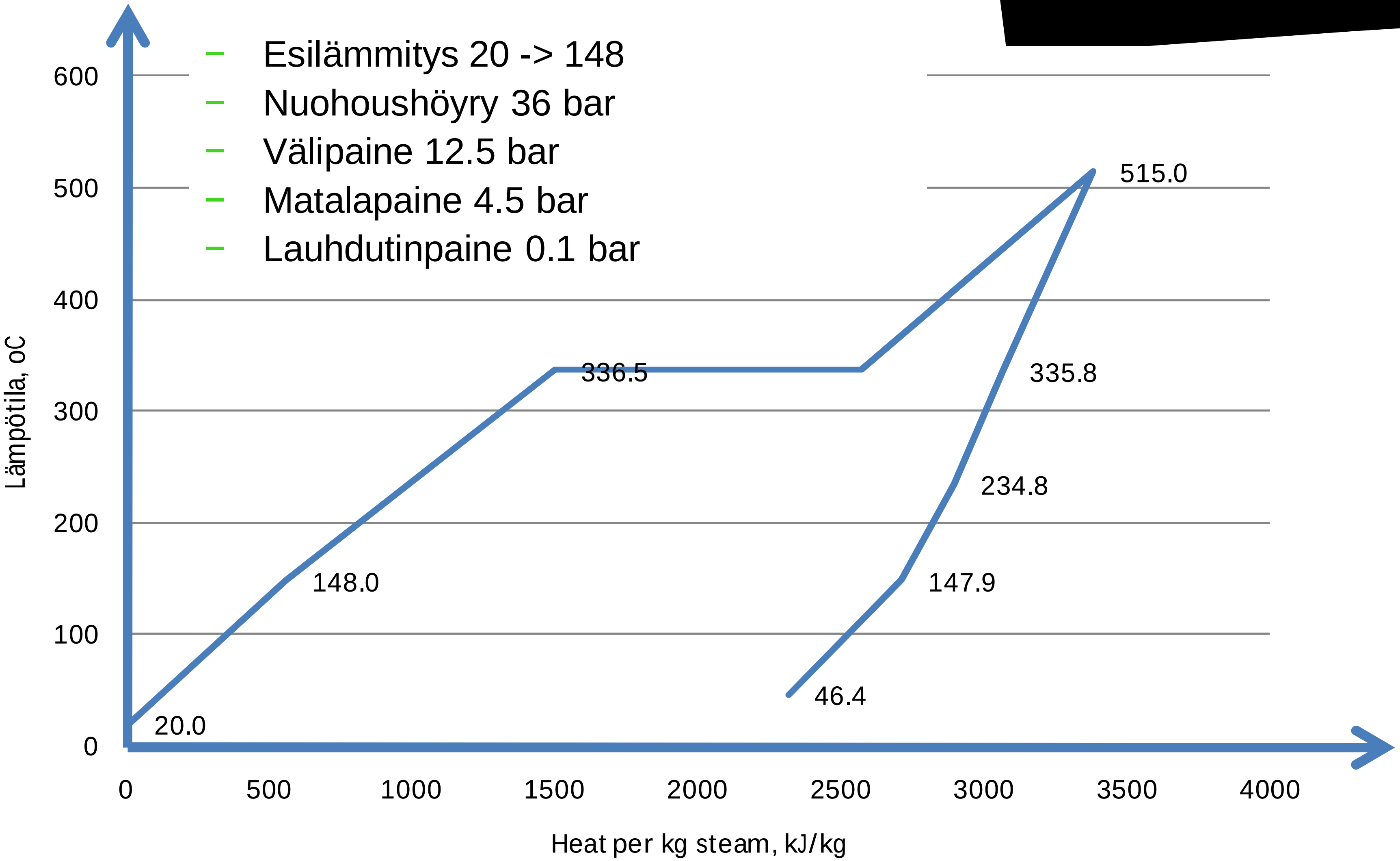
| **Tapaus** | | **A** | **B** | **C** | **D** | **E** | **F** |
|---|---|---|---|---|---|---|---|
| Kapasitetti | tds/d | 5500 | 5500 | 5500 | 5500 | 5500 | 5500 |
| Kuiva-aine | % | 82.0 | 85.0 | 85.0 | 85.0 | 85.0 | 85.0 |
| HP höyry | bar(a) | 94.0 | 104.0 | 124.0 | 164.0 | 124.0 | 264.0 |
| HP höyry | °C | 490.0 | 505.0 | 515.0 | 540.0 | 515.0 | 540.0 |
| Höyryvirtaus (SK) | kg/s | 215.0 | 226.4 | 232.5 | 232.0 | 224.0 | 218.5 |
| | % | 0.0 | 5.3 | 8.1 | 7.9 | 4.1 | 1.6 |
| Sellutehdas käyttö | MW | 87.6 | 88.1 | 88.9 | 90.2 | 88.2 | 93.2 |
| Tehtaan käyttö | MW | 91.1 | 91.7 | 92.4 | 93.8 | 91.8 | 96.8 |
| Sähkön tuotanto | MW | 149.3 | 153.9 | 161.8 | 175.6 | 162.3 | 177.9 |
| Sähkö myyntiin | MW | 58.2 | 62.2 | 69.4 | 81.7 | 70.5 | 81.1 |
| Hyötysuhde | % | 20.4 | 20.4 | 21.4 | 23.2 | 21.5 | 23.5 |
| | | | | | | | |
| Lisäsähkö | MW | 0.0 | 4.0 | 11.2 | 23.6 | 12.3 | 22.9 |
| | % | 0.0 | 6.8 | 19.3 | 40.5 | 21.1 | 39.4 |

# Soodakattila sähkönkäyttö

| **Tapaus** | | **A** | **B** | **C** | **D** | **E** | **F** |
|---|---|---|---|---|---|---|---|
| Ilmapuhallin | kW | 2275 | 2296 | 2296 | 2296 | 2296 | 2296 |
| Savukaasupuh. | kW | 2570 | 2534 | 2534 | 2534 | 2534 | 2534 |
| SV-pumppu | kW | 3055 | 3556 | 4347 | 5719 | 4187 | 8606 |
| Muu käyttö | kW | 1500 | 1500 | 1500 | 1500 | 1500 | 1500 |
| Yhteensä | kW | 9401 | 9886 | 10677 | 12049 | 10518 | 14937 |

# Kattilaprosessi – Case C

- Esilämmitys 20 -> 148
- Nuohoushöyry 36 bar
- Välipaine 12.5 bar
- Matalapaine 4.5 bar
- Lauhdutinpaine 0.1 bar



# Turbiini – Case C

Open your mind. LUT.
Lappeenranta University of Technology

Savukaasu antaa lämpöä

3384.5-562.5 = 2822.0 kJ/kg

Nuohoushöyry 36 bar

3384.5-3069.2 = 315.3 kJ/kg 11.2 %

Välipainehöyry 12.5 bar

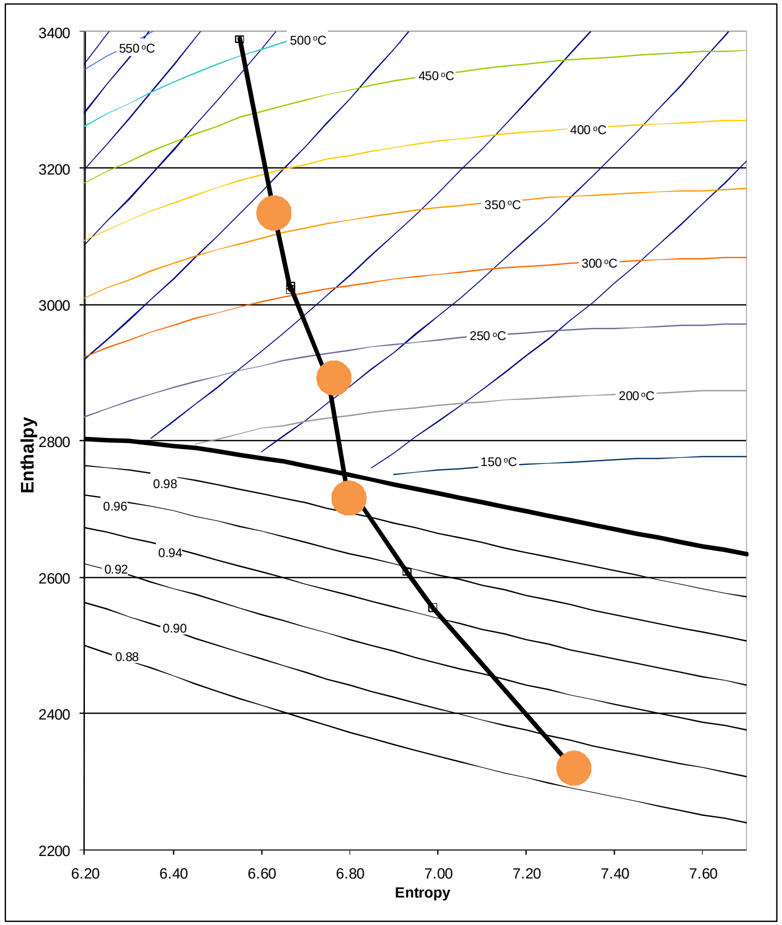
3384.5-2897.8 = 486.7 17.2 %

Matalapainehöyry 4.5 bar

3384.5-2714.9 = 669.6 23.7 %

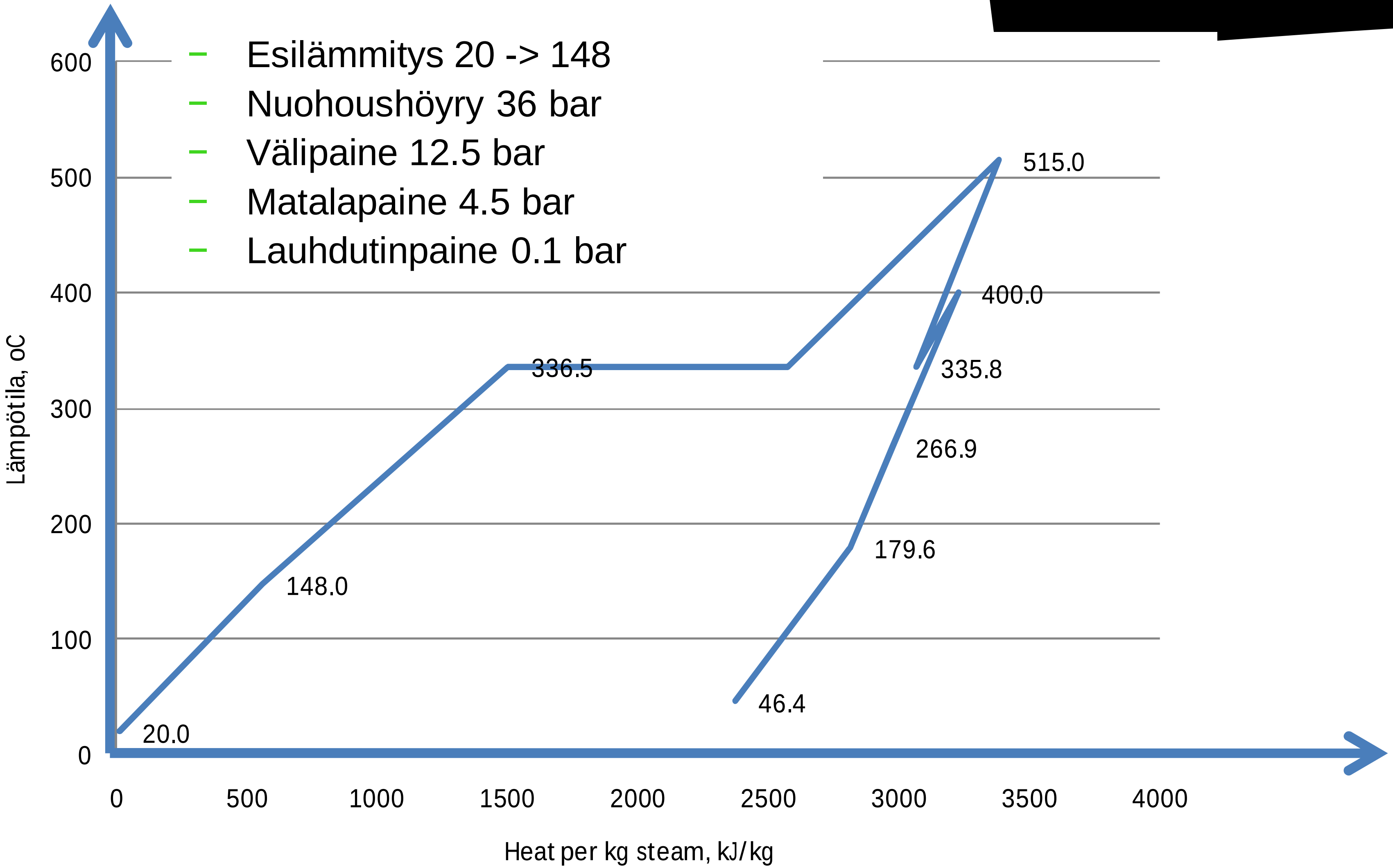
Lauhdutin 0.1 bar

3384.5-2319.4 = 1065.1 37.7 %



# Kattilaprosessi – Case E

- Esilämmitys 20 -> 148
- Nuohoushöyry 36 bar
- Välipaine 12.5 bar
- Matalapaine 4.5 bar
- Lauhdutinpaine 0.1 bar



# Turbiini – Case E

Savukaasu antaa lämpöä

3384.5-562.5+3225.9-3099.1 = 2948.7kJ/kg

Nuohoushöyry 36 bar

3384.5-3069.2 = 315.3 11.2 %

Välipainehöyry 12.5 bar

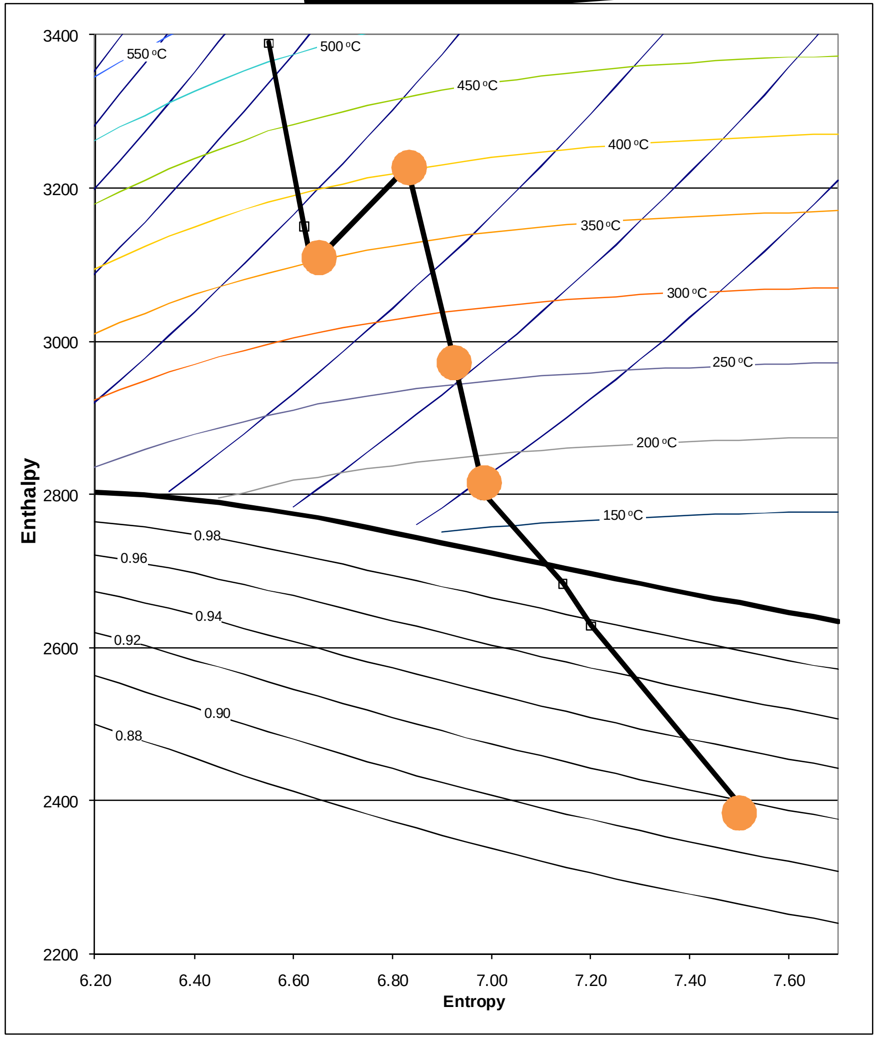
315.3+3225.9-2972.1 = 569.0 19.1 %

Matalapainehöyry 4.5 bar

315.3+3225.9-2714.9 = 727.4 27.7 %

Lauhdutin 0.1 bar

315.3+3225.9-2319.4 = 1168.2 41.0 %



# Vertailu jos voimalaitos

Voimalaitosprosessissa niin Case E että Case C kaikki höyry paisuu

Suora:

| | | |
|---|---|---|
| - Savukaasu antaa lämpöä | 3384.5- 562.5 | = 2822.0 kJ/kg |
| - Sähköä lauhdutin 0.1 bar | 3384.5-2319.4 | = 1065.1 kJ/kg |
| - Jos höyryä 233.5 kg/s niin | 233.5*1065.1 | = 248.7 MW |

Välitulistus:

| | | |
|---|---|---|
| - Savukaasu antaa lämpöä | 3384.5-562.5+3225.9-3099.1 | |
| | | = 2948.7 kJ/kg |
| - Sähköä lauhdutin 0.1 bar | | = 1168.2 kJ/kg |
| - Jos höyryä 221.8 kg/s* niin | 221.8*1168.2 | = 259.1 MW (+4.2 %) |

*Höyryä vähemmän koska välitulistus

# Vertailu - vastapaine

Savukaasu antaa lämpöä saman verran sekä Case E että Case C.

Suurin osa höyrystä paisuu vain osan prosessista.

Tuotantoero paisuu kuitenkin lauhdutinpaineeseen.

| | Höyryä | | Energia | | Sähköä | |
|---|---|---|---|---|---|---|
| **Paisunta** | välitul. | suora | välitul. | suora | välitul. | suora |
| | kg/s | kg/s | kJ/kg | kJ/kg | MW | MW |
| ***124-36*** | 221.8 | 233.5 | 315.3 | 315.3 | 69.9 | 73.6 |
| ***36-12.5*** | 207.9 | 219.6 | 253.7 | 171.4 | 52.8 | 37.6 |
| ***12.5-4.5*** | 173.9 | 185.6 | 158.4 | 182.9 | 27.5 | 34.0 |
| ***4.5-0.1*** | 25.6 | 37.3 | 440.8 | 395.5 | 11.3 | 14.8 |
| | | | | | **161.5** | **160.0** |

*Vastapaineen takia lauhdeperään vain pieni virta

Open your mind. LUT.
Lappeenranta University of Technology

Esa K. Vakkilainen

# LIITE X

**Patrik Yrjas, Åbo Akademi**

# SKYREC - Laboratory tests of superheater materials – final report

**4.6.2010**

# Skyrec

## Final report

## Confidential

**Patrik Yrjas, Dorota Bankiewicz**

Report written at the Laboratory of Inorganic Chemistry/ÅA
lead by prof. Mikko Hupa

**February 2010**

# Preface

This report is based on the results obtained from the laboratory tests performed at the Åbo Akademi University at Laboratory of Inorganic Chemistry. The experiments were carried out during 2009 in agreement with Suomen Soodakattilayhdistys – Finnish Recovery Boiler Committee. This report presents a summary of all tests performed in the project. Due to the high number of SEM and X-ray pictures, only chosen samples with identified corrosion will be presented also in a form of pictures. All the results (SEM/EDX) will be, however, delivered together with the report.

The goal of the project was to estimate the resistance/behaviour of the chosen boiler steam/superheater tube materials under alkali sulfates and alkali sulfates + alkali chlorides containing synthetic ashes in a reducing atmosphere.

The tests were performed using a laboratory method for studying high temperature corrosion developed at Åbo Akademi. The method is based on the estimation of the oxide layer thickness or/and depth of the material degradation. The recognition of the oxide layer composition is also included.

The laboratory work was carried out by Piia Leppäsalo. The SEM/EDX analyses were done by Linus Silvander. The equilibrium curves were calculated and produced by Daniel Lindberg. The analyses of the results, meeting materials and final report have been written by Dorota Bankiewicz in co-operation with, reviewed and commented by Patrik Yrjas.

1 Attachment: CD with SEM/EDX results from all performed tests

The content of the report is confidential and is the property of *Suomen Soodakattilayhdistys – Finnish Recovery Boiler Committee.*

*Authors*

*Åbo Akademi University,*
*June 2010*

# Table of Contents

# 1. Introduction

There is a need for increasing energy conversion efficiency nowadays. The reason for the low steam temperatures in the black liquor fired boilers lies in the corrosiveness of the deposits formed on the tubes of heat exchangers during black liquor combustion. For this reason sodium, along with sulfur and chlorine in the fuel, are considered important elements in the view of fireside corrosion in the black liquor firing recovery boilers. The fuel impurities such as chlorine, sulfur, sodium, and potassium are believed to affect the deposit chemistry changing for example its melting behavior. Therefore, the studies related to effect of deposit chemistry, temperature and combustion conditions on high temperature corrosion of steam tube materials is needed to understand and develop control of the fireside attack on superheater tubes in real recovery boilers [1, 2]. Based on earlier investigation the influence of reducing conditions remained unclear. During the combustion process in the recovery boilers, the carryover particles convey often unburned C which increases risk of fireside corrosion. For that reason, tests in a simulated reducing atmosphere were performed within this project. Four different synthetic ashes containing main black liquor components were used in the laboratory testing of different steam tube materials used in the recovery boilers.

# 2. Experimental

Four different superheater materials were delivered by the customer of the project and used in the experiments. Table 1 presents the detailed steel compositions (weight-%).

**Table 1 The detailed compositions of the tested steels (wt%)**

| | 10CrMo9-10 | T91 | Sanicro 28 | HR11N |
|---|---|---|---|---|
| **Fe** | 95,96 | 88,82 | 36,11 | 28,81 |
| **Cr** | 2,24 | 8,76 | 27,36 | 28,67 |
| **Mo** | 1,00 | 0,95 | 3,51 | 0,96 |
| **Mn** | 0,45 | 0,45 | 1,15 | 0,91 |
| **Si** | 0,25 | 0,35 | 0,46 | 0,27 |
| **Ni** | | 0,19 | 31,38 | 40,24 |
| **V** | | 0,21 | | |
| **C** | 0,07 | 0,10 | 0,01 | |
| **Nb** | | 0,08 | | |
| **N** | | 0,05 | | 0,15 |
| **Al** | | 0,02 | | |
| **P** | 0,01 | 0,01 | 0,01 | |
| **S** | 0,01 | | 0,01 | |

The materials can be classified as two low alloy steels: ferritic (10CrMo9-10) and martensitic (T91), high nickel austenitic stainless steel (S28) and nickel based austenitic stainless steel (HR11N). The test specimens had a size of approximately 20x20 mm and a thickness of 5 mm. Before the experiments all steel specimens were polished in ethanol using first a 600 and then a 1000 grid SiC paper, cleaned in ultrasound bath and covered halfway with a protective paste. The covering with a protective paste was implemented in order to be able to determine the original surface after the corrosion test. The protective paste used in the experiments is a commercially available fire sealant - 1200ºC, composed of sodium silicate 10-30% and produced by Bostik. Before the tests, the specimens were pre-oxidised in a furnace for 24 h at 200$^o$C and covered with a certain salt mixture (of 0.25g/specimen), which is also called synthetic ash. On the top of the salt 0.005 g of active C was weighted. Then the material samples (up to 5 at a time) were exposed to high temperature in a horizontal tube furnace for 168 h (7 days), at 450°C - 600°C. The furnace was equipped with a tightly closed glass reactor The composition of the gas flowing through the reactor during the tests was 5% CO, 95% $N_2$ with a flow of 2.0 l/min. The furnace with the inner reactor is shown in Figure 1.

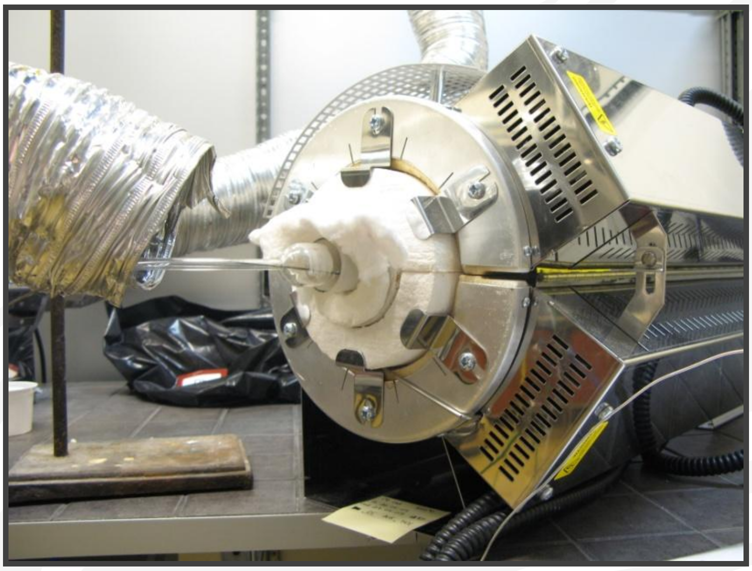


**Figure 1 The horizontal tube furnace with an inner glass reactor**

The chemical compositions of the synthetic ashes used in the experiments are shown in Figure 2. The names: salt 5, salt 8, salt 9 and salt 10 are introduced with respect to previous project dealing with the same salts and are used for comparison and recognition purposes. Broadly speaking, the chosen composition of the tested salts could be explained as follows:

salt 5 – reference salt – only potassium sulfate containing black liquor does not exist

salts 8 and 10 – “represent” black liquors with low and low/medium Cl content salt 9 – no potassium – unlikely for the black liquor. Prepared in order to check what is the role of K.

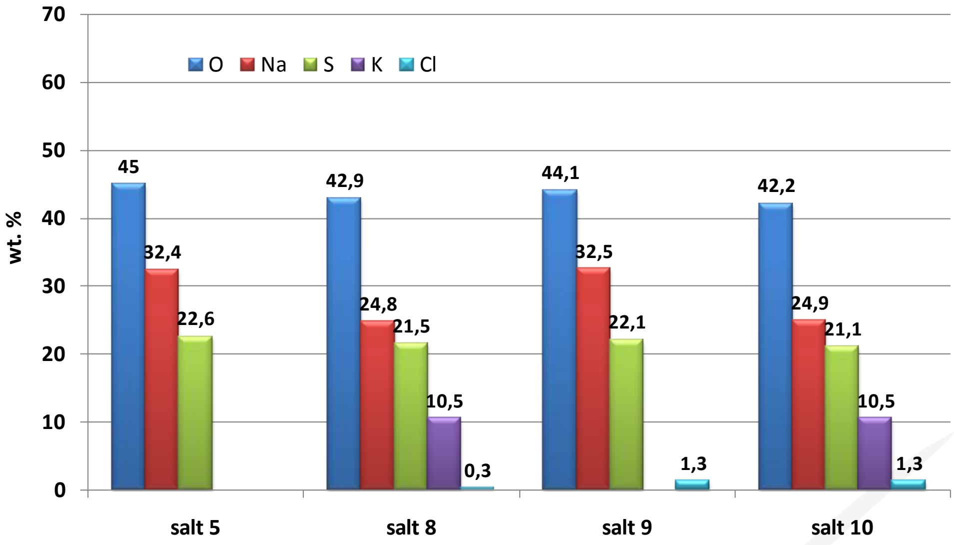


**Figure 2 The chemical compositions of the synthetic ashes used in the corrosion tests (wt%)**

After the corrosion test, the specimens were allowed to cool down to room temperature inside furnace with a continuous flow of the gas mixture through the reactor. The samples were then placed in a mould and cast in epoxy, then cut off in the middle to reveal the specimen's cross-section. The cross-section surfaces were further polished in kerosene, using 1000 and 1200 grid SiC paper, cleaned in petroleum ether and ultrasound bath. The samples were then ready to be analyzed with SEM/EDX in order to identify various chemical elements.

The corrosion products were identified using x-ray images. The corrosion layer thickness was determined using scanning electron microscope back-scatter images. Several SEM images were combined into one panoramic picture. After that the panoramic pictures were digitally treated by using contrast differences. An example of the treatment stages of a typical SEM panoramic picture is shown in Figure 3. After the panoramic images have been colored, the thickness of the oxide layer was determined for each vertical line of pixels and recalculated into µm.

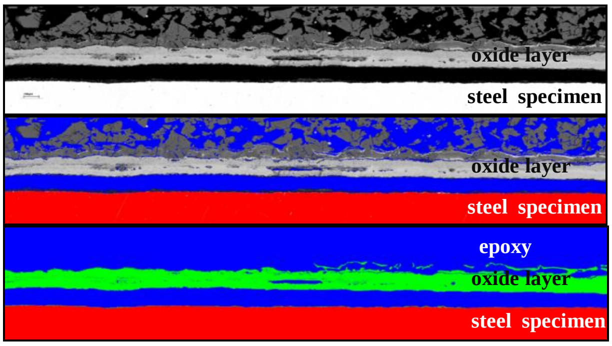


**Figure 3 A schematic view of SEM pictures coloring stages in order to determine the oxide layer thickness**

The corrosion layer was defined as the thickness of the oxide layer for each line and the corrosion attack was expressed as a mean thickness of the oxide layer [3, 4].

# 3. Results and discussion

Five different (with respect to $Cl^-$ and $K^+$ content) salts were used in the corrosion tests. The current section describes separately the tests for each salt.

## 3.1. Tests with Salt 5 ($Na_2SO_4$)

**Salt 5** characteristic:

$T_0$ = 884ºC

No $Cl^-$

No $K^+$

In Table 2 a full test matrix with Salt 5 is presented. One repeatability test for one of the steels was performed during each test. The *corrosion product thickness (μm)* for each steel (if countable) is listed in the table.

**Table 2 Corrosion test matrix for Salt 5**

| | Salt | Steel | Temp | Corrosion products thickness |
|---|---|---|---|---|
| *1* | $Na_2SO_4$ | **10CrMo** | 450 | |
| *2* | $Na_2SO_4$ | **T91** | 450 | |
| *3* | $Na_2SO_4$ | **Sanicro 28** | 450 | |
| *4* | $Na_2SO_4$ | **HR11N** | 450 | |
| *5* | $Na_2SO_4$ | **10CrMo** | 450 | |
| *6* | $Na_2SO_4$ | **10CrMo** | 500 | |
| *7* | $Na_2SO_4$ | **T91** | 500 | |
| *8* | $Na_2SO_4$ | **Sanicro 28** | 500 | |
| *9* | $Na_2SO_4$ | **HR11N** | 500 | |
| *10* | $Na_2SO_4$ | **T91** | 500 | |
| *11* | $Na_2SO_4$ | **10CrMo** | 550 | |
| *12* | $Na_2SO_4$ | **T91** | 550 | |
| *13* | $Na_2SO_4$ | **Sanicro 28** | 550 | |
| *14* | $Na_2SO_4$ | **HR11N** | 550 | |
| *15* | $Na_2SO_4$ | **Sanicro 28** | 550 | |
| *16* | $Na_2SO_4$ | **10CrMo** | 600 | **24** |
| *17* | $Na_2SO_4$ | **T91** | 600 | **6** |
| *18* | $Na_2SO_4$ | **Sanicro 28** | 600 | |
| *19* | $Na_2SO_4$ | **HR11N** | 600 | **2** |
| *20* | $Na_2SO_4$ | **HR11N** | 600 | |

Results from the tests show that up to 550ºC Salt 5 does not induce corrosion. No oxide layer was observed on the samples at 450, 500 and 550ºC. At 600 ºC, a 24 µm and a 6 µm thick oxide layer was formed on 10CrMo and T91, respectively (see Figures 4 and 5). A very thin oxide layer, consisting of a mixture of Fe, Cr, and Ni, was formed on HR11N. However, the oxide layer was just ~2µm, which is considered very low and still indicates a good resistance under these conditions.

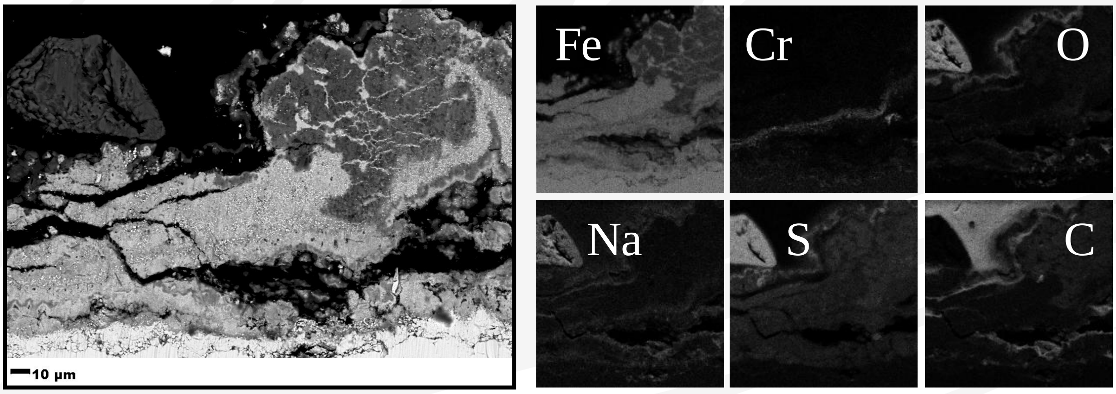


**Figure 4 SEM image and x-ray maps of 10CrMo exposed to Salt 5 at 600°C, 168h**

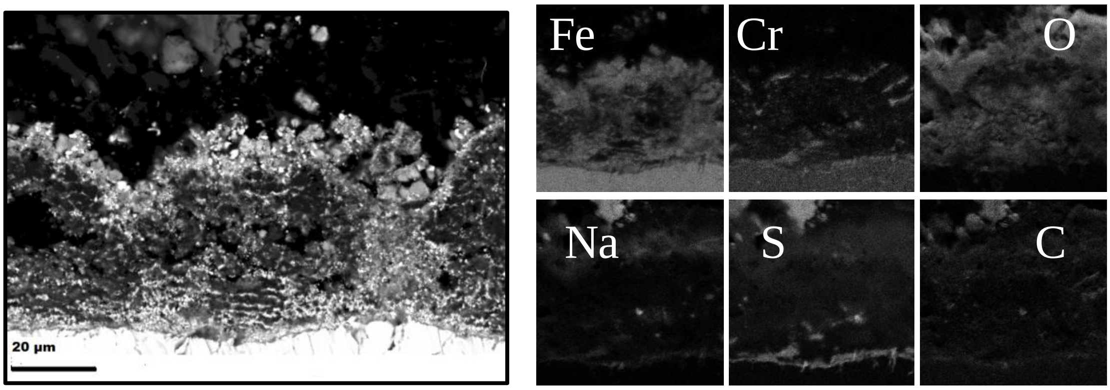


**Figure 5 SEM image and x-ray maps of T91 exposed to Salt 5 at 600ºC, 168h**

## 3.2. Tests with Salt 8 ($Na_2SO_4$ + NaCl + $K_2SO_4$ + KCl)

**Salt 8** characteristic:

$T_0$ = 526ºC

0.3 wt% of $Cl^-$

10.5 wt% of $K^+$

In Table 3 a full test matrix with Salt 8 is presented. One repeatability test for one of the steels was performed during each test. The *corrosion product thickness (µm)* for each steel (if countable) is listed in the table.

**Table 3 Corrosion test matrix for Salt 8**

| | Salt | Steel | Temp | Corr prod. thickness |
|---|---|---|---|---|
| *21* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **10CrMo** | 450 | **11** |
| *22* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **T91** | 450 | **9** |
| *23* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **Sanicro 28** | 450 | |
| *24* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **HR11N** | 450 | |
| *25* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **10CrMo** | 450 | **3** |
| *26* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **10CrMo** | 500 | **3** |
| *27* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **T91** | 500 | |
| *28* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **Sanicro 28** | 500 | |
| *29* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **HR11N** | 500 | |
| *30* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **T91** | 500 | |
| *31* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **10CrMo** | 550 | |
| *32* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **T91** | 550 | |
| *33* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **Sanicro 28** | 550 | |
| *34* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **HR11N** | 550 | |
| *35* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **Sanicro 28** | 550 | |
| *36* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **10CrMo** | 600 | **334** |
| *37* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **T91** | 600 | |
| *38* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **Sanicro 28** | 600 | |
| *39* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **HR11N** | 600 | |
| *40* | $Na_2SO_4$+$K_2SO_4$+NaCl+KCl | **HR11N** | 600 | |

In these tests both $Cl^-$ and $K^+$ were present. The amount of added chlorine as KCl was very small. Likewise to previous case where Salt 5 was tested, also Salt 8 did not show detrimental effects up to 550 ºC. However, a small oxide layer growth was still noticed at 450ºC for both 10CrMo and T91. At 600 ºC only 10CrMo was attacked, and both Fe and Cr were detected in the oxide layer, in addition to the grain boundary corrosion that was observed. The grain boundary corrosion caused separation of big iron grains (see Figure 6) from the bulk material which were then lifted up by the growing oxide layer and found then mixed with the oxide scale/salt mixture. The oxide layer measured on 10CrMo was over 330 µm thick. Chlorine was not found in the sample most probably due to a very small amount of KCl added to the salt.

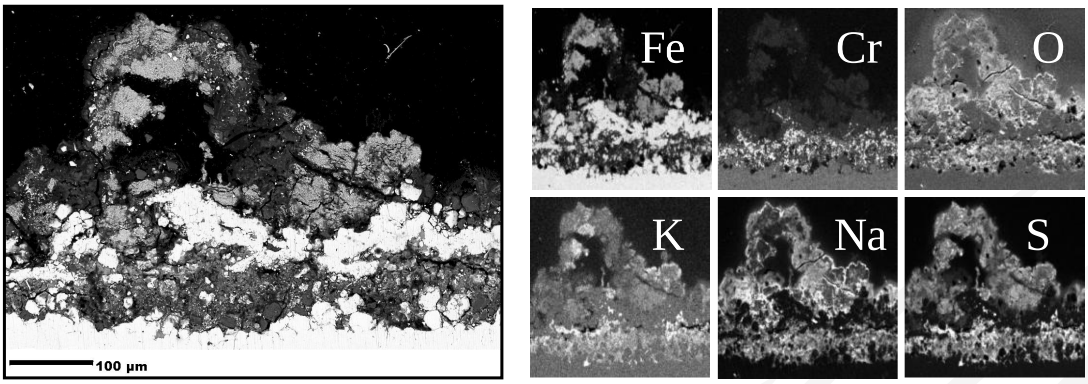


**Figure 6 SEM image and x-ray maps of 10CrMo exposed to Salt 8 at 600 ºC, 168h**

The tests at 600ºC temperature were above the first melting point (526ºC ) and the formation of a melt can be observed in the presented images (Fig 6).

### 3.3. Tests with Salt 9 ($Na_2SO_4$ + NaCl)

**Salt 9** characteristic:
$T_0$ = 621ºC
1.3 wt% of $Cl^-$
No $K^+$

In Table 4 a full test matrix with Salt 9 is presented. One repeatability test for one of the steels was performed during each test. *Corrosion products thickness (µm)* for each steel (if countable) is also gathered in the table.

When comparing to the two previously described salts, Salt 9 contained the highest amount of chlorine which in this case was equal to 1.3 wt%. No potassium was present. Up to 500ºC all materials behaved well and no detrimental effect of the environment was noticed. At 550ºC only 10CrMo was covered with a Fe and Cr oxide layer. The inner part of the oxide scale was dense-looking and Cr rich with traces of S while the outer part of the oxide was partially porous and poorly adherent (see Figure 7). At 600ºC 10CrMo showed no reaction with salt similarly to the other tested materials. Quite interesting behavior was observed with the Ni based and high Cr content HR11N material (see red box in Table 4). There were two samples of HR11N material in the oven during this test (Figure 8).

**Table 4 Corrosion test matrix for Salt 9**

| | Salt | Steel | Temp | Corr prod. thickness |
|---|---|---|---|---|
| *41* | $Na_2SO_4$+NaCl | **10CrMo** | 450 | |
| *42* | $Na_2SO_4$+NaCl | **T91** | 450 | **1** |
| *43* | $Na_2SO_4$+NaCl | **Sanicro 28** | 450 | |
| *44* | $Na_2SO_4$+NaCl | **HR11N** | 450 | |
| *45* | $Na_2SO_4$+NaCl | **10CrMo** | 450 | **3** |
| *46* | $Na_2SO_4$+NaCl | **10CrMo** | 500 | **2** |
| *47* | $Na_2SO_4$+NaCl | **T91** | 500 | |
| *48* | $Na_2SO_4$+NaCl | **Sanicro 28** | 500 | |
| *49* | $Na_2SO_4$+NaCl | **HR11N** | 500 | |
| *50* | $Na_2SO_4$+NaCl | **T91** | 500 | |
| *51* | $Na_2SO_4$+NaCl | **10CrMo** | 550 | **13** |
| *52* | $Na_2SO_4$+NaCl | **T91** | 550 | |
| *53* | $Na_2SO_4$+NaCl | **Sanicro 28** | 550 | |
| *54* | $Na_2SO_4$+NaCl | **HR11N** | 550 | |
| *55* | $Na_2SO_4$+NaCl | **Sanicro 28** | 550 | |
| *56* | $Na_2SO_4$+NaCl | **10CrMo** | 600 | |
| *57* | $Na_2SO_4$+NaCl | **T91** | 600 | |
| *58* | $Na_2SO_4$+NaCl | **Sanicro 28** | 600 | |
| *59* | $Na_2SO_4$+NaCl | **HR11N** | 600 | **62** |
| *60* | $Na_2SO_4$+NaCl | **HR11N** | 600 | **0** |

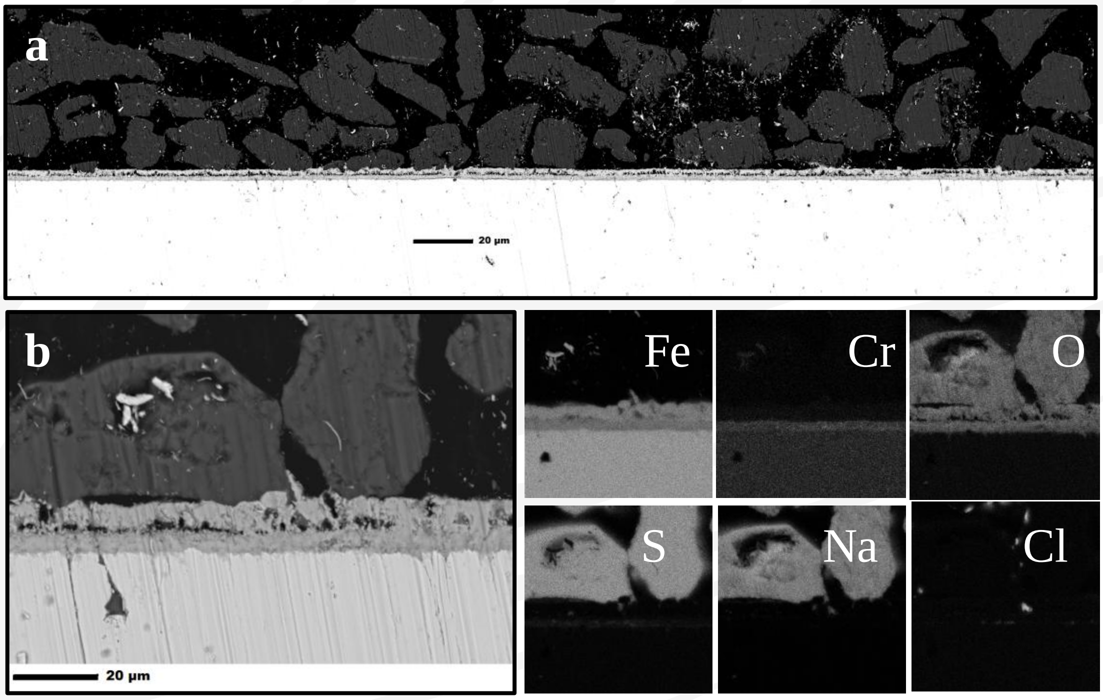


**Figure 7 a) Part of 10CrMo panorama picture after 168h tests at 550°C test with Salt 9, b) SEM image and x-ray maps**

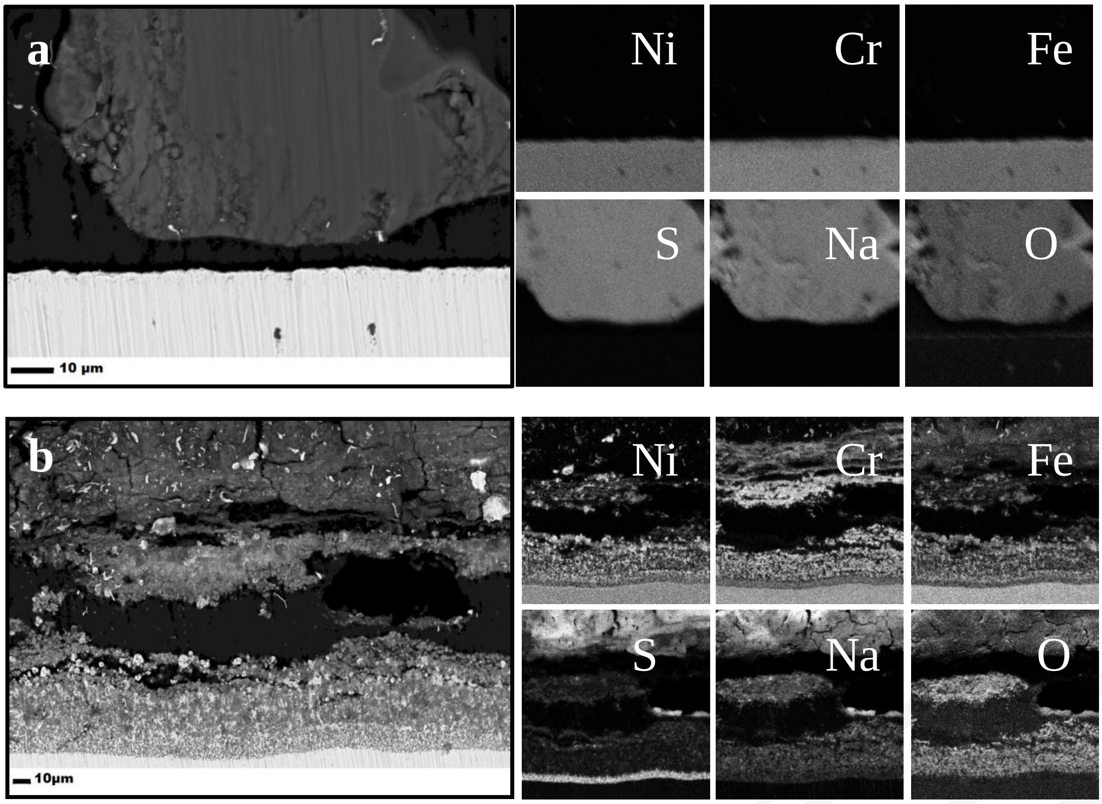


**Figure 8 SEM image and x-ray maps of HR11N duplicates exposed to Salt 9 at 600°C, 168h, a) no reaction occurred, b) severe corrosion attack**

One of the HR11N samples showed no reaction (see Figure 8a) with the salt while the other sample was destroyed quite severely (see Figure 8b). The measured internal attack together with oxide layer was over 60 µm thick. Mainly depletion of the alloying elements from the steel surface was observed. The depleted layer was almost entirely oxidised, however, the very bottom of depleted layer was S-rich and without oxygen (see Figure 8, x-ray maps).

It is not fully clear why the two HR11N samples showed completely different response under the same conditions. A double check was done to confirm that the materials had the same compositions. However, later in the report in Chapter 4 one explanation is proposed.

## 3.4. Tests with Salt 10 ($Na_2SO_4$ + $K_2SO_4$ + KCl)

**Salt 10** characteristic:

$T_0$ = 522°C

1.3 wt% of $Cl^-$

10.5 wt% of $K^+$

In Table 5 a full test matrix with Salt 10 is presented. One repeatability test for one of the steels was performed during each test. *Corrosion products thickness (μm)* for each steel (if countable) is listed in the table.

**Table 5 Corrosion test matrix for Salt 10**

|  | Salt | Steel | Temp | Corr prod. thickness |
|---|---|---|---|---|
| *61* | $Na_2SO_4+K_2SO_4+KCl$ | **10CrMo** | 450 |  |
| *62* | $Na_2SO_4+K_2SO_4+KCl$ | **T91** | 450 |  |
| *63* | $Na_2SO_4+K_2SO_4+KCl$ | **Sanicro 28** | 450 |  |
| *64* | $Na_2SO_4+K_2SO_4+KCl$ | **HR11N** | 450 |  |
| *65* | $Na_2SO_4+K_2SO_4+KCl$ | **10CrMo** | 450 |  |
| *66* | $Na_2SO_4+K_2SO_4+KCl$ | **10CrMo** | 500 |  |
| *67* | $Na_2SO_4+K_2SO_4+KCl$ | **T91** | 500 |  |
| *68* | $Na_2SO_4+K_2SO_4+KCl$ | **Sanicro 28** | 500 |  |
| *69* | $Na_2SO_4+K_2SO_4+KCl$ | **HR11N** | 500 |  |
| *70* | $Na_2SO_4+K_2SO_4+KCl$ | **T91** | 500 |  |
| *71* | $Na_2SO_4+K_2SO_4+KCl$ | **10CrMo** | 550 | **2** |
| *72* | $Na_2SO_4+K_2SO_4+KCl$ | **T91** | 550 | **2** |
| *73* | $Na_2SO_4+K_2SO_4+KCl$ | **Sanicro 28** | 550 | **2** |
| *74* | $Na_2SO_4+K_2SO_4+KCl$ | **HR11N** | 550 | **2** |
| *75* | $Na_2SO_4+K_2SO_4+KCl$ | **Sanicro 28** | 550 | **2** |
| *76* | $Na_2SO_4+K_2SO_4+KCl$ | **10CrMo** | 600 | **306** |
| *77* | $Na_2SO_4+K_2SO_4+KCl$ | **T91** | 600 | **54** |
| *78* | $Na_2SO_4+K_2SO_4+KCl$ | **Sanicro 28** | 600 | **53** |
| *79* | $Na_2SO_4+K_2SO_4+KCl$ | **HR11N** | 600 | **76** |
| *80* | $Na_2SO_4+K_2SO_4+KCl$ | **HR11N** | 600 | **24** |

The last of tested salts in this project contained the highest amounts of potassium and chlorine which were 1.3 wt% and 10.5 wt% respectively. Up to 500ºC no corrosion was observed. At 550ºC all tested materials had visible inclusions, however, they were of negligible thickness and can be omitted. The situation changed at 600ºC where all materials suffered significant corrosion attacks. 10CrMo suffered the most (see Figure 9). The corrosion products and type of corrosion was very similar to the test with Salt 8 at 600ºC. The only difference between those tests was the amount of Cl added. Salt 8 contained 0.3 wt% of $Cl^-$ while Salt 10 contained 1.3 wt% of $Cl^-$. Separated metal grains were lifted up by the growing oxide layer and found then mixed with the metal oxides/salt mixture in a similar way as before. It was observed that areas between the grains were depleted from chromium and filled with sulphur and potassium (see Figure 6). T91 steel also suffered from grain boundary corrosion but no cracks on the steel surface were observed. Particles of metallic Fe were spread in the salt while Cr in the form of oxide was well mixed in it. In the cases of high alloy steels, S28 and HR11N, the surfaces showed significant Cr depletion. Directly beneath the depleted steel surface a sulfur rich layer together with sodium was present (Figures 11 and 12).

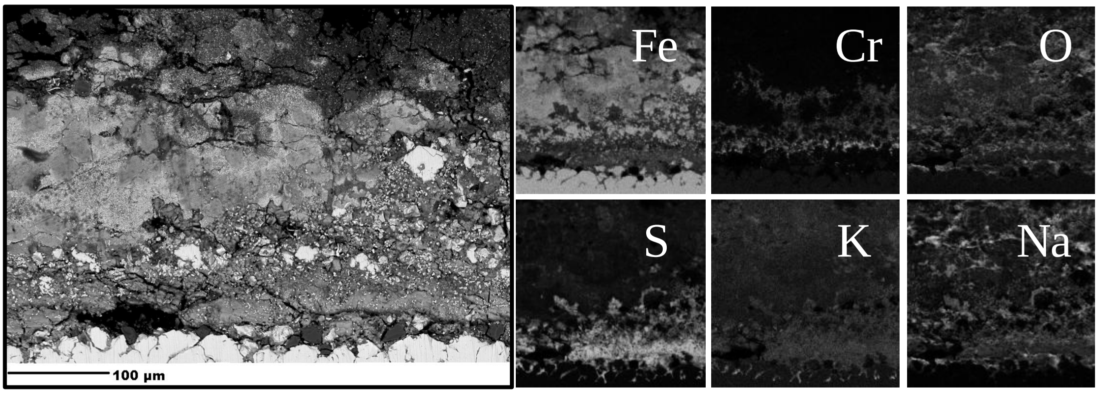


Figure 9 SEM image and x-ray maps of 10CrMo exposed to Salt 10 at 600°C, 168h

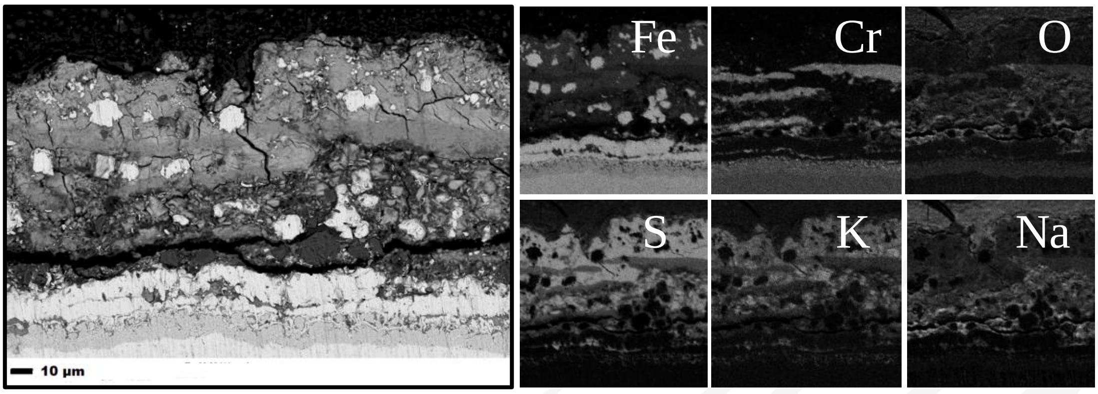


Figure 10 SEM image and x-ray maps of T91 exposed to Salt 10 at 600°C, 168h

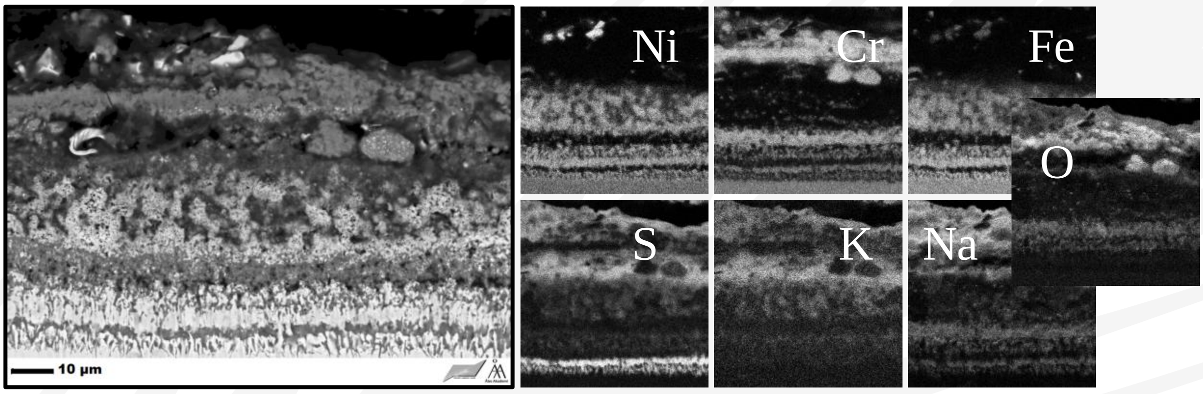


Figure 11 SEM image and x-ray maps of S28 steel exposed to Salt 10 at 600°C, 168h

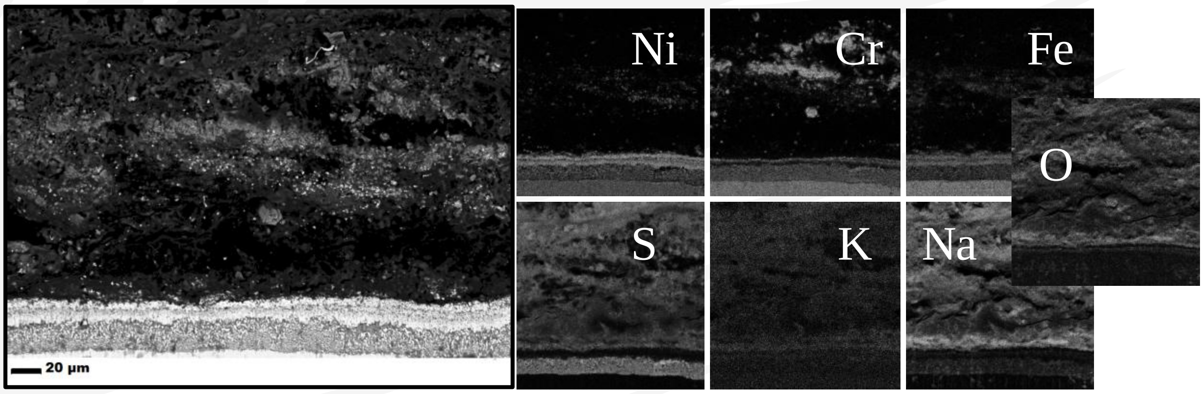


Figure 12 SEM image and x-ray maps of HR11N exposed to Salt 10 at 600°C, 168h

## 3.5. Reducing vs. ambient atmosphere

In a previous project (SOTU2) the same salts have been used for corrosion tests in ambient atmosphere. A comparison of these results for Salts 5, 8, 9, and 10 in ambient and reducing atmosphere is presented below on separate graphs (Fig 13). Tests that have not been performed are marked with the green “x”. No bar means - oxide layer thickness below the detection limit. Considering that the tests in ambient atmosphere have already been discussed and reported e.g. [2], visible differences between tested atmospheres are shortly described.
The graphs show that reducing atmosphere generally did not cause significant problems in the tests at temperatures 550°C and lower. The corrosion rates were higher for the corresponding cases in ambient atmosphere where the corrosion rate was significant already at 500°C and even worse at 550°C. Under reducing conditions the corrosion became severe at 600°C with Salt 10 (containing both potassium and chlorine in the highest amount among tested salts mixtures) as also in ambient atmosphere. However, direct comparison of the harmfulness between ambient and reducing atmosphere in the tests with Salt 10 at 600°C is not possible since different material reacted differently.

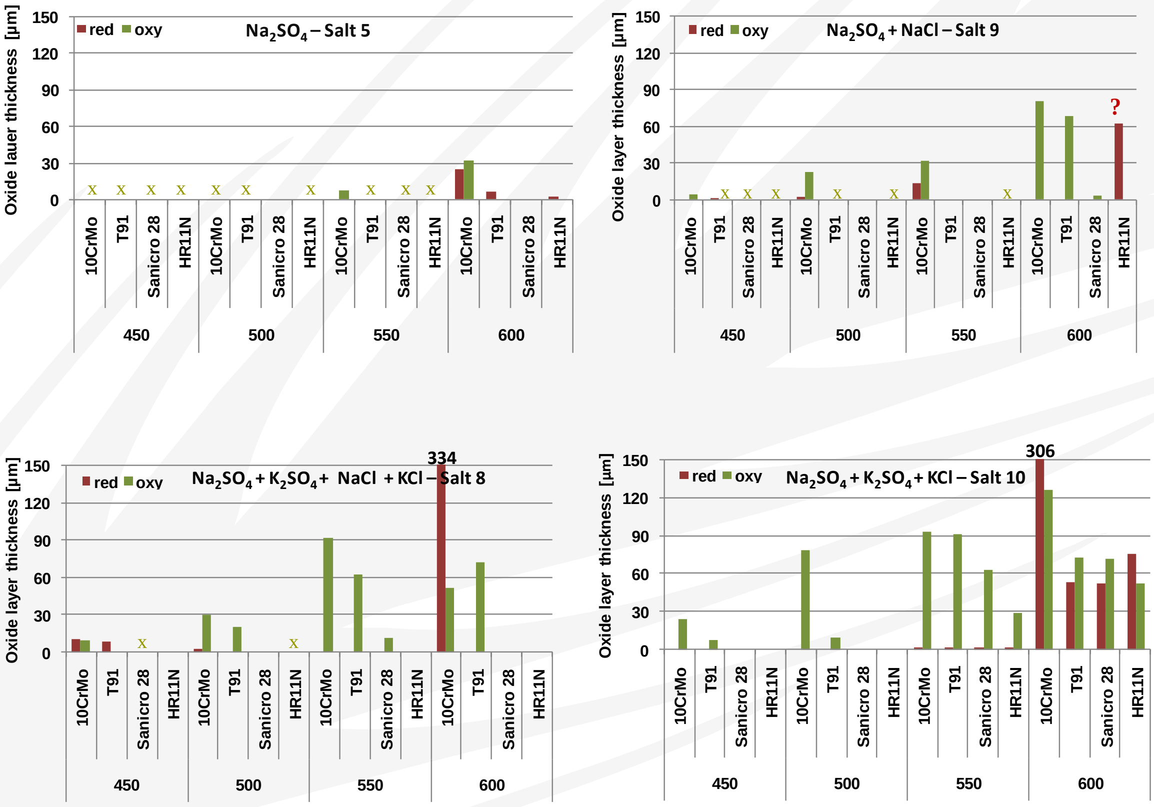


**Figure 13 The mean oxide layer/corrosion product thickness of the tested materials in ambient (*green bars* - oxy) and reducing atmosphere (*red bars*- red). The corrosion tests duration 168h.**

Anyhow, both atmospheres together with Salt 10 and high temperature had a highly destructive effect on the performance of the tested materials. The case with HR11N at 600ºC with Salt 9 (see also Figure 8) is discussed in more detail in the chapter below.

# 4. Thermodynamic calculations and considerations

Additionally to the laboratory tests, thermodynamic calculations describing the melting behaviour of the salts used in the experiments have been performed. Figures 14a, 14b, 14c and 14d present the melting curves of the salts.

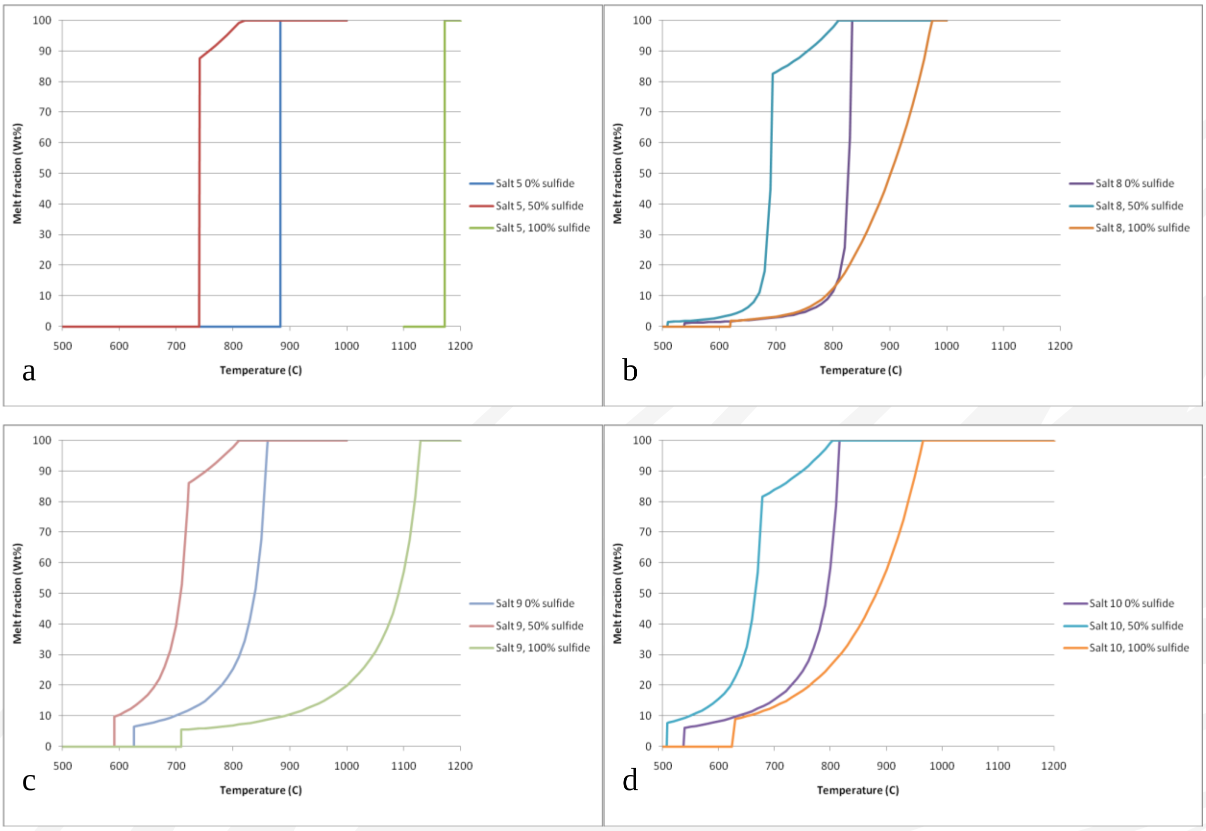


**Figure 14 The calculated melting behaviour of the salts a) #5, b) #8, c) #9, d) #10 presented as the amount of molten phase in the salt as a function of temperature. The calculations were performed assuming that 0 mol %, 50 mol % or 100 mol% of sodium sulfate reacted and formed sodium sulfide. Calculations done by Daniel Lindberg.**

It can be noticed that a 100% reduction of sodium sulfate to sodium sulfide shifts the $T_0$ of the salts to 100ºC higher or more. On the other hand, a partial reduction of the salt mixtures lowers $T_0$ down to 590°C in case of Salt 9 or even down to 510°C – Salts 8 and 10. In addition, amount of melt increases with increasing temperature. If we now study the partially reduced salt that would have the lowest melting point (Salt 10), a noticeable melt should have appeared in the corrosion tests already at 550°C. However, only partial melting of the particles gluing them together was observed at 550°C while the sample at 600°C looked completly different (Figure 15).

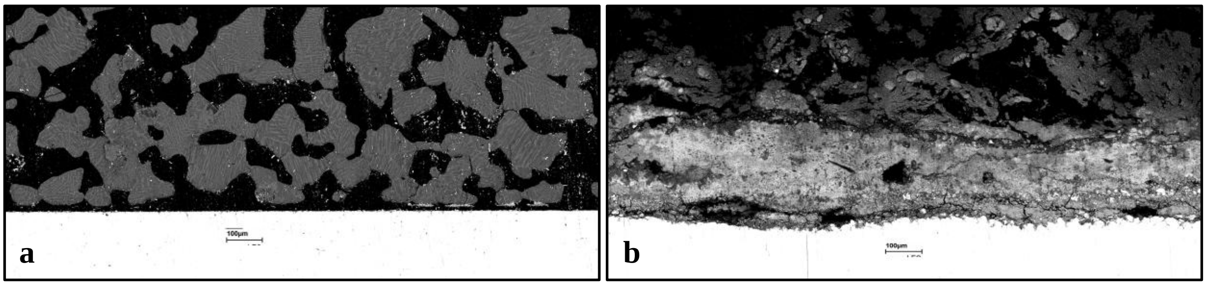


**Figure 15 The panorama pictures of 10CrMo9-10 steel exposed to Salt 10 at a) 550ºC and b) 600ºC.**

This indicates that there was no significant sulphate reduction to sulfide at test temperatures below 600°C, which is supported by Li and van Heiningen [6] who showed that sulfate reduction starts at a temperature between 600-630ºC for a mixture of activated carbon and sodium sulfate. This also explains the results with HR11N covered with Salt 9, which in one case resulted in no corrosion and in the other case corroded heavily. Comparing these two HR11N-cases, we can see that in the corroded case a Na and S containing layer just above the metal surface (Figure 8b) indicating some reduction of sulphate to sulfide and simultaneously the formation of a melt, while in the other case (Figure 8a) no such layer can be observed.

Based on these observations one can conculde that no significant reduction of sulfate to sulfide occurred below 600°C and even at 600°C this reaction was limited. In combination with the corrosion results this also further suggests that the corrosion in reducing conditions is strongly dependent on $Na_2S$ formation in combination with a melt being present.

# 5. Conclusions

1. For the salts where no potassium was added and just 0.3 wt% of $Cl^-$ (Salts 5 and 9) only low corrosion rates were observed. The exception was 10CrMo with Salt 5 at 600ºC where the corrosion rate was slightly increased as with the HR11N nickel based austenitic stainless steel with Salt 9 at 600ºC. An explanation based on the temperature sensitivity of the sulfate reduction was proposed.
2. The results showed that salts containing both potassium and chlorine in the salt mixture (when comparing four tested salts) induced corrosion:
   a. at reducing conditions for all steels ≥ 550ºC

  - b. at ambient conditions for low grade steels especially ≥ 500ºC, for all steels ≥ 550ºC ($T_0$ of the K containing salts slightly above 500ºC)
3. In reducing conditions and high temperature (600ºC):
   - a. Low grade steels were destroyed mainly by grain boundary corrosion
   - b. Austenitic steels underwent heavy depletion of Cr from the surface
4. *Sulfur* was often found on the corrosion front beneath the depleted surface of the bulk material suggesting formation of metal sulfides. This was typically but not exclusively observed in the cases of high alloy steels, S28 and HR11N.
5. Reducing conditions induced mainly internal attack of the steel
6. In ambient conditions growth of the oxide layer was promoted
7. Ambient atmosphere appeared to be more harmful than reducing
8. Thermodynamic calculations in combination with the results and the literature give indications that the full reduction of the tested salts did not occur at temperatures below 600ºC and even at 600ºC the reduction reaction may have been limited

Based on the performed tests as well as on the presented thermodynamic calculations further research on the reducing conditions (salt reduction reactions) itself should be done. The following optional tests have been suggested:

1. To increase the amount of active C/sample and mix it well with the salt
2. To increase the test temperature in order to attain a stronger reduction of $Na_2SO_4$ to $Na_2S$
   - a. 610, 620, 630, 640, 650ºC (active C as a reducing agent)
   - b. heat up the samples to e.g. 630ºC, keep it there for a certain certain time to achieve a sulphate reduction and then decrease the temperature to the test temperature. However, this treatment may influence the materials differently, and may in some cases give unclear results
3. To create reducing conditions by different methods:
   - a. BL-char on the salt
   - b. BL-char/salt mixture

Option 3 was already considered in this work, however, since BL-char contains chlorine and it is known that the corrosion can be very sensitive to the amounts of Cl it was decided to use active carbon as the reducing agent.

# References

[1] Otsuka, N. *Effects of fuel impurities on the fireside corrosion of boiler tubes in advanced power generating systems—a thermodynamic calculation of deposit chemistry*. Corrosion Science 44 (2), 265-283

[2] Skrifvars, B-J., Backman, R., Hupa, M., Salmenoja, K., Vakkilainen, E. *Corrosion of superheater steel materials under alkali salt deposits Part 1: The effect of salt deposit composition and temperature.* Corrosion Science 50, 1274-1282 (2008)

[3] Westén-Karlsson, M. *Assessment of a Laboratory Method for Studying High Temperature Corrosion Caused by Alkali Salts.* Lic. Thesis, Åbo Akademi University, Åbo, Finland 2008, ISBN 978-952-12-2116-3

[4] Bankiewicz, D., Yrjas, P., Hupa, M. *High temperature corrosion of steam tube materials exposed to zinc salts.* Energy&Fuels 23 (7), 3469-3474 (2009)

[5] Skrifvars, B-J., Westén-Karlsson, M., Hupa, M., Salmenoja, K. *Corrosion of superheater steel materials under alkali salt deposits Part 2: SEM analyses of different steel materials.* Corrosion Science 52, 1011-1019 (2010)

[6] Li, J., van Heiningen, A. R. P. *Kinetics of Solid State Reduction of Sodium Sulphate by Carbon.* Journalof Pulp and Paper Science vol. 22, no 5 (1995)

# LIITE XI

## SKYREC - FRBC’s Material recommendation – table of contents

## ESIPUHE

## SISÄLLYSLUETTELO

# LIITE XII

Timo Karjunen, Boildec Oy
SKYREC - Field tests of furnace materials – testi 1 raportti
27.4.2010

Tilaaja Soodakattilayhdistys 26.4.2010

## TULIPESÄSONDIKOE NRO 1

Kokeessa oli tarkoitus altistaa koemateriaalit tulipesäolosuhteille 1000 tunnin ajan niin, että koemateriaalien pintalämpötila on 440°C. Kokeessa testattavia materiaaleja olivat 3R12 (304L), 3RE28 (AISI310S), San28 ja San38.

Koe aloitettiin asentamalla sondi paikoilleen 2.3.2010. Sondin paine nostettiin päivän aikana hitaasti tasolle 6 bar (abs), johon se jätettiin vuorokaudeksi. Paine nostettiin asetusarvoonsa 9,5 bar (abs) 3.3.2010 klo 10:00, josta testijakso lasketaan alkavaksi. Tässä paineessa lämpötila sondin höyrystinosan, jonka etuseinän muodostavat testimateriaalit, sisällä on n. 390°C.

Koemateriaalien lämpötilaa seurattiin kokeen aikana kahdella termoelementillä. Mittaustulosten mukaan koemateriaalien lämpötila höyrystinosan etuseinän keskellä oli keskimäärin 407 - 411°C. Koemateriaalien pintalämpötiloja ei mitattu, mutta niiden arvioidaan olleen keskimäärin 432 - 435°C.

Termoelementit vikaantuivat 8.3. ja 21.3., joten mittaustietoa lämpötiloista on ainoastaan osasta koejaksoa. Sondin painemittauksen tulosten perusteella olosuhteet sondissa pysyivät vakaina eikä kattilan kuormassa tapahtunut muutoksia koko koejakson aikana. On siten perusteltua olettaa, että koemateriaalien lämpötilat eivät merkittävästi muuttuneet sen jälkeen, kun termoelementit vikaantuivat, ja lämpötilamittausten tuloksia voidaan siten pitää koko koejakson lämpötiloja edustavina.

Sondissa havaittiin 17.3. pieni vuoto, jonka korjaamisesta aiheutui 22 h pituinen keskeytys sondin käyttöön.

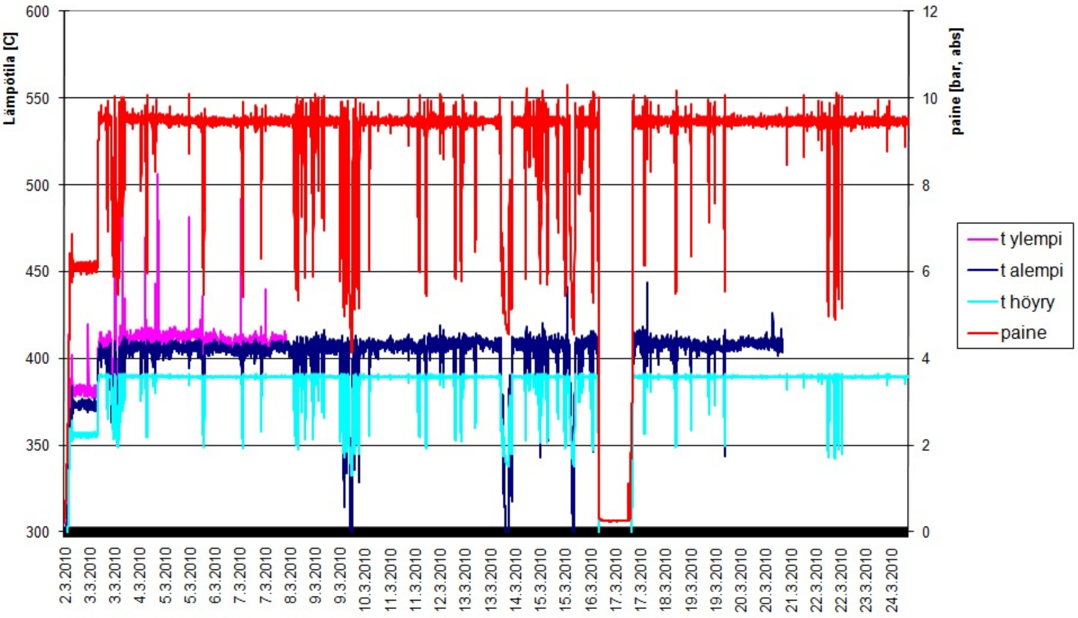
Sondiin jäähdytysilmaa syöttävää puhallinta ohjaava painemittaus vikaantui 31.3. Jäähdytysilman varasyöttö oli järjestetty paineilmajärjestelmästä. Paineilman virtausta kontrolloivat venttiilin ohjausta säädettiin sondin paineen perusteella asetusarvona 10 bar (abs). Kun normaalisäädössä käytetyn painelähettimen vikaantuminen huomattiin 6.4., laskettiin paineilmajäähdytyksen säädön paineen asetusarvo arvoon 9,5 bar (abs). Paineen asetusarvon nousu 0,5 bar verran nosti sondin lämpötilaa alle 3°C verran noin viikoksi. Muutoksen vaikutus koemateriaalien keskilämpötiloihin kokeessa oli siten vähäinen, luokkaa 0,5°C koko koejakson yli arvioituna.

Koe lopetettiin 15.4.2010 klo 8:30, jolloin sondi oli ollut toiminnassa yhteensä 1006 tuntia. Tästä ajasta sondin paine oli yli 9 bar (abs) 906 tuntia eli yli 90 % kokeen kokonaiskestosta.

## Mittaustulokset

Lämpötilamittaukset oli asennettu ylimpään (3R12) ja alimpaan (San38) koepalaan koepalojen ylä-/alareunasta keskelle porattuihin reikiin. Termoelementit on pyritty asentamaan niin, että ne mittaavat kummankin koepalan lämpötilaa palan keskeltä sekä pituus-, leveys- että syvyyssuunnassa.

Lämpötilamittausten tulokset koejakson alkupuoliskolta (2. - 24.3) on esitetty kuvassa 1. Kuvassa on myös sondin paine ja paineen perusteella laskettu lämmönsiirtoöljyn höyrystymislämpötila.



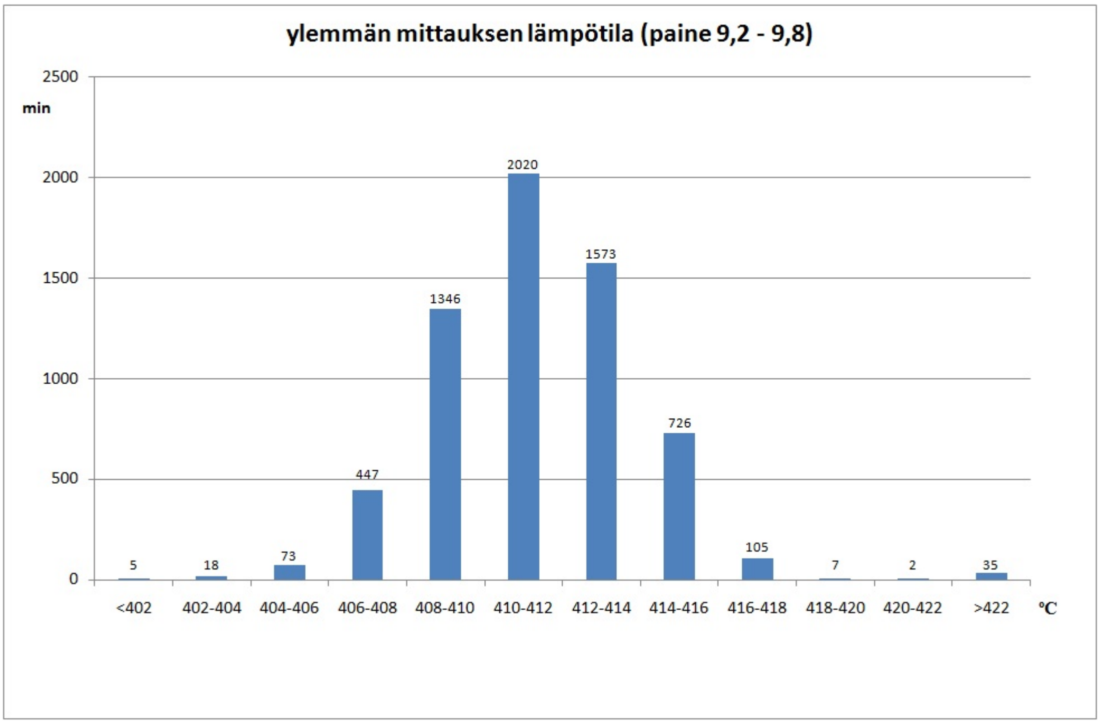
**Kuva 1.** Sondin paine, painetta vastaava lämmönsiirtoöljyn höyrystymislämpötila sekä koemateriaalien lämpötilat 2. – 24.3. (koejakson alkupuolisko)

Kuten kuvasta 1 nähdään, sondin paine pysyi koko jakson ajan alueella 4,0 – 10,2 bar lukuun ottamatta jaksoa, jolloin sondi otettiin pois paikoiltaan vuodon korjaamista varten.

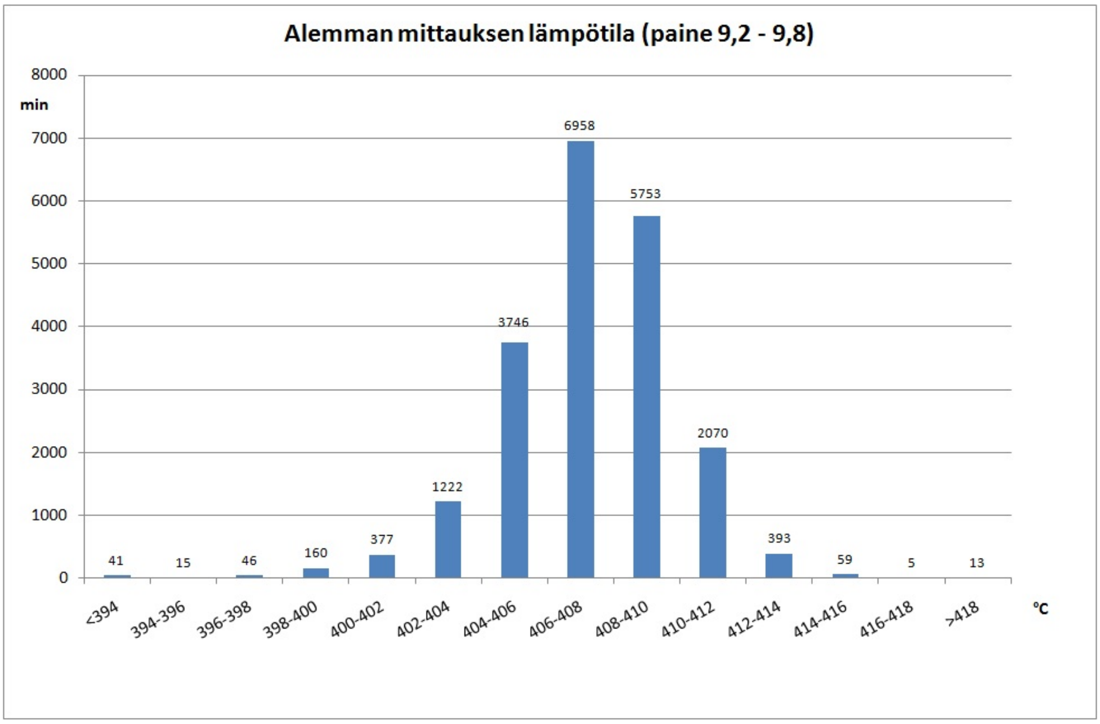
Erityisen positiviista oli, että sondin paine ei kertaakaan laskenut hyvin matalaksi, toisin kuin aikaisemmissa kokeissa. Ilmeisesti syynä paineen laskuun on sondin altistuminen lipeäsateelle, ts. lipeän roiskuminen suoraan sondin höyrystinosaan. Aikaisemmissa kokeissa tapahtuneisiin paineen laskuihin liittyi toisinaan koemateriaalien lämpötilojen karkaamista, jonka syynä oli oletettavasti lämmönsiirtokriisi höyrystinosassa. Koelaitteisto näyttäisi nyt toimivan niin, että tällaisia ongelmia ei enää esiinny.

Kuvasta 1 voidaan todeta, että koemateriaalien lämpötila on melko tasaisesti hieman yli 400°C, mutta lämpötilatrendeissä näkyy joitakin piikkejäkin, jotka ovat korkeimmillaan 530°C (ylempi koemateriaali) ja 440°C (alempi koemateriaali).

Piikkien osuus koko mittausjaksolla oli hyvin vähäinen lämpötilojen painottuessa voimakkaasti alueelle 400 - 420°C, ks. kuvat 2 ja 3. Kuvissa on esitetty mittaustulosten jakauma jaksoilta, joilla sondin paine oli lähellä asetusarvoa (9,5 bar abs). Ylemmän 3R12-palan lämpötila oli yli 450 °C 25 min ja 500 - 530 °C 4 min ajan. Alemman San38-palan lämpötila nousi puolestaan 440 °C lämpötilaan kaksi kertaa minuutiksi.

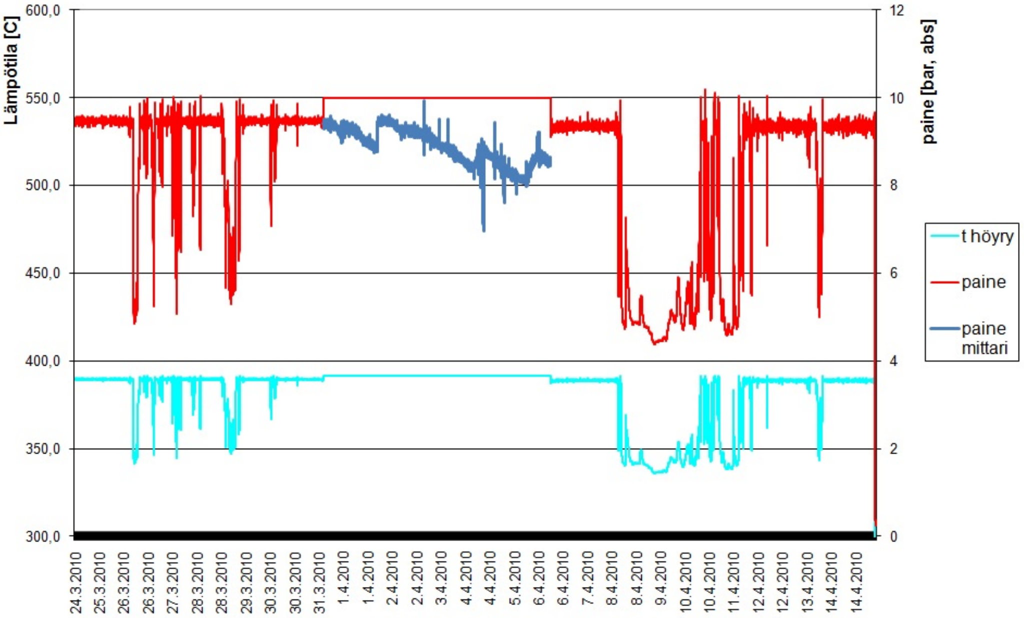


**Kuva 2.** Ylemmän lämpötilamittauksen tulosjakauma sondin paineen ollessa 9,2 – 9,8 bar.



**Kuva 3.** Alemman lämpötilamittauksen tulosjakauma sondin paineen ollessa 9,2 – 9,8 bar.

Viimeinen toiminnassa ollut termoelementti vikaantui 21.3., joten koejakson jälkipuoliskolta on käytettävissä ainoastaan sondin painemittauksen tulokset, kuva 4.

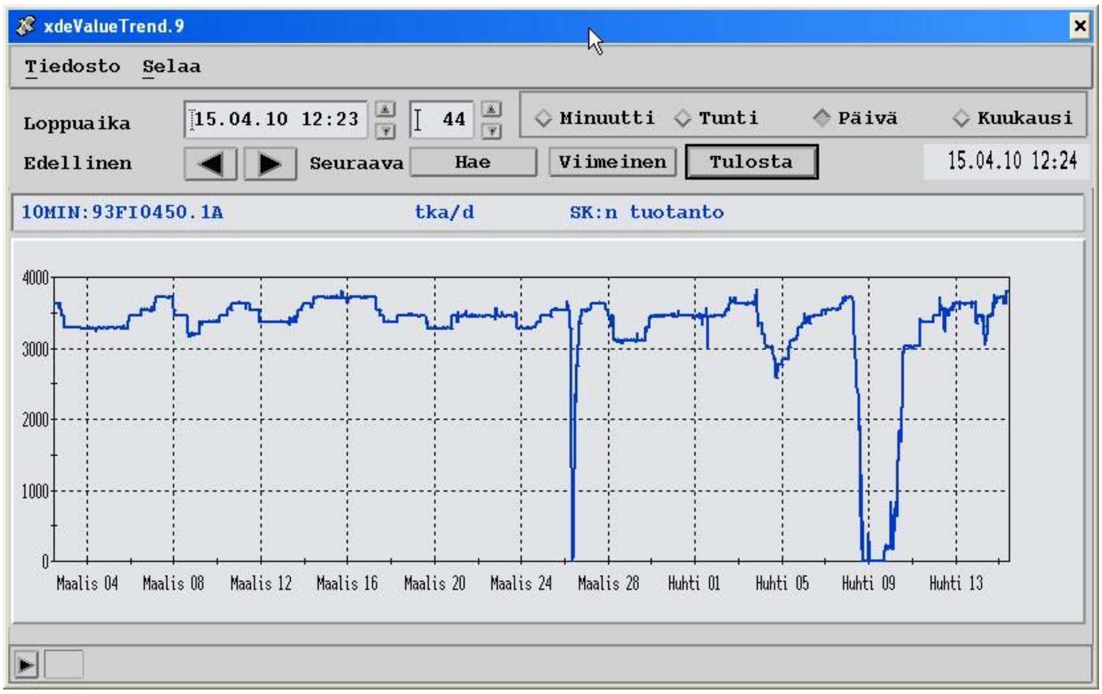


**Kuva 4.** Sondin paine ja painetta vastaava lämmönsiirtoöljyn höyrystymislämpötila 24.3. – 15.4.

Kuvassa 4 esitetyn jakson keskivaiheilla näkyy sinisellä värillä erotettu käyrä ("painemittari"), joka kuvaa tuloksia jaksolla, jolla jäähdytysilmapuhaltimen säädössä käytetty painemittaus oli vikaantunut ja tulos on siten virheellinen.

Mittauksen vikaantuminen havaittiin verrattaessa ko. painemittauksen tulosta toiseen, paineilman syötön säädössä käytetyn painemittauksen tulokseen. Tämän mittauksen tuloksia ei tallennettu dataloggerille. Vertailu vikaantuneen painemittarin tilalle vaihdetun uuden mittarin tuloksiin, jotka ovat esitetty kuvassa 4 (punainen trendiviiva oikeassa reunassa), osoitti, että paineilman syötön säädössä käytetty painemittaus toimi tarkasti ja luotettavasti.

Sondin paine pysyi koejakson loppupuolen hyvin hallinnassa lukuun ottamatta jaksoja, joilla sondin paine laski tasolle 4 – 8 bar kattilan kuorman putoamisen takia (26.3. ja 8.-10.4., ks. kuva 5).


Loppuaika 15.04.10 12:23 44
15.04.10 12:24
10MIN:93FI0450.1A tka/d SK:n tuotanto

**Kuva 5.** Kattilan kuorma koejaksolla

Kattilan kuorma oli koejakson alussa, kun lämpötilamittaukset vielä toimivat, normaali, joten tuolloin mitattujen lämpötilojen voidaan olettaa olevan edustavia koko koejaksolle (myös koejakson loppupuoliskolle, jossa lämpötilamittaukset eivät enää toimineet luotettavasti).

## YHTEENVETO

Koe nro 1 saatiin onnistuneesti päätökseen niin, että

- kokeen kokonaiskesto oli yli 1000 h, jona aikana sondin paine (ja siten myös koemateriaalien lämpötilat) oli lähellä tavoitearvoa noin 900 tunnin ajan
- lämpötilamittausten tulosten mukaan koemateriaalien lämpötila seinämän keskellä oli keskimäärin 407 - 412°C
- laskennallisesti arvioidut pintalämpötilat testimateriaaleilla olivat keskimäärin 432 - 435°C
- lämpötilamittausten tulosten mukaan testimateriaalien maksimilämpötilat olivat koko ajan alle 530°C
- testimateriaalien lämpötilat olivat 450 - 530°C enimmillään muutamien tuntien ajan koko koejaksolla (alun 6 vrk aikana 25 min)
- sondin paine saatiin hallittua niin, että sondin paine ei laskenut kertaakaan niin matalalle, että koemateriaalien lämpötilat olisivat voineet karata lämmönsiirtokriisin takia.

Jatkossa kokeet pyritään tekemään samanlaisissa olosuhteissa kuin nyt tehty koe, ts. säätäen sondin paineeksi kokeen aikana 9,5 bar (abs).

Koelaitteistossa yritetään parantaa lämpötilamittausten suojausta niin, että mittaukset kestävät jatkossa koko koejakson.

# LIITE XIII

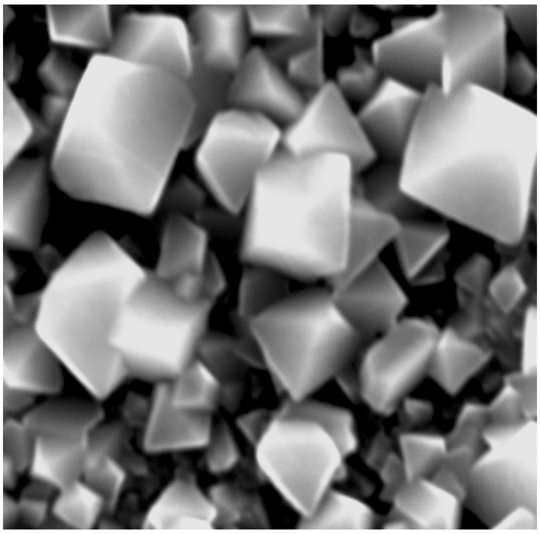
Mikko Vepsäläinen, VTT

# SKYREC - Effect of water quality and different chemicals on magnetite layer properties – lopullinen raportti

21.4.2010

TUTKIMUSRAPORTTI -
LUONNOS

VTT-R-



# Alkaloivien amiinien vaikutus hiiliteräksen magnetiittikalvon ominaisuuksiin

| | |
|---|---|
| Kirjoittajat: | Mikko Vepsäläinen, Petri Kinnunen, Timo Saario, Pekka Pohjanne, Stella Rovio |
| Luottamuksellisuus: | Luottamuksellinen |

Raportin nimi

# Alkaloivien amiinien vaikutus hiiliteräksen magnetiittikalvon ominaisuuksiin

| | |
|---|---|
| Asiakkaan nimi, yhteyshenkilö ja yhteystiedot<br>Suomen Soodakattilayhdistys ry | Asiakkaan viite<br>16A0913 / S87 |
| Projektin nimi<br>Miten eri kemikaalit ja veden laatu vaikuttavat hiiliteräksen magnetiittikalvon ominaisuuksiin? | Projektin numero/lyhytnimi<br>35172 / SKYREC CS |
| Raportin laatija(t)<br>Mikko Vepsäläinen, Petri Kinnunen, Timo Saario, Pekka Pohjanne, Stella Rovio | Sivujen/liitesivujen lukumäärä<br>21/3 |
| Avainsanat<br>Amiinit, Alkalointi, Magnetiitti | Raportin numero<br>VTT-R- |

Tiivistelmä

Tutkimuksessa selvitettiin alkaloivien amiinien termistä hajoamista ja vaikutusta hiiliteräksen pinnalle syntyvän magnetiittikerroksen ominaisuuksiin 340 °C lämpötilassa. Tutkittavia kemikaaleja olivat morfoliini, sykloheksyyliamiini ja 2-amino-2-metyyli-1-propanoli ja referenssinä käytettiin ammoniakkia. Kyseiset yhdisteet ovat yleisesti käytössä soodakattiloissa käytettävissä vesikemikaaliseoksissa. Kokeiden aikana kemikaalien hajoamista seurattiin on-line pH-mittauksella ja vesinäytteistä määritettiin amiinien pitoisuudet kapillaarielektroforeesilla. Magnetiitin muodostumista hiiliteräsnäytteiden pinnalle seurattiin potentiaali- ja impedanssimittauksilla hiotuista ja esihapetetuista näytteistä.

Tutkituista amiineista morfoliinin terminen kestävyys oli paras ja 2-amino-2-metyyli-1-propanolin heikoin. Määritettyjen hajoamistuotteiden pitoisuudet olivat vähäisiä kokeissa käytetyillä kemikaaliannoksilla. Vähähappisessa vedessä hajoamistuotteina syntyy lähinnä pienemmän molekyylipainon amiineja ja erilaisia alkoholeja, ei orgaanisia happoja. Pienten hajoamistuotemäärien tarkka analysointi vaatii kvalitatiivisia tutkimusmenetelmiä.

Potentiaalimittausten mukaan hiiliteräsnäytteiden pinnalle muodostui suojaava magnetiittikerros alle 12 h koeajalla. Potentiaali sijaitsi magnetiitin termodynaamisella stabiilisuusalueella kaikilla näytteillä. EIS-mittausten mukaan alkaloivat amiinit vaikuttivat hiiliteräksen magnetiittikalvon ominaisuuksiin. Warburg-kertoimien mukaan rauta-ionien diffuusio oksidikerroksen läpi nopeutui alkaloivien amiinien vaikutuksesta. Kokeen viimeisistä mittauksista laskettujen aineensiirtovastusten mukaan korroosionopeuksissa ei kuitenkaan ollut merkittävää eroa eri näytteiden välillä. Kemikaalien toisistaan poikkeava hajoamisnopeus vaikeuttaa kuitenkin eri amiinien vaikutuksen vertailemista.

| | |
|---|---|
| Luottamuksellisuus | Luottamuksellinen |

Espoo 22.4.2010

| Laatija | Tarkastaja | Hyväksyjä |
|---|---|---|
| Mikko Vepsäläinen<br>Tutkija | Petri Kinnunen<br>Tiimipäällikkö | Pentti Kauppinen<br>Teknologiapäällikkö |

VTT:n yhteystiedot

VTT, Kemistintie 3, PL 1000, 02044 VTT puh. 020 722 111 fax. 020 722 7002

Jakelu (asiakkaat ja VTT)

Suomen soodakattilayhdistys, 1 kpl
VTT:n kirjaamo, 1kpl

# Alkusanat

Työ on tehty Espoon VTT:llä talven 2009 ja kevään 2010 aikana Suomen Soodakattilayhdistys ry:n toimeksiannosta. Työn on jatkoa aiemmille kirjallisuustutkimuksille "Suomen soodakattiloissa käytössä olevat vesi-höyrykierron hapenpoisto- ja alkalointikemikaalit ja niiden reaktiot" ja "Orgaaniset yhdisteet syöttö- ja kattilaveden käsittelyssä" sekä kokeelliselle tutkimukselle "Vesihöyrykierron kemikaalien reaktiot kattilaolosuhteissa".

Espoo 22.4.2010

Tekijät

# Sisällysluettelo

# 1 Johdanto

Voimalaitoksissa käytetään amiineja pääasiassa alkalointiin ja hapen poistoon. Alkaloivien amiinien etuja, verrattuna ammoniakkiin, ovat niiden erilaiset jakaantumiskertoimet ja jakaantuminen lauhteisiin. Valitsemalla vesikiertoon syötettävään amiiniseokseen erilaisen jakaantumiskertoimen sisältäviä amiineja, voidaan lauhteen pH pitää kattilamateriaalien korroosionkestävyyden kannalta oikealla alueella.

Alkaloivat amiinit hajoavat kattilaolosuhteissa hydrolysoitumalla tai hapettumalla. Ongelmallisimpia hajoamistuotteita ovat lyhytketjuiset orgaaniset hapot, kuten muurahais- ja etikkahappo, ja hiilidioksidi. Nämä yhdisteet kulkeutuvat höyryn mukana ja rikastuvat ensilauhteeseen. Gilbert ja Lamarre [1] ovat esittäneet, että morfoliini hajoaa alhaisessa happipitoisuudessa ensin diaminoetanoliksi tai 2-(2-aminoetoksi)etanoliksi ja edelleen ammoniakiksi, metyyli- ja etyyliamiiniksi ja etyleeniglykoliksi. Etyyliamiini ja etyleeniglykoli voivat edelleen hajota hapettumalla mm. etikka-, oksaali- ja muurahaishapoksi. 2-amino-metyyli-1-propanolista muodostuu hydrolysoitumalla 2-metyyli-1,2-propaanidiolia ja hapen läsnä ollessa myös asetaattia ja formiaattia. Myös muiden amiinien kohdalla happipitoisuuden nousu yleensä lisää orgaanisten happojen muodostumista laboratoriokokeiden ja koekattilan syöttöveden esilämmittimellä tehdyissä kokeissa [2]. Alkaloivien amiinien hajoamisesta yli 300 °C lämpötilassa on hyvin vähän tietoa.

Hajoamistuotteiden vaikutus rakennemateriaaleihin liittyy pääasiassa pH:n muutokseen, joka vaikuttaa virtauksen kiihdyttämään korroosioon (flow assisted corrosion, FAC). Asetaatilla on myös esitetty olevan vaikutusta materiaalien jännityskorroosioon, mutta tätä ei ole osoitettu yksiselitteisesti [3].

Magnetiittikalvon ($Fe_3O_4$) muodostumista hiiliteräksen pinnalle on tutkittu VTT:llä ydinvoimalaitosten vesikiertoon liittyvissä materiaalitutkimuksissa [4]. Suojaavan kerroksen muodostuminen hiiliteräksen pinnalle alkalisessa, hapettomassa vedessä tunnetaan varsin hyvin. $Fe_3O_4$-kerroksen on todettu olevan luonteeltaan kaksikerroksinen. Alempi kerros koostuu tiiviistä, hienojakoisesta materiaalista kun taas päällimmäinen kerros kostuu väljästi pakkautuneista suuremmista partikkeleista.

Magnetiittikalvon kasvua voidaan seurata sähkökemiallisten tutkimusmenetelmien avulla. Impedanssispektroskopialla (electrochemical impedance spectroscopy, EIS) saadaan selville oksidikerroksen sähköiset ja aineen kuljetukseen liittyvät ominaisuudet. Näiden perusteella voidaan päätellä, kuinka suojaava ja pysyvä passiivikerroksesta muodostuu. Kirjallisuudesta ei löydy viitteitä tutkimuksiin, joissa olisi tehty EIS-mittauksia 340 °C lämpötilassa. Korkea lämpötila ja paine asettavat erityisiä haasteita koejärjestelyille muun muassa johtimien eristysten suhteen. Kemikaalien toiminnan ja materiaalien kestävyyden varmistaminen korkeassa lämpötilassa on kuitenkin tärkeää, koska soodakattiloiden lämpötiloja sekä paineita ja siten energiatehokkuutta pyritään nostamaan.

# 2 Tavoite

Tutkimuksen tavoitteena oli selvittää, kuinka alkaloivat amiinit vaikuttavat hiiliteräksen pinnalle muodostuvan magnetiittikerroksen ominaisuuksiin 340 °C lämpötilassa. Kokeilla selvitettiin myös alkaloivien amiinien termisen hajoamisen nopeutta ja syntyvien hajoamistuotteiden pitoisuuksia. Tuloksia voidaan hyödyntää laadittaessa ohjeita voimalaitosten vesikemian hallintaan.

# 3 Rajaukset

Vastoin alkuperäistä tutkimussuunnitelmaa, tässä tutkimuksessa käytetystä koelaitteistosta ei ollut mahdollista ottaa näytteitä höyrytilasta, minkä vuoksi tässä tutkimuksessa ei pystytty selvittämään magnetiittikalvon muodostumista höyryssä tai amiinien ja hajoamistuotteiden jakaantumista höyryn ja nesteen välillä. Amiinien hajoamistuotteista määritettiin vain orgaaniset hapot (muurahais- ja etikkahappo) ja ammoniakki. Tarkempi hajoamistuotteiden ja -reittien selvittäminen vaatisi lisäkokeita ja kvalitatiivisia analyysejä vesinäytteistä esimerkiksi GC-MS (Gas Cromatography - Mass Spectrometry) ja HPLC-MS (High Performance Liquid Chromatography - Mass Spectrometry) menetelmillä.

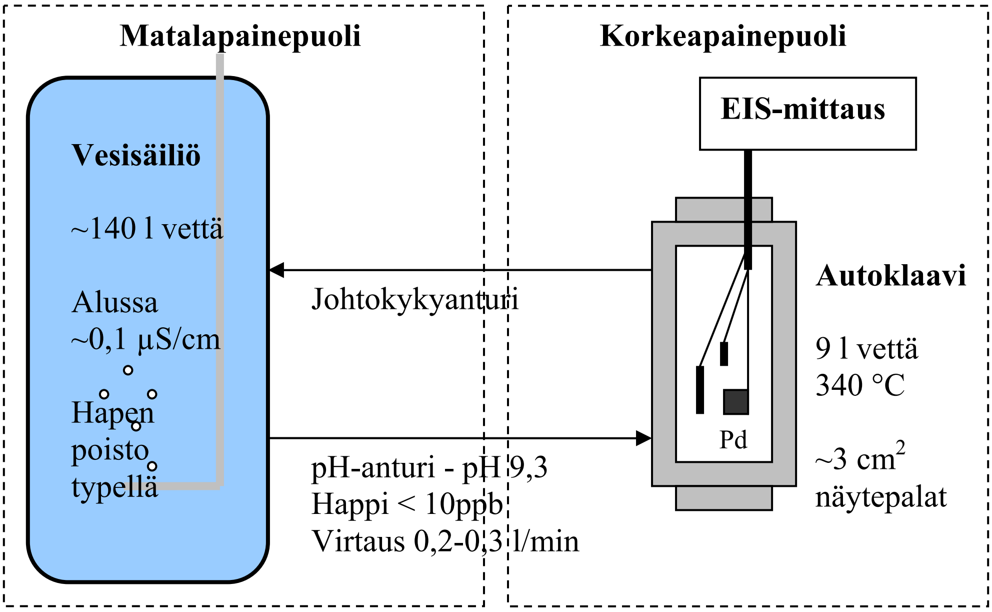
Sähkökemiallisten mittausten osalta veden heikko johtokyky asetti käytetyille menetelmille rajoitteita ja mm. voltametrisia määrityksiä ei tehty tässä tutkimuksessa. Tutkimuksen alussa oli huomattavia ongelmia korkeasta lämpötilasta johtuen johtimien eristyksissä ja paineen sekä lämpötilan säädöissä. Ongelmien vuoksi luovuttiin panos-tyyppisestä koejärjestelystä ja kokeet tehtiin vesipiirissä, jossa oli jatkuva kierto korkea- ja matalapainepuolen välillä. Tutkimusympäristössä tehdyt muutokset osoittautuivat tutkimuksen kannalta hyödyllisiksi, koska kemikaalien käyttäytymistä voitiin seurata vesipiirissä olevien online-mittareiden avulla. Johdinten eristyksessä päästiin hyvään lopputulokseen käyttämällä läpiviennin eri kohdissa eri materiaaleja (teflon, $Al_2O_3$ ja $ZrO_2$) lämpötilasta riippuen.

# 4 Menetelmät

## 4.1 Koelaitteisto

Kokeissa käytettiin kiertovesipiiriä 3 (kuva 1). Ennen kokeen aloittamista vesipiiristä tyhjennettiin edellisen kokeen vedet ja säiliö täytettiin (135-145 l) ionivaihdetulla vedellä. Vettä kuplitettiin typellä ja kierrätettiin ioninvaihtimen läpi ennen kokeen aloittamista, kunnes johtokyky oli laskenut tasolle 0,1 µS/cm ja happipitoisuus oli <10 ppb. Kokeen aikana kiertovesisäiliössä pidettiin n. 0,5 bar ylipaine typen avulla ja hidas typpikuplitus.

Kokeen alussa vesipiirin matalapainepuolelle annosteltiin referenssikokeessa ammoniakkia ja muissa kokeissa alkaloivaa amiinia, kunnes pH vesipiirissä oli 9,3±0,1. Virtaus matalapaineosasta korkeapaineosaan oli kokeen aikana n. 0,25 l/min, jolloin viipymäajaksi autoklaavissa tulee n. 0,6h. Koetta aloitettaessa korkeapaineosan paine säädettiin ~160 bar, jonka jälkeen autoklaavi lämmitettiin 340 °C esilämmittimen ja autoklaavin vastusten avulla.

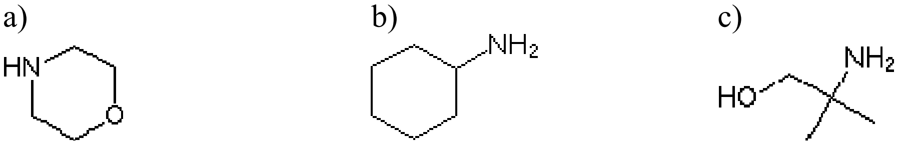


**Kuva 1:** Kaaviokuva tutkimuksessa käytetystä koelaitteistosta.

Vesipiirin matalapainepuolelta mitattiin veden johtokyky, pH ja happipitoisuus online-mittareiden avulla. Happipitoisuus ja pH mitattiin autoklaaviin menevästä ja johtokyky autoklaavista palaavasta vesilinjasta.

## 4.2 Kokeissa käytetyt alkaloivat amiinit

Kokeissa käytettävät amiinit hankittiin Sigma-Aldrichilta ja niiden puhtaus oli ≥99 %. Kokeissa käytettävät amiinit olivat morfoliini, 2-amino-2-metyyli-1-propanoli ja sykloheksyyliamiini ja ne kuuluvat ns. alkaloiviin amiineihin. Amiinien rakenne on esitetty kuvassa 2.



**Kuva 2:** Tutkimuksessa käytettyjen alkaloivien amiinien rakenteet; a) morfoliini (molekyylipaino 87,12 g/mol), b) sykloheksyyliamiini (molekyylipaino 99,12 g/mol) ja c) 2-amino-2-metyyli-1-propanoli (molekyylipaino 89,14 g/mol).

Amiineja tai ammoniakkia annosteltiin kunnes vesipiirin pH oli kaikissa kokeissa 9,3±0,1. Käytettyjen amiinien erilaisista emäsvakioista johtuen kemikaalien pitoisuudet vedessä vaihtelivat kokeesta riippuen. Amiinien tarkka lähtöpitoisuus määritettiin kapillaarielektroforeesilla (capillary electrophoresis, CE) (taulukko 2).

Vesinäytteet otettiin matalapainepuolelta ennen autoklaavin lämmittämistä, kun koelämpötila 340 °C oli saavutettu ja n. 15 h, 40 h ja 70 h kuluttua (340 °C saavuttamisen jälkeen). Vesinäytteistä määritettiin CE-tekniikalla oletettujen hajoamistuotteiden pitoisuudet. CE-määritysten ajo-olosuhteet on esitetty taulukossa 1. Kokeiden aikana amiinien hajoamista seurattiin myös online-pH-mittarilla.

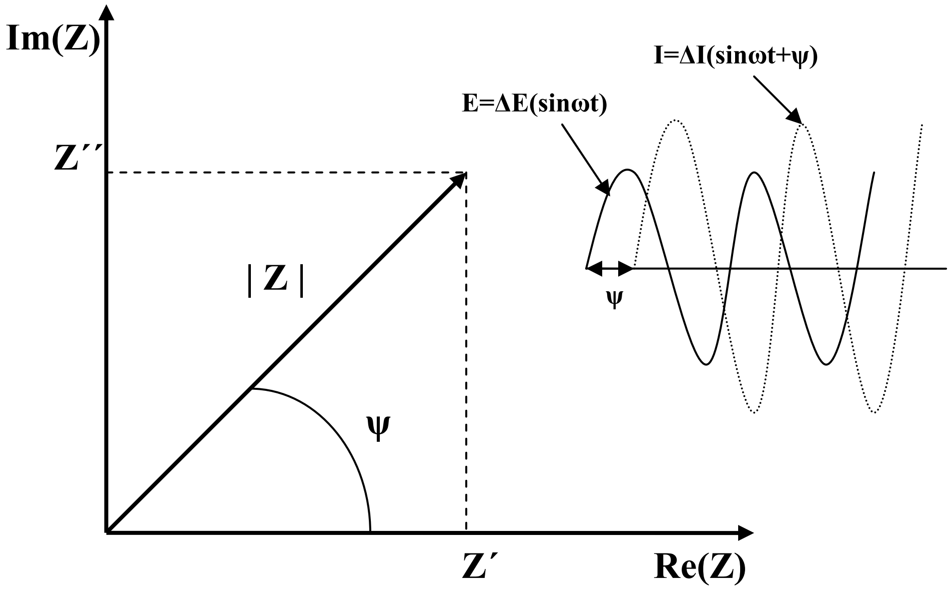
**Taulukko 1:** Ajo-olosuhteet CE-määrityksissä eri yhdisteryhmille

| Parametri | Hapot | Amiinit |
|---|---|---|
| Erotusjännite | 15 kV | 25 kV |
| Polariteetti | negatiivinen ---> positiivinen | positiivinen ---> negatiivinen |
| Injektio | 2 psi 30 s | 2 psi 30 s |
| Detektio | | |
| - aallonpituus | 281 nm | 210 nm |
| - detektiotapa | epäsuora detektio | epäsuora detektio |

## 4.3 EIS-mittaukset

Sähkökemiallinen impedanssispektroskopia (electrochemical impedance spectroscopy, EIS) on menetelmä, jota käytetään materiaalien pintakerroksen ominaisuuksien tutkimuksissa. Mittauksessa tutkittavaan näytteeseen kohdistetaan sini-muotoinen jännitesignaali eri taajuuksilla ja sen synnyttämä sähkövirta mitataan. Tuloksista voidaan laskea jännite- ja virtasignaalien välinen vaihe-ero ja vaihtovirtavastus eli impedanssi.

Impedanssi on vektorisuure, joka voidaan esittää kuvan 3 mukaisesti. |Z| on impedanssi itseisarvo eli vektorin suuruus ja vaihekulman, $\theta$, avulla voidaan esittää vektorin suunta. Impedanssi voidaan jakaa reaaliseen ($Z'=|Z|\cos\psi$) ja imaginaariseen ($Z''=|Z|\sin\psi$) osaan.



**Kuva 3:** Impedanssi vektorina.

Impedanssispektroskopiaa käytetään sähkökemiallisten reaktiomekanismien tutkimuksissa, materiaalien dielektristen ja aineensiirtoon liittyvien ominaisuuksien tutkimuksissa ja metallien passiivikerroksen ominaisuuksien selvityksissä.

EIS-mittauksilla saadaan tietoa sekä hitaista aineensiirron kontrolloimista että nopeista kineettisesti kontrolloiduista prosesseista. Nämä prosessit näkyvät mittaussignaaleissa, kun taajuutta vaihdellaan. Yleensä tuloksia tarkasteltaessa käytetään ns. sijaiskytkentäpiirejä, jotka koostuvat yleensä vastuksista ja kondensaattoreista. Sijaiskytkentäpiirin avulla mitatusta signaalista saatuja prosesseja voidaan kytkeä fysikaaliskemiallisiin ilmiöihin.

Tässä tutkimuksessa EIS-tuloksista esitetään ns. Nyquist-kuvaajat, joissa impedanssi on esitetty reaali- ja imaginaariosien avulla. Hiotuille näytteille esitetään myös sijaiskytkentäpiirin Warburg-impedanssista lasketut arvot aineensiirtovastukselle ($R_w$) ja diffuusiokertoimelle (D).

EIS-mittauksia varten autoklaaviin vaihdettiin ennen jokaista koetta uusi hiottu hiiliteräspala ja esihapetettu hiiliteräspala. Näytteiden pinta-alat olivat n. 3 $cm^2$. Kaikki näytteet hiottiin ennen kokeita 4000 grit hiomapaperilla ja huuhdeltiin etanolilla ja ionivaihdetulla vedellä. Esihapetettua näytettä pidettiin 340 °C lämpötilassa ammoniakkipitoisessa vedessä n. 72h ennen koetta. Sähkökemiallisia mittauksia varten autokolaaviin tuotiin myös vastaelektrodit ja referenssielektrodi. Referenssielektrodina käytettiin palladiumia (Pd), joka polarisoitiin virtalähteen avulla "vetyviivalle" eli potentiaaliin, jossa vetyä muodostuu elektrodin pinnalla veden hajotessa ja Pd:n potentiaali pysyy tasaisena. Kun veden pH tunnetaan, voidaan potentiaali laskea ns. Nernstin yhtälön avulla standardina käytettävälle SHE (standard hydrogen electrode) skaalalle. Koelaitteiston referenssielektrodin (Pd) polarisoinnin ja EIS-mittauksen vastaelektrodeina käytettiin platinalankaa. Johtojen eristys tarkistettiin kokeiden alussa vastusmittauksella.

Impedanssimittauksissa käytettiin Autolab PGSTAT20 -potentiostaattia. Impedanssi mitattiin taajuusalueelle $8*10^4$- $1*10^{-3}$ Hz ja a.c. jännitteen amplitudi oli 30 mV. Yhden spektrin mittaus kesti n. 3,5 h. Hiotun näytteen mittaus keskeytettiin kerran päivässä yhden mittaussyklin ajaksi, jonka aikana mitattiin esihapetetun näytteen impedanssispektri.

EIS-mittauksissa elektrodien läpivienneissä käytettiin AISI 316 johtimia, jotka eristettiin rungosta teflonilla ja keraamisilla eristeillä. Autoklaavin sisällä eristettä ei käytetty kuin johtimien kiinnityksissä. Paljaana olevat johtimet voivat osaltaan vaikuttaa mittaussignaaliin, mutta johtimien ja näytekappaleiden pinta-alasuhteiden vuoksi vaikutus ei ole merkittävä.

## 4.4 Ex-situ mittaukset

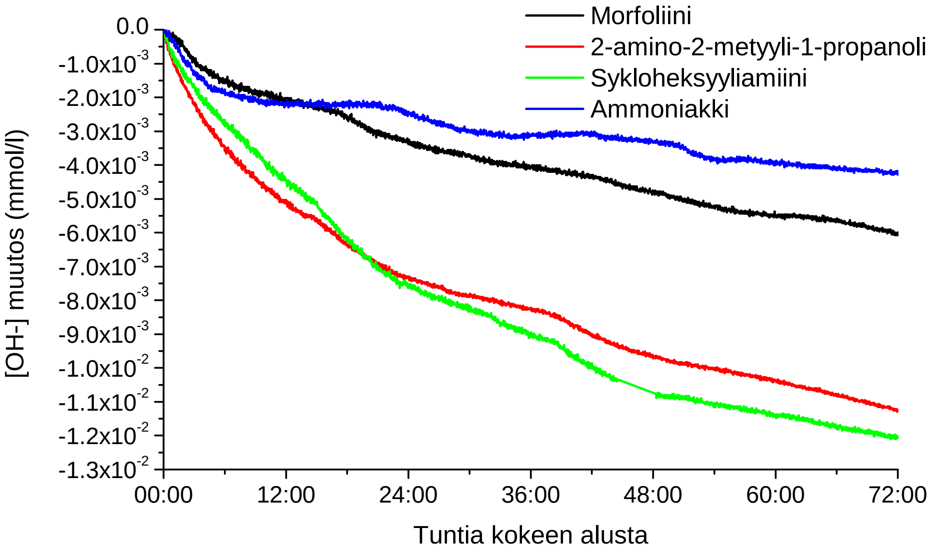
Kokeiden jälkeen näytteiden pinnat kuvattiin pyyhkäisyelektronimikroskoopilla (SEM) magnetiittikerroksen topografian selvittämiseksi 30-, 5000- ja 15000-kertaisella suurennoksella. Hiotuista näytteistä tehtiin myös poikkileikkaushieet, joista määritettiin sisemmän oksidikerroksen paksuus. Tässä raportissa esitetään pinnan topografiakuvat ja poikkileikkaushieiden kuvat 5000-kertaisella suurennoksella.

# 5 Tulokset

## 5.1 Alkaloivien amiinien hajoaminen

### pH:n muutos kokeen aikana

Kokeen aikana vesipiirin pH:n muutosta seurattiin on-line mittauksen avulla. Amiinien hajoamisessa syntyvät orgaaniset yhdisteet, ammoniakki ja hiilidioksidi vaikuttavat pH:n muutokseen. Hajoamisen lopputuotteena muodostuva ammoniakki haihtuu todennäköisesti kiertovesisäiliön kaasutilaan, minkä seurauksena pH muuttuu kokeen edetessä. Kuvassa 4 on esitetty pH:n muutoksesta laskettu hydroksyyli-ionipitoisuuden, [OH$^-$], muutos kokeen aikana. [OH$^-$] muutoksesta nähdään pH:n muutosta tarkemmin erot eri kemikaalien hajoamisen välillä.



**Kuva 4:** Hydroksyyli-ionipitoisuuden muutos kokeen aikana amiineja tai ammoniakkia sisältävässä vedessä.

[OH$^-$] on laskettu veden ionitulon, $K_W = 1{,}00 * 10^{-14}$ (25 °C) ja pH:n avulla kaavan 1 mukaisesti.

$$\left[OH^-\right] = 10^{-(14-pH)} \qquad (1)$$

Kuvan 4 tuloksista nähdään, että sykloheksyyliamiinilla ja 2-amino-2-metyyli-1-propanolilla hydroksyyli-ionipitoisuus laski selvästi nopeammin kuin morfoliinilla ja ammoniakilla. Hydroksyyli-ionipitoisuuteen vaikuttavat sekä amiinin pitoisuuden lasku termisen hajoamisen edetessä ja sitä vastaava muutos amiinin ionisoitumisessa että muodostuvien hajoamistuotteiden rakenne ja ominaisuudet. Mahdollisista hajoamistuotteista ammoniakki ja amiinit nostavat [OH$^-$]:ta ja orgaaniset hapot ja hiilidioksidi laskevat sitä. Vähähappisissa olosuhteissa orgaanisten happojen muodostuminen on kuitenkin epätodennäköistä.

Ammoniakin tapauksessa vähäinen [OH$^-$] muutos kokeen alussa johtuu todennäköisesti ammoniakin jakaantumisesta veden ja kiertovesisäiliön kaasutilan välillä. Hitaan kuplituksen vuoksi ammoniakki häviää myös hiljalleen kaasutilasta, mikä havaitaan hitaampana [OH$^-$] muutoksena. Morfoliinista muodostuu aiempien tutkimusta mukaan hajoamistuotteina muita amiineja, kuten metyyli- ja etyyliamiineja, jotka hidastavat pH:n laskua [2].

Hydroksyyli-ionipitoisuuden muutoksen avulla laskettiin myös reaktionopeusvakiot kemikaalien hajoamiselle. Laskennassa on otettu huomioon amiinien konsentraatiosta riippuva ionisoitumisaste ja myös, että autoklaavissa oleva vesitilavuus on n. 1/14 kokonaistilavuudesta. [OH$^-$] riippuu yhdisteiden pitoisuuksien lisäksi niiden emäsvakioista, pK$_b$, ja amiinin pitoisuus liuoksessa voidaan laskea kaavojen 3 avulla yhtälön 2 reaktiolle, kun tunnetaan [OH$^-$]. Laskennassa on käytetty seuraavia emäsvakioiden arvoja; morfoliini 3,1 * 10$^{-6}$, sykloheksyyliamiini 440 * 10$^{-6}$ ja 2-amino-2-metyyli-1-propanoli 55 * 10$^{-6}$ [5].

$$B + H_2O \leftrightarrow BH^+ + OH^- \tag{2}$$

$$\begin{aligned} &[BH^+] + [B] = \text{Amiinin pitoisuus} \\ &[BH^+] = [OH^-] \\ &K_b = \frac{[BH^+]*[OH^-]}{[B]} = \frac{[OH^-]^2}{[B]} \\ &[B] = \frac{[OH^-]^2}{K_b} \end{aligned} \tag{3}$$

Lasketut ensimmäisen kertaluvun reaktionopeusvakiot amiinien hajoamiselle 340 °C:ssa ovat; morfoliinille 5,27*10$^{-5}$ s$^{-1}$ (puoliintumisaika 4 h), sykloheksyyliamiinille 6,10*10$^{-5}$ s$^{-1}$ (puoliintumisaika 3 h) ja 2-amino-2-metyyli-1-propanolille 8,71*10$^{-5}$ s$^{-1}$ (puoliintumisaika 2 h). Reaktionopeusvakioiden laskennassa on oletettu, että muutos [OH$^-$] riippuu ainoastaan syötettävän amiinin pitoisuudesta eikä syntyvillä hajoamistuotteilla ole vaikutusta hydroksyyli-ionipitoisuuteen.

## Amiinien hajoamistuotteiden määritys kapillaarielektroforeesilla

CE-menetelmällä määritetyt amiinien ja oletettujen hajoamistuotteiden pitoisuudet on esitetty taulukossa 2. Morfoliini oli käytetyistä amiineista heikoin emäs, minkä vuoksi sen lähtöpitoisuus oli korkeampi kuin sykloheksyyliamiinilla ja 2-amino-2-metyyli-1-propanolilla.

CE-määritysten mukaan morfoliinin hajoamisnopeus oli selvästi hitaampi kuin sykloheksyyliamiinin ja 2-amino-2metyyli-1-propanolin hajoamisnopeus. Morfoliinista muodostuu hajotessa muita amiineja, mikä selittää mitatut sykloheksyyliamiinipitoisuudet lämmittämisen jälkeen. Sykloheksyyliamiinipitoisuudet ovat kuitenkin erittäin korkeita suhteessa hajonneen morfoliinin määrään ja sykloheksyyliamiini on epätodennäköinen hajoamistuote morfoliinin termisessä hajoamisessa. Kyseessä onkin todennäköisesti joku muu yhdiste esim. toinen amiini, joka eluoituu samassa kohdassa ja antaa erilaisen vasteen suhteessa konsentraatioon.

Sykloheksyyliamiini hajosi nopeammin kuin morfoliini, mutta hitaammin kuin 2-amino-2metyyli-1-propanoli. Myös on-line pH-mittauksen mukaan 2-amino-2-metyyli-1-propanolin terminen hajoaminen oli nopeinta. Sykloheksyyliamiinin ja 2-amino-2metyyli-1-propanolin hajoamistuotteina muodostui ammoniakkia. Tulosten mukaan ammoniakkipitoisuus kuitenkin laski kokeen aikana eli ammoniakkia todennäköisesti haihtui kiertovesisäiliön kaasutilaan. Pieniä asetaattipitoisuuksia mitattiin jokaisessa kokeessa, mutta merkittävää muutosta ajan funktiona näissä pitoisuuksissa ei ollut havaittavissa. Asetaatin ja formiaatin pitoisuuden muutokset olivat todennäköisesti käytetyillä amiinipitoisuuksilla niin alhaisia, ettei eroa havaita käytetyllä analyysimenetelmällä. Kuten aiemminkin todettiin, hapettomissa olosuhteissa orgaanisten happojen muodostuminen on epätodennäköistä.

**Taulukko 2:** CE-tekniikalla mitatut amiinien ja hajoamistuotteiden pitoisuudet (mg/l), toteamisrajat (LOD mg/l) ja määritysrajat (LOQ mg/l) eri yhdisteille (AMP=2-amino-2-metyyli-1-propanoli ja CHA=sykloheksyyliamiini). Taulukossa tulos on merkitty ND:llä (not detected), kun yhdistettä ei ole havaittu.

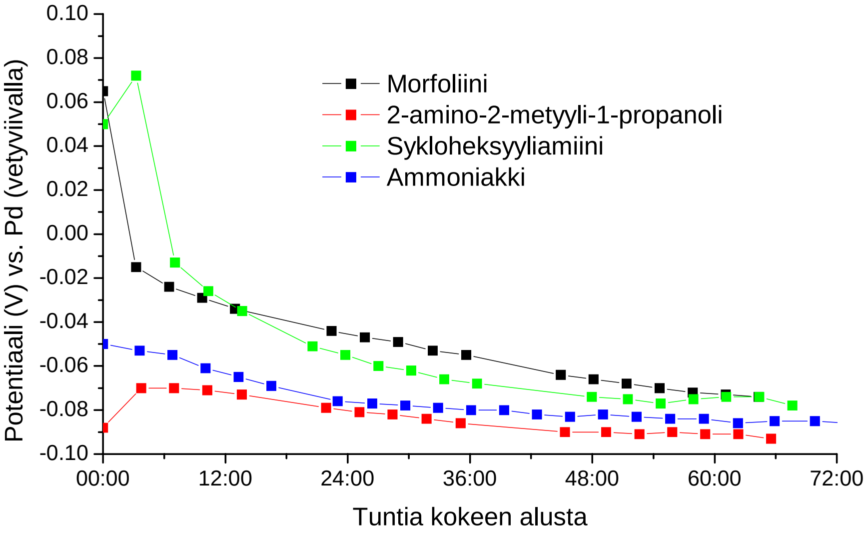
| | Näyte | Morfoliini | CHA | AMP | Formiaatti | Asetaatti | Ammonium |
|---|---|---|---|---|---|---|---|
| **Morfoliini** | Ref (90 °C) | 3,6 | ND | ND | < LOD | 0,3 | < LOQ |
| | Ref (340 °C) | 3,5 | 0.7 | ND | < LOD | 0,3 | < LOQ |
| | Koeaika 16h | 3,50 | 0.5 | ND | < LOD | 0,3 | < LOQ |
| | Koeaika 40h | 3,3 | 0.5 | ND | < LOD | 0,3 | ND |
| | Koeaika 69h | 3,4 | 0.5 | ND | < LOD | 0,4 | < LOQ |
| **AMP** | Ref (90 °C) | <LOQ | ND | 1,5 | < LOD | < LOQ | < LOQ |
| | Ref (340 °C) | ND | ND | 1,3 | < LOD | < LOQ | < LOQ |
| | Koeaika 15h | <LOQ | <LOQ | <LOQ | < LOD | < LOQ | 1,2 |
| | Koeaika 40h | ND | ND | ND | < LOD | 0,4 | ND |
| | Koeaika 70h | ND | ND | ND | < LOD | 0,4 | ND |
| **CHA** | Ref (90 °C) | ND | 2,1 | ND | < LOD | 0.4 | < LOQ |
| | Ref (340 °C) | ND | 1,7 | ND | < LOD | < LOQ | < LOQ |
| | Koeaika 15h | <LOQ | 1,7 | ND | < LOD | 0,4 | < LOQ |
| | Koeaika 40h | <LOQ | 1,0 | ND | < LOD | 0,3 | < LOQ |
| | Koeaika 70h | <LOQ | <LOQ | ND | < LOD | < LOQ | 0,5 |
| | **LOD** | 0,25 | 0,25 | 0,25 | 0,1 | 0,1 | 0,25 |
| | **LOQ** | 0,5 | 0,5 | 0,5 | 0,25 | 0,25 | 0,5 |

## 5.2 Magnetiittikalvon muodostuminen

### Hiiliteräksen lepopotentiaalin mittaus

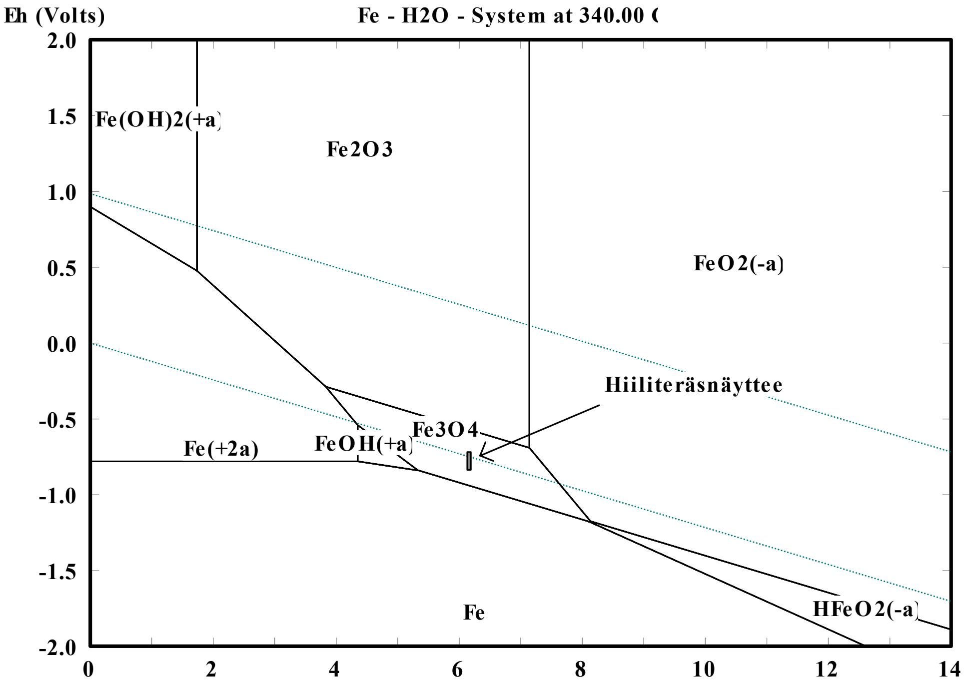
Kokeiden aikana seurattiin hiotun hiiliteräsnäytteen potentiaalin muutosta. Veden alhaisen happipitoisuuden johdosta (<10 ppb) metallin potentiaali oli lähellä vetyviivaa (eli Pd-referenssiä) kaikissa kokeissa (kuva 5). Kokeen alussa hiiliteräsnäytteen potentiaali oli morfoliinia ja sykloheksyyliamiinia käytettäessä korkeammalla kuin ammoniakilla ja 2-amino-2-metyyli-1-propanolilla. Kuten aiemmin todettiin, kyseiset amiinit hajosivat myös hitaammin kuin 2-amino-2-metyyli-1-propanoli. Metallin potentiaalissa ei ollut merkittävää eroa >12 h kokeen aloittamisen jälkeen eri amiinien välillä. Potentiaalin muutos kuvaa muutoksia metallin pinnalla tapahtuvissa reaktioissa eli tulosten mukaan voidaan todeta pysyvän passiivikerroksen muodostuneen 12 h koeajalla.

Esihapetettujen hiiliteräsnäytteiden potentiaalista oli vain muutama mittauspiste. Näiden mittausten mukaan näytteiden potentiaali oli samalla alueella kuin hiottujen näytteiden eli välillä -0.03 V ja -0.09 V.



**Kuva 5:** Hiotun hiiliteräsnäytteen potentiaalin muutos ajan funktiona eri amiineilla tehdyissä kokeissa ( T ≈ 340 °).

Multeq-ohjelmalla arvioitu veden pH 335 °C:ssa amiineja käytettäessä oli välillä 6,13-6.22. Kun tiedetään lisäksi näytteiden potentiaalit, voidaan E-pH-kuvaajan (kuva 6) avulla todeta, että hiiliteränäytteiden potentiaali sijaitsee magnetiitin stabiilisuusalueella. Tämän perusteella voidaan päätellä, että näytteiden pinnalle muodostuu termodynaamisesti kestävä magnetiittikerros ($Fe_3O_4$).

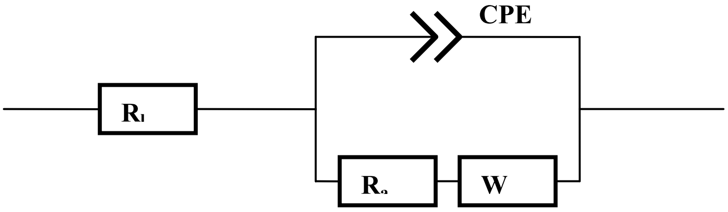


**Kuva 6:** E-pH-kuvaaja raudalle 340 °C. Kuvaajaan on merkitty alue, jossa hiiliteränäytteiden potentiaalit sijaitsivat.

## EIS-mittaukset kokeen aikana

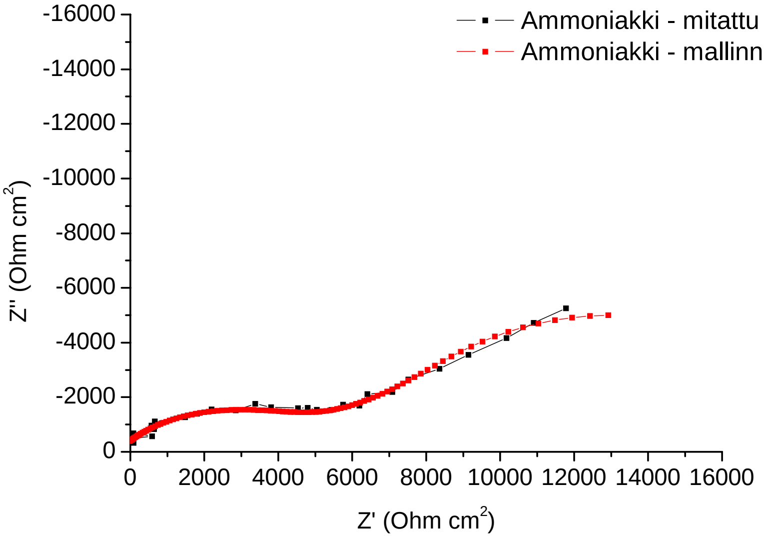
Esihapetettujen ja hiottujen näytteiden impedanssispektrien muoto oli eri amiineja sisältävissä vesissä samankaltainen. Veden heikko johtokyky näkyi erittäin suurena liuosvastuksena, joka vähennettiin tuloksista. Impedanssispektreissä oli selvästi näkyvillä keskitaajuuksilla $10^{2}$-$10^{-1}$ Hz kapasitiivinen vaste, joka on seurausta oksidipinnalla tapahtuvista prosesseista. Matalilla taajuuksilla $10^{-1}$-$10^{-3}$ Hz oli nähtävissä toinen prosessi, joka vastaa rauta-ionien diffuusiota oksidikerroksen läpi ja noudattaa aineenkuljetusta kuvaavaa Warburg-impedanssia. Tämä on todennäköisesti korroosionopeutta rajoittava prosessi.

EIS-tulosten mallinnuksessa käytetty sijaiskytkentäpiiri ja esimerkki mallinnuksesta saaduista arvoista on esitetty kuvissa 7 ja 8. $R_l$ on elektrolyyttiliuoksen vastus, joka vaihtelee johtokyvyn ja elektrodien välimatkan mukaan. Tämä komponentti on vähennetty kaikista tuloksista, jolloin sen arvo mallinnuksessa on n. 0 $\Omega cm^2$. CPE (constant phase element) kuvaa oksidipinnalla tapahtuvan elektroninsiirtoreaktion ominaisuuksia. CPE:tä käytetään kuvaamaan pintojen kapasitiivisia ominaisuuksia, kun pinta ei ole ideaalinen, mikä voi johtua esimerkiksi pinnankarheudesta tai kapasitanssin voimakkaasta taajuusriippuvuudesta. W on matalilla taajuuksilla näkyvä aineensiirtoa edustava Warburg-impedanssi ($Z_w$), jonka termeistä saadaan laskettua Warburg-kerroin ($\sigma$). Warburg-kertoimen ja aineensiirtoreaktioon osallistuvan ionin diffuusiokertoimen (D) välinen yhteys on yhtälön 4 mukainen.



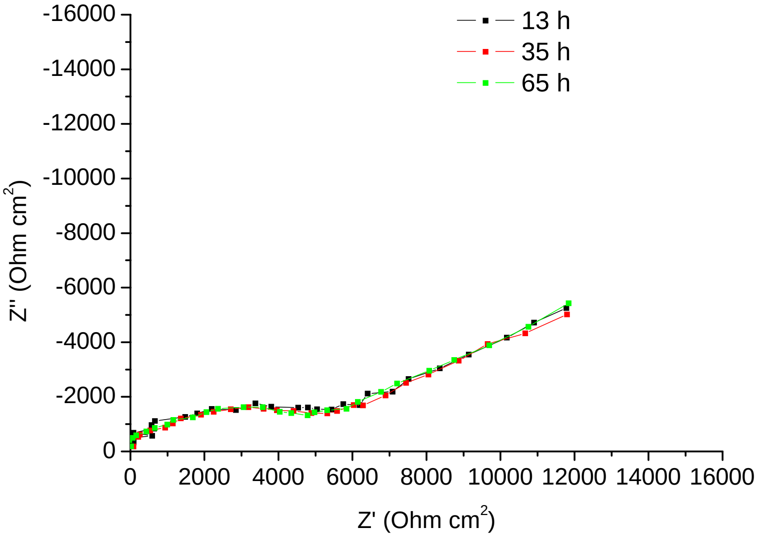
**Kuva 7:** Tulosten mallinnuksessa käytetty sijaiskytkentäpiiri.

$$
\begin{aligned}
Z_w &= \sigma\omega^{-1/2} - i\sigma\sigma^{-1/2} \\
\sigma &= \frac{RT}{z^2F^2A\sqrt{2}}(c_O^p\sqrt{D})^{-1}
\end{aligned}
\qquad (4)
$$

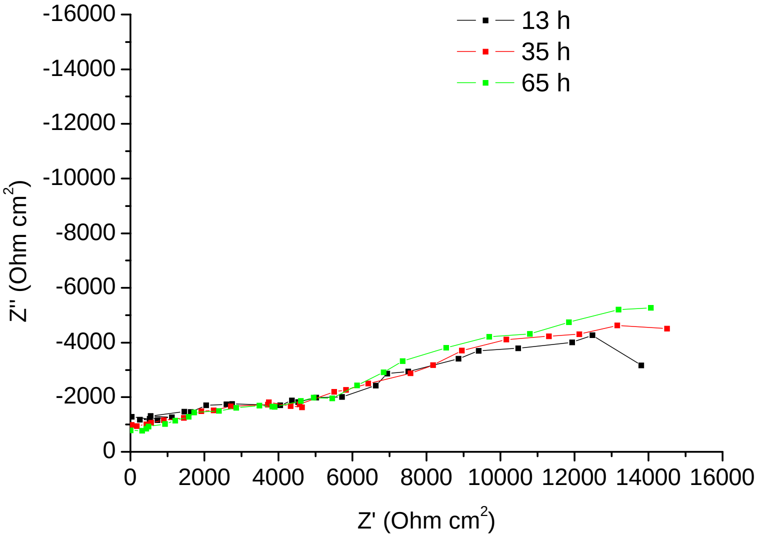


**Kuva 8:** Hiotun hiiliteräsnäytteen Nyquist-kuvaaja ammoniakkia sisältävässä vedessä 65h kokeen aloittamisen jälkeen ja sitä vastaava, sijaiskytkentäpiirin avulla laskettu, malli.

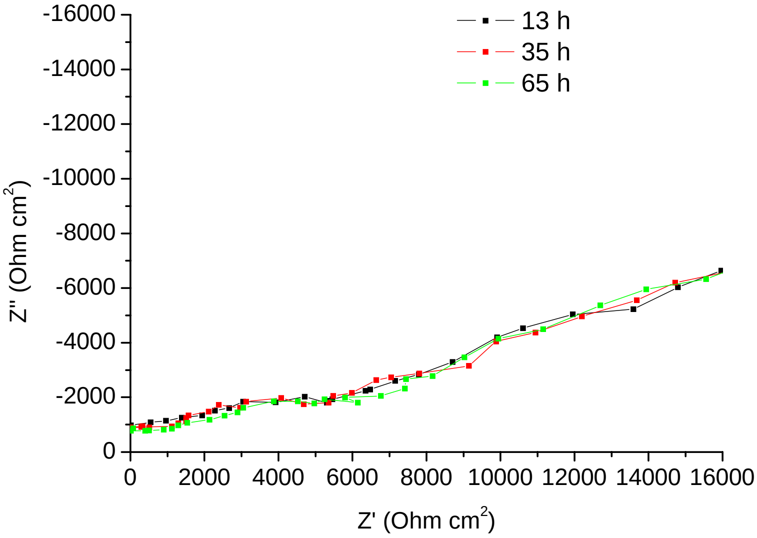
Hiottujen näytteiden EIS-spektrit on esitetty kuvissa 9-12. Neljän ensimmäisen mittauksen aikana, eli alle 13 tunnin koeajalla, spektreissä oli huomattavan paljon kohinaa. Kohina voi olla seurausta olosuhteiden muutoksesta metallin pinnalla eli tässä tapauksessa magnetiittikerroksen muodostumisesta. EIS-spektreistä nähdään, että ammoniakkia ja 2-amino-2-metyyli-1-propanolia sisältävässä vedessä näytteiden spektrit eivät muuttuneet merkittävästi 13 tunnin koeajan jälkeen. Tuloksia tarkasteltaessa on otettava huomioon, että 2-amino-2metyyli-1-propanoli hajosi täysin <40h kokeen aloittamisen jälkeen. Morfoliinilla ja sykloheksyyliamiinilla tehdyissä kokeissa matalien taajuuksien vaihekulma kasvoi kokeen aikana eli rauta-ionien diffuusio oksidikerroksen läpi hidastui amiinin hajotessa.



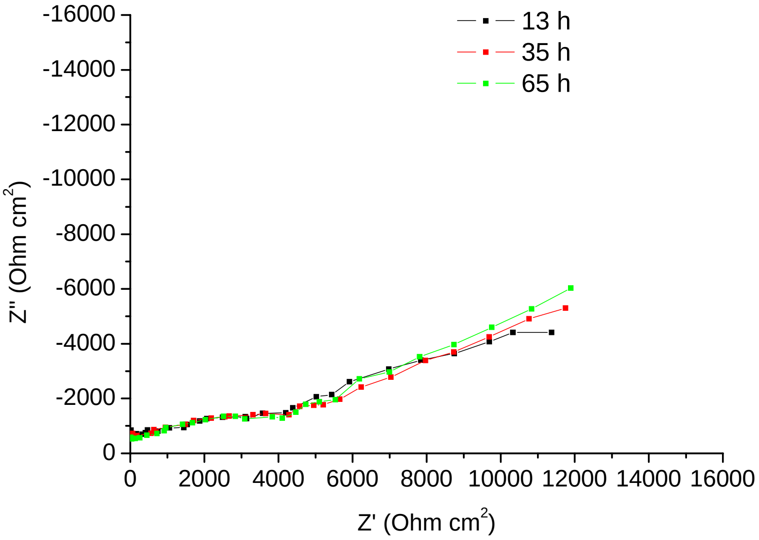
**Kuva 9:** Hiotun hiiliteräsnäytteen Nyquist-kuvaajat 13 h, 35 h ja 65 h kokeen aloittamisen jälkeen ammoniakkia sisältävässä vedessä.



**Kuva 10:** Hiotun hiiliteräsnäytteen Nyquist-kuvaajat 13 h, 35 h ja 65 h kokeen aloittamisen jälkeen morfoliinia sisältävässä vedessä.

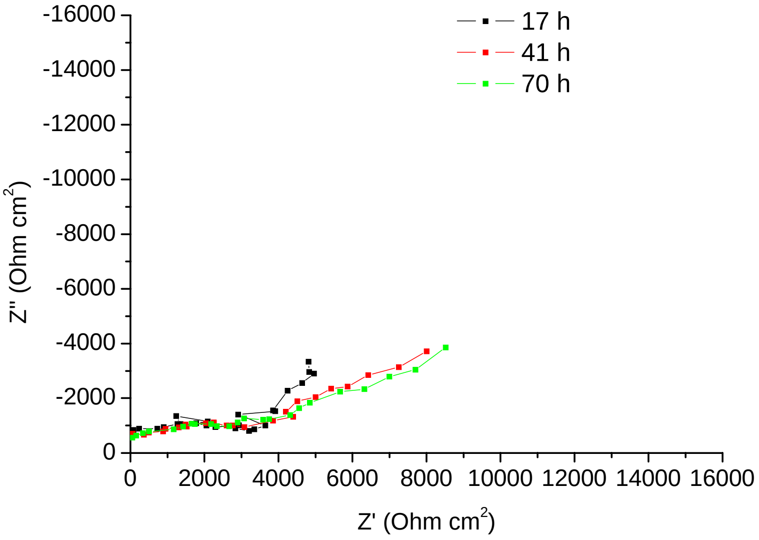


**Kuva 11:** Hiotun hiiliteräsnäytteen Nyquist-kuvaajat 13 h, 35 h ja 65 h kokeen aloittamisen jälkeen 2-amino-2-metyyli-1-propanolia sisältävässä vedessä.

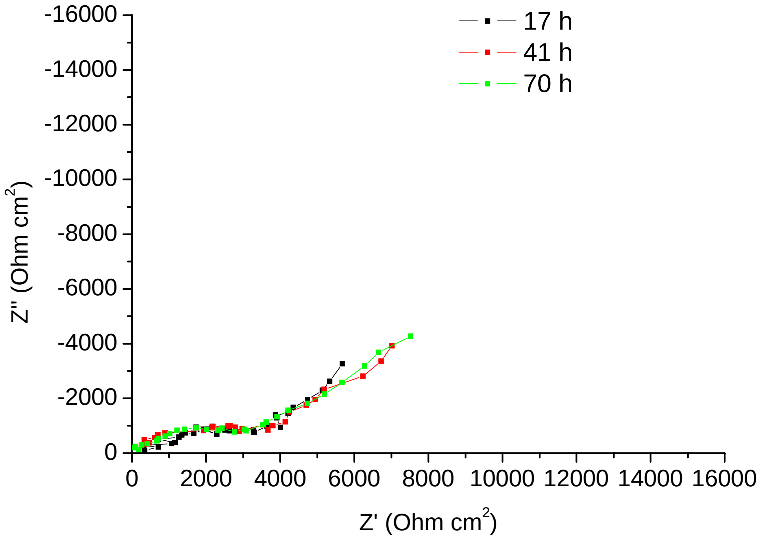


**Kuva 12:** Hiotun hiiliteräsnäytteen Nyquist-kuvaajat 13 h, 35 h ja 65 h kokeen aloittamisen jälkeen sykloheksyyliamiinia sisältävässä vedessä.

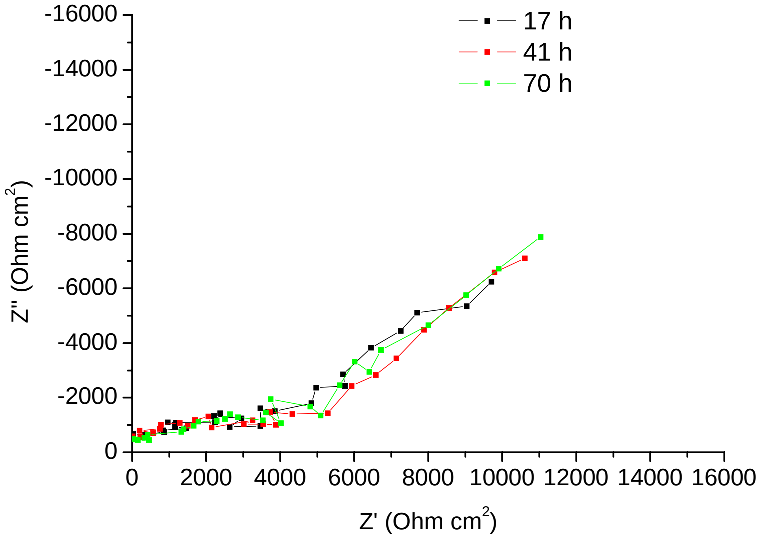
Esihapetetun hiiliteräsnäytteen EIS-spektrissä tapahtui selvä muutos kokeen aikana ainoastaan morfoliinia sisältävässä vedessä (kuvat 13-15). Matalien taajuuksien impedanssin itseisarvo kasvoi ja vaihekulma laski kokeen edetessä. Esihapetetulla näytteellä kemiallisen ympäristön muuttuessa ammoniakkiliuoksesta amiiniliuokseksi diffuusionopeus oksidin läpi kasvoi. Morfoliini hajosi hitaammin kuin muut amiinit, jolloin kemikaali pääsi vaikuttamaan oksidikerroksen ominaisuuksiin pidempään kuin muut amiinit. Warburg-kertoimien mukaan diffuusio oli kuitenkin hitaampaa esihapetettujen näytteiden läpi jokaisella amiinilla, josta esimerkkinä kuva 16.



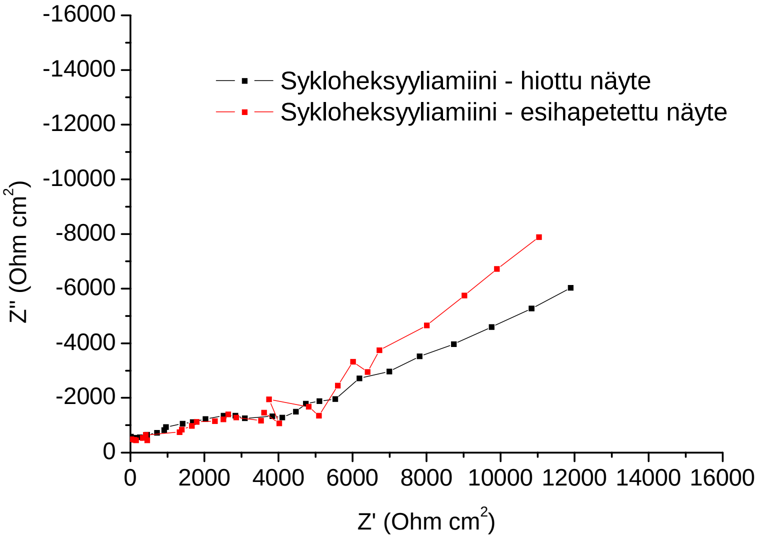
**Kuva 13:** Esihapetetun hiiliteräsnäytteen Nyquist-kuvaajat 17 h, 41 h ja 70 h kokeen aloittamisen jälkeen morfoliinia sisältävässä vedessä.



**Kuva 14:** Esihapetetun hiiliteräsnäytteen Nyquist-kuvaajat 17 h, 41 h ja 70 h kokeen aloittamisen jälkeen 2-amino-2-metyyli-1-propanolia sisältävässä vedessä.



**Kuva 15:** Esihapetetun hiiliteräsnäytteen Nyquist-kuvaajat 17 h, 41 h ja 70 h kokeen aloittamisen jälkeen sykloheksyyliamiinia sisältävässä vedessä.



**Kuva 16:** Hiotun ja esihapetetun näytteen Nyquist-kuvaajat sykloheksyyliamiinilla tehdyn kokeen lopussa.

Taulukossa 3 on esitetty hiiliteräsnäytteiden EIS-tuloksista lasketut aineensiirtovastusten arvot kokeen lopussa. Aineensiirtovastus kuvaa rauta-ionien diffuusiosta johtuvaa vastusta ja on käänteen verrannollinen korroosionopeuteen.

**Taulukko 3:** Hiiliteräsnäytteiden Warburg-impedanssista lasketut aineensiirtoa kuvaavien aineensiirtovastusten ($R_w$) arvot kokeen lopussa.

| **Näyte** | **Hiottu näyte $R_w$ ($\Omega$ cm$^2$)** | **Esihapetettu näyte $R_w$ ($\Omega$ cm$^2$)** |
|---|---|---|
| Ammoniakki | 14185 | |
| Morfoliini | 13499 | 13508 |
| 2-amino-2-metyyli-1-propanoli | 19913 | 14849 |
| Sykloheksyyliamiini | 15769 | 16441 |

Taulukon 3 tulosten mukaan 2-amino-2-metyyli-1-propanoliliuoksessa olleen hiotun hiiliteräsnäytteen korroosionopeus oli kokeen lopussa pienempi kuin muiden näytteiden. Kyseinen kemikaali myös hajosi nopeammin kuin muut amiinit. Muiden näytteiden korroosionopeuksissa ei ollut merkittävää eroa aineensiirtovastusten mukaan.

EIS-mallinnuksen tulosten ja oksidikerroksen paksuuden avulla laskettu diffuusiokerroin hiotulle hiiliteräsnäytteelle, ammoniakilla tehdyn kokeen lopussa, oli $1,1 \cdot 10^{-17}$ cm$^2$s$^{-1}$. Morfoliiniliuoksessa olleen hiiliteräsnäytteen diffuusiokerroin oli suurempi kuin muilla amiineilla ja ammoniakilla. Diffuusiokertoimeen laskentaan sisältyy kuitenkin huomattava epävarmuus, koska suojaavan oksidikerroksen paksuutta ei voida luotettavasti arvioida liitteen 1 SEM-kuvien avulla.

### SEM-kuvat

Elektronimikroskoopilla otetut kuvat on esitetty liitteessä 1. Näytteiden pinnoilta otetuissa kuvissa näkyy hyvin pinnan rakenteen kaksiosaisuus. Tiheään pakkautuneiden oksidipartikkelien päällä oli harvempi suuremmista partikkeleista koostuva kerros.

Näytepalojen uloimmassa pintakerroksessa oli näkyvissä selviä eroja kokeiden välillä. 2-amino-2-metyyli-1-propanoli- ja sykloheksyyliamiini-kokeissa olleiden näytteiden pinnalla oli vähemmän suuria oksidipartikkeleita kuin ammoniakki- ja morfoliini-kokeissa olleiden palasten pinnalla. Esihapetettujen näytteiden pinnoilla oli enemmän suuria oksidipartikkeleita, mutta erot hiottuihin näytteisiin olivat vähäisiä. Erot amiinien välillä olivat samat kuin hiotuilla näytteillä.

Magnetiittikerroksen kaksikerroksisuus näkyi myös poikkileikkaushieissä erityisesti ammoniakkiliuoksessa olleissa hiiliteränäytteissä. Ammoniakkia sisältävässä vedessä oksidikerroksesta muodostui hieman ohuempi kuin amiineja sisältävässä vedessä, mutta alempi kerros oli tasaisemmin näytteiden pinnalla. Magnetiittikerroksen paksuus hiottujen näytteiden pinnalla oli 0,7-1,3 µm.

## 6 Tulosten tarkastelu ja johtopäätökset

Alkaloivien amiinien hajoamisesta saatiin tietoa online-mittausten (johtokyky ja pH) ja CE-määritysten avulla. Tulokset tukevat hyvin toisiaan ja nyt määritetyt reaktionopeusvakiot ovat samansuuntaisia kirjallisuudesta löytyvien arvojen kanssa. Shenberger et. al määrittämät reaktionopeusvakioiden arvot, koekattilalla tehdyissä tutkimuksissa, olivat morfoliinille $7{,}47 * 10^{-5}\ s^{-1}$ ja 2-amino-2-metyyli-1-propanolille $4{,}68 * 10^{-4}\ s^{-1}$ [2]. Morfoliinin reaktionopeusvakiot vaihtelevat kuitenkin huomattavan paljon eri tutkimusten välillä [6]. Online-mittausten ja CE-määritysten tulosten mukaan morfoliini oli termisesti kestävin 340 °C lämpötilassa. Sykloheksyyliamiini hajosi nopeammin kuin morfoliini, mutta hitaammin kuin 2-amino-2-metyyli-1-propanoli. Vähähappisessa vedessä hajoamismekanismeista tulee kyseeseen lähinnä hydrolysoituminen eli hajoamistuotteina ei muodostu orgaanisia happoja [2]. Todennäköisiä hajoamistuotteita ovat pienemmän molekyylipainon amiinit ja erilaiset alkoholit.

EIS-tulosten mukaan amiineilla oli vaikutusta hiiliteräksen pinnalle muodostuvan oksidikerroksen ominaisuuksiin. Morfoliinia ja sykloheksyyliamiinia sisältävässä vedessä rauta-ionien diffuusio hiottujen näytteiden pinnalle muodostuneen oksidin läpi hidastui amiinin hajotessa. Morfoliiniliuoksessa myös esihapetetun näytteen oksidikerroksen ominaisuudet muuttuivat. Aineensiirtovastusten mukaan näytteiden korroosionopeuksissa ei kuitenkaan ollut merkittävää eroa kokeen lopussa.

Metallinäytteiden potentiaali- ja EIS-mittausten mukaan pysyvä magnetiittikalvo muodostui näytteiden pinnalle < 12h kokeen aloittamisen jälkeen kaikilla amiineilla ja ammoniakilla. Potentiaali sijaitsi kaikilla näytteillä magnetiitin termodynaamisella stabiilisuusalueella. SEM-kuvien mukaan morfoliini- ja ammoniakki-kokeissa olleiden hiiliteräsnäytteiden pinnalla oli enemmän suuria oksidipartikkeleita kuin sykloheksyyliamiini- ja 2-amino-2-metyyli-1-propanoli-kokeissa olleiden näytteiden pinnalla. Tämä voi olla seurausta korkeamman pH:n aiheuttamasta liuenneiden rauta-ionien saostumisesta oksidikerroksen pinnalle suurina oksidipartikkeleina. Varsinainen suojaava kerros muodostuu kuitenkin metallin ja oksidin rajapinnalla, joten oksidin ja veden rajapinnalla saostuneet oksidipartikkelit eivät vaikuta merkittävästi kerroksen kykyyn suojata metallia.

Tulevissa tutkimuksissa olisi hyödyllistä seurata online-mittauksella myös kationinvaihtimen jälkeistä johtokykyä, joka kertoo orgaanisten happojen määrän muutoksesta. Hajoamisreittien selvittämiseksi tulisi käyttää kvalitatiivisia tutkimusmenetelmiä, esimerkiksi GC-MS ja HPLC-MS tekniikoita, ja hajoamistuotteiden pitoisuuksien määrittämisessä on päästävä 10 ppb tasolle. Tutkimuksissa on pyrittävä lyhentämään viipymäaikaa autoklaavissa ja kasvatettava kiertovesisäiliön vesitilavuutta suhteessa autoklaavin tilavuuteen, jolloin autoklaavissa tapahtuva kemikaalien hajoaminen ei ole merkittävää ja amiineja voidaan vertailla luotettavammin. Tämän tutkimuksen tulosten mukaan alkaloivat amiinit vaikuttavat magnetiittikerroksen ominaisuuksiin ja kerroksesta muodostuu erilainen kuin ammoniakkipitoisessa vedessä. Tulevissa tutkimuksissa olisikin hyvä selvittää kattavammin eri amiinien vaikutusta magnetiittikerroksen pitkäaikaiskestävyyteen/stabiilisuuteen. Lisäksi tulee selvittää myös kattilan häiriötilanteiden vaikutusta (esim. häiriöt kemikaalien syötössä ja happipitoisuuden tilapäinen nousu) magnetiittikerroksen pysyvyyteen.

# 7 Yhteenveto

Tutkimuksessa selvitettiin alkaloivien amiinien termistä hajoamista ja vaikutusta hiiliteräksen pinnalle syntyvän magnetiittikerroksen ominaisuuksiin 340 °C lämpötilassa. Tutkittavia kemikaaleja olivat morfoliini, sykloheksyyliamiini ja 2-amino-2-metyyli-1-propanoli ja referenssinä käytettiin ammoniakkia. Kyseiset yhdisteet ovat yleisesti käytössä soodakattiloissa käytettävissä vesikemikaaliseoksissa. Kokeiden aikana kemikaalien hajoamista seurattiin on-line pH-mittauksella ja vesinäytteistä määritettiin amiinien pitoisuudet kapillaarielektroforeesilla. Magnetiitin muodostumista hiiliteräsnäytteiden pinnalle seurattiin potentiaali- ja impedanssimittauksilla hiotuista ja esihapetetuista näytteistä.

Tutkituista amiineista morfoliinin terminen kestävyys oli paras ja 2-amino-2-metyyli-1-propanolin heikoin. Määritettyjen hajoamistuotteiden pitoisuudet olivat vähäisiä kokeissa käytetyillä kemikaaliannoksilla. Vähähappisessa vedessä hajoamistuotteina syntyy lähinnä pienemmän molekyylipainon amiineja ja erilaisia alkoholeja, ei orgaanisia happoja. Pienten hajoamistuotemäärien tarkka analysointi vaatii kvalitatiivisia tutkimusmenetelmiä.

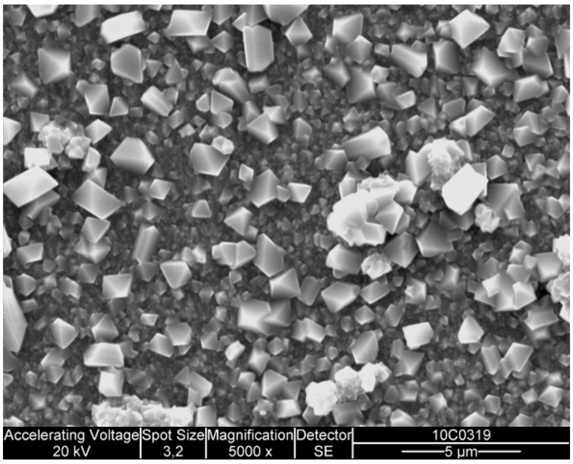
Potentiaalimittausten mukaan hiiliteräsnäytteiden pinnalle muodostui suojaava magnetiittikerros alle 12 h koeajalla. Potentiaali sijaitsi magnetiitin termodynaamisella stabiilisuusalueella kaikilla näytteillä. EIS-mittausten mukaan alkaloivat amiinit vaikuttivat hiiliteräksen magnetiittikalvon ominaisuuksiin. Warburg-kertoimien mukaan rauta-ionien diffuusio oksidikerroksen läpi nopeutui alkaloivien amiinien vaikutuksesta. Kokeen viimeisistä mittauksista laskettujen aineensiirtovastusten mukaan korroosionopeuksissa ei kuitenkaan ollut merkittävää eroa eri näytteiden välillä. Kemikaalien toisistaan poikkeava hajoamisnopeus vaikeuttaa kuitenkin eri amiinien vaikutuksen vertailemista.

# Lähdeviitteet

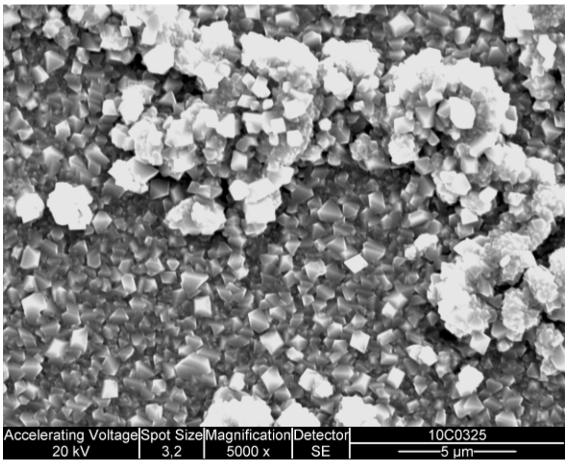
1. Passell, T.O., (Ed), Advanced studies in Chemistry Control with Morpholine, EPRI, Palo Alto, July 1992, TR-100758.
2. Passell, T.O., (Ed), Loop testing of Alternative Amines for All-Volatile Treatment Control in PWRs, EPRI, Palo Alto, July 1992, TR-100756.
3. VGB Instruction Sheet "Organic Matter and Dissolved Carbon Dioxide in the Steam Water Circuit of Power Plant", (M418 Le) 2002, VGB, Essen, Germany, 43s.
4. Bojinov, M., Gaonkar, K., Ghosh, S., Kain, V., Kumar, K., Saario, T., Characterisation of the oxide layer on carbon steel during hot conditioning of primary heat transport systems in heavy-water reactors, Corros. Sci. 51 (2009) 1146-1156.
5. Vidqvist, M., Kattilavesikemikaalit - hydratsiini, ammoniakki vai amiinit?, Promaint-lehti, 2 / 2008 p. 26-29.
6. Hildén, J., Pohjanne, P., Orgaaniset yhdisteet syöttö- ja kattilaveden käsittelyssä, VTT tutkimusraportti VTT-R-010993-09, Espoo 2009.

# Liite 1. SEM-kuvat

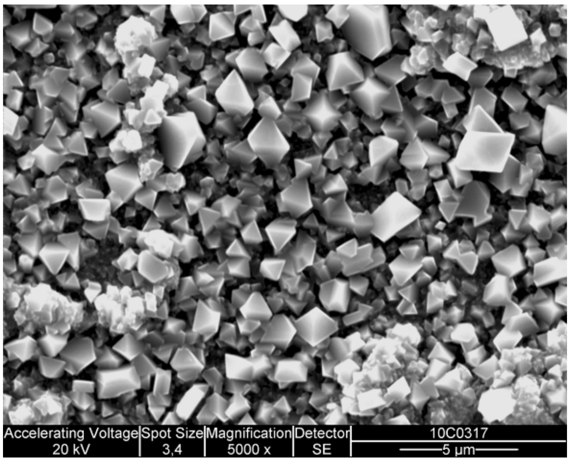
### 5000-kertainen suurennos hiotuista näytteistä kokeen jälkeen



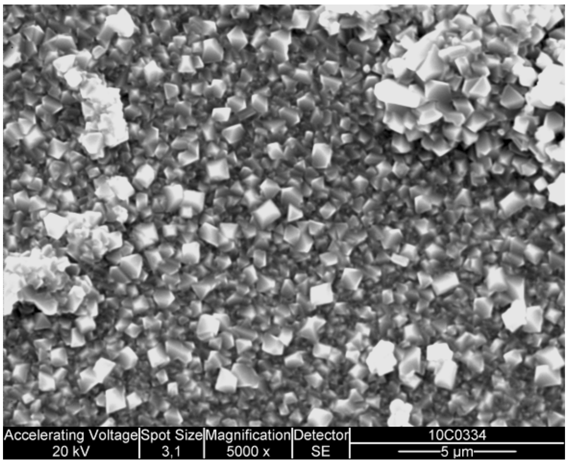
**Ammoniakki**



**Sykloheksyyliamiini**

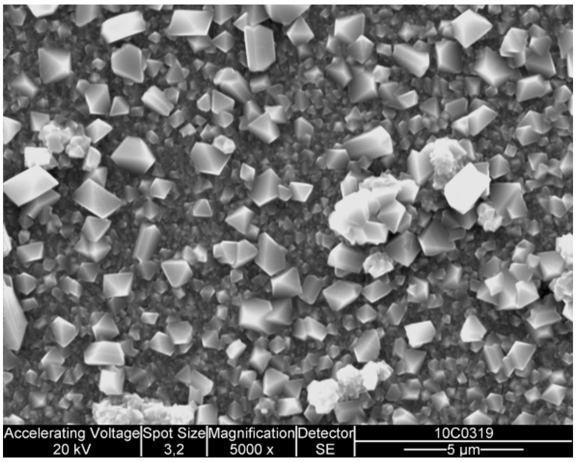


**Morfoliini**

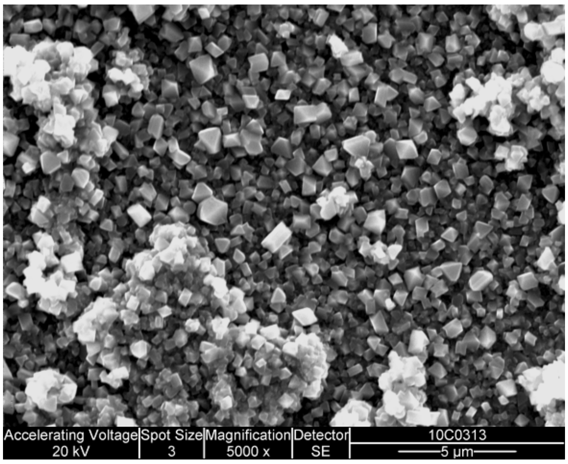


**2-amino-2metyyli-1-propanoli**

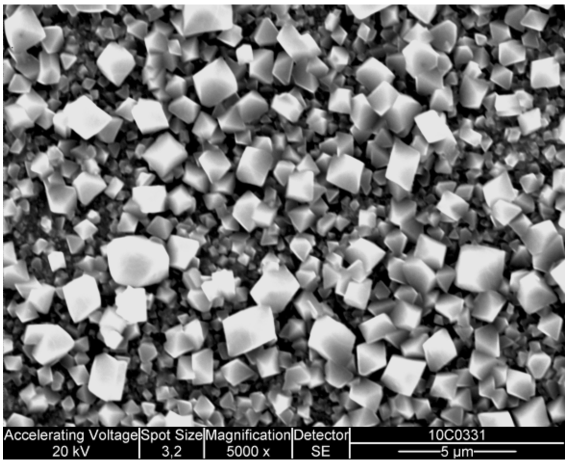
## 5000-kertainen suurennos esihapetetuista näytteistä kokeen jälkeen



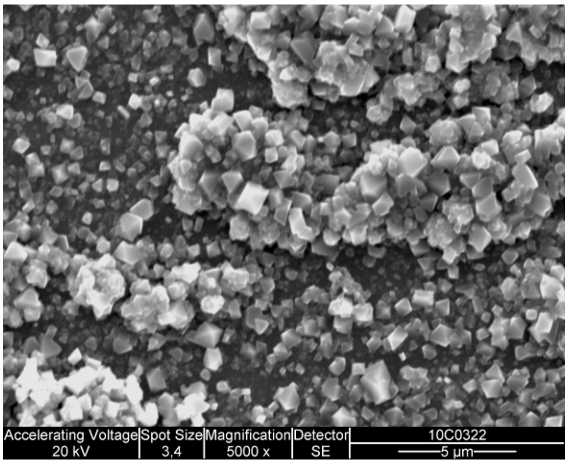
Ammoniakki



Sykloheksyyliamiini

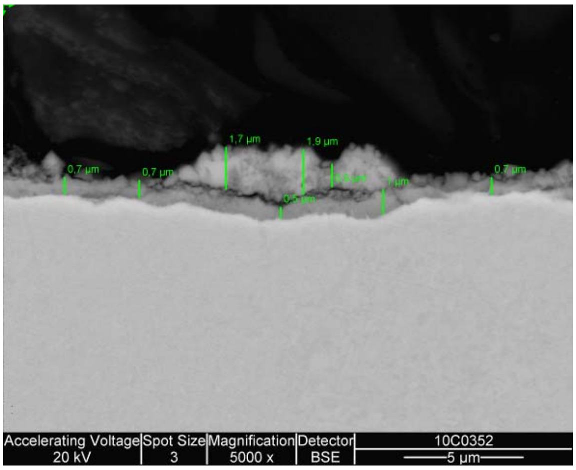


Morfoliini

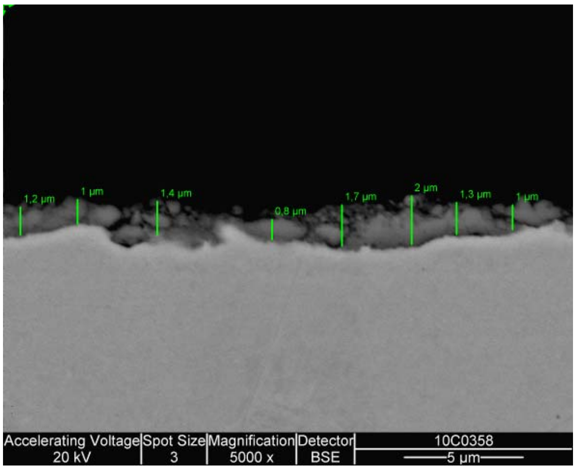


2-amino-2-metyyli-1-propanoli

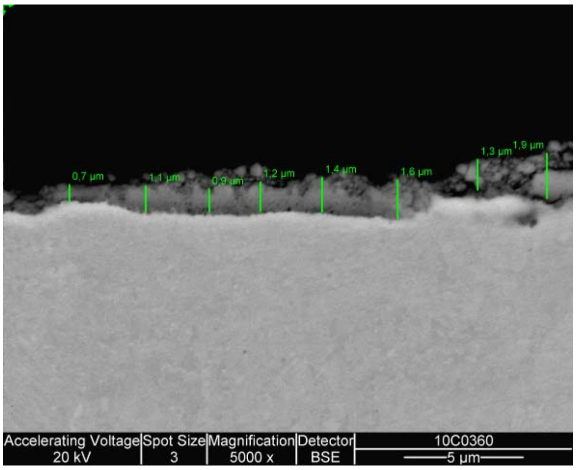
## 5000-kertainen suurennos hiottujen näytteiden poikkileikkaushieiden magnetiittikerroksista



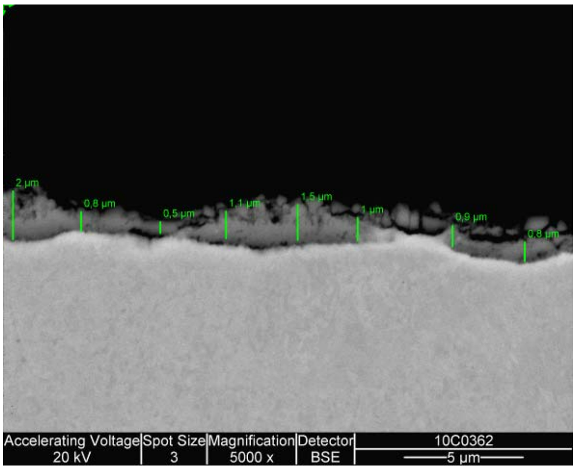
**Ammoniakki**



**Sykloheksyyliamiini**



**Morfoliini**



**2-amino-2-metyyli-1-propanoli**

# LIITE XIV

Tero Luukkonen, OY

# SKYREC - Reduction of TOC from recovery boiler make-up water – jatkotutkimusehdotuksia

2.6.2010

Tero Luukkonen 14.6.2010
Jatkotutkimussuunnitelma

# Aktiivihiilisuodatuksen ja UV-käsittelyn soveltaminen suolanpoistolaitokseen lisäveden TOC-tason alentamisessa

## 1 Tausta ja tavoite

Projekti on osa Soodakattilan sähköenergiatehokkuuden nostaminen uudelle tasolle -projektia ja sen Kattilaveden ja höyryn laadun varmistaminen -osaprojektia. Projekti on jatkotutkimus Oulun yliopiston kemian laitoksella tehtyyn pro gradu -työhön ”Soodakattilalaitoksen lisäveden orgaanisen aineen (TOC) alentaminen”.

Projektin tavoitteena on varmentaa ja optimoida aktiivihiilisuodattimen toimivuutta TOC:n poistossa tehdasympäristössä sekä tehdä lisäselvityksiä esimerkiksi suodattimen mitoituksesta ja aktiivihiilen käyttöjakson pituudesta.

Lisäksi selvitetään ja kokeillaan UV-valon käyttöä osana suolanpoistolaitosta.

## 2 Toteutus

### 2.1 Vaiheet, työpaketit, tehtävät

Tutkimuksessa selvitetään mahdollisuutta integroida aktiivihiilisuodatus osaksi suolanpoistolaitosta. Suolanpoistolaitoksessa pääosan orgaanisesta aineesta (TOC) poistavat anioninvaihtimet. Aiemmassa tutkimuksessa todettiin, että aktiivihiilisuodatuksella voidaan poistaa merkittävä osa jäljelle jääneestä orgaanisesta aineesta. Lisäksi saatiin viitteitä, että poistoprosessi on ainakin osittain biologinen.

Aktiivihiilisuodattimen toimintamekanismia tutkitaan tekemällä pesäkelukumäärityksiä suodatusjakson edetessä. Suodattimen toimintaa seurataan myös mittaamalla hiilen ominaispinta-alaa BET-menetelmällä. Tutkitaan käynnistyykö biologinen prosessi ilman avustusta vai tarvitaanko aluksi mikrobeja sisältävää ns. make up -vettä. Aktiivihiilen käyttöjakson pituus selvitetään tekemällä riittävän pitkä TOC-mittaussarja.

Selvitetään kuinka paljon aktiivihiilisuodatuksessa alentunutta TOC-tasoa voidaan lisäalentaa sitä seuraavalla suolanpoistolla (MB-vaihdin). Tämä tutkimusvaihe toteutetaan käytännössä lisäämällä aktiivihiilisuodattimen (AC) jälkeen pilot-kokoluokan sekavaihdin. Suunniteltu kytkentä on: K – A1 – A2 – AC – MB. Aktiivihiilen biologinen toiminta voi mahdollisesti pilkkoa huonosti poistuvan varauksettoman orgaanisen aineen varauksellisiksi yhdisteiksi, jotka poistuvat MB-vaihtimessa. Tähän kytkentään liitetään online pH- ja johtokykymittaukset ennen ja jälkeen aktiivihiilisuodattimen ja niiden tieto kerätään teollisuuslaitoksen tietojärjestelmään.

Tutkitaan UPM:n Pietarsaaren soodakattilan lisäveden puhdistamista aktiivihiilisuodattimella. Tutkimus toteutetaan viemällä pilot-suodatin Pietarsaareen ja tekemällä riittävän pitkä mittaussarja. Analyysit suoritetaan Oulun yliopistolla.

UV-valolla tehtävät kokeet pyritään toteuttamaan pilot-mittakaavan laitteistolla, jossa kytkentä on: K – A1 – A2 – UV – MB. Riittävän voimakkaalla UV-valolla (aallonpituus 185 nm) orgaaniset yhdisteet saadaan hajoamaan varauksellisiksi, pienemmiksi yhdisteiksi, jotka voidaan poistaa sekavaihtimella.

Veden ja siinä olevan orgaanisen aineen koostumuksen analyyseja tehdään ennen ja jälkeen aktiivihiilisuodatuksen ja UV-käsittelyn. Orgaanisten yhdisteiden kvalitatiivisia analyysejä tehdään myös raakaveden puhdistusprosessin ja soodakattilan vesi-höyrykierron eri vaiheista. Veden kvalitatiiviset analyysit toteutetaan tilaustyönä tähän erikoistuneessa laboratoriossa. Tarkoitukseen soveltuva analyysitekniikka on esimerkiksi LC-OCD. Formiaatti- ja asetaattipitoisuuksien analyysit voidaan tehdä käyttäen yliopiston ionikromatografia, jossa on tarkoitukseen sopiva, puhdas kolonni.

Tärkeitä selvitettäviä asioita ovat myös aktiivihiilisuodattimen ja UV-laitteiston mitoitukseen ja investoinnin suuruuteen liittyvät kysymykset. Mitoitussuunnittelu toteutetaan yhteistyössä laitetoimittajan kanssa.

## 2.2 Organisointi

Työntekijänä toimii FM Tero Luukkonen.

Työ suoritetaan Oulun yliopiston CEWIC-projektin tai vaihtoehtoisesti kemian laitoksen hallinnoimana.

## 2.3. Aikataulu

Tutkimus tullaan pääosin suorittamaan kesän 2010 aikana (kesä – syyskuu). Alla olevassa kaaviossa on jaoteltu tehtäviä kuukausittain. Aktiivihiilisuodattimen käyttöjakson selvitys voi jatkua syyskuun jälkeen tuntiveloituksena.

Tulokset raportoidaan (käyttöjakson selvitystä lukuunottamatta) 30.9., mikäli projekti pääsee alkamaan kesäkuun alkupuolella.

| **Kesäkuu** | **Heinäkuu** | **Elokuu** | **Syyskuu** | |
|---|---|---|---|---|
| • Laitteistojen rakentaminen tehdasympäristöön<br>• Koeajojen aloitus (biologian käynnistys)<br>• Analyysejä (TOC, pesäkeluvut, BET)<br>• Tilattavien analyysien kilpailutus | • Koeajojen jatkuminen<br>• Analyysejä (TOC, ionikrom., pesäkeluvut, BET) | • Koeajojen jatkuminen<br>• Analyysejä (TOC, ionikrom., pesäkeluvut, LC-OCD, BET) | • Koeajojen jatkuminen<br>• Pietarsaaren kokeet<br>• Analyysejä (TOC, BET)<br>• Tulosten raportointi | • Käyttöjakson selvitys (esim. seuraavat 3 kk) |

## 2.4. Budjetti ja rahoitus

Rahoituksen ja budjetin osalta on esitetty kaksi vaihtoehtoa: CEWIC-hanke (vaihtoehto 1) ja kemian laitoksen hallinnoima hanke (vaihtoehto 2). Jotta projekti voidaan toteuttaa tuettuna CEWIC-hankkeena, mukaan rahoitukseen täytyy saada vähintään yksi Pohjois-Pohjanmaalla toimiva yritys/toimija Soodakattilayhdistyksen lisäksi. CEWIC tukee hanketta tällöin 50 %:lla yritysten antamasta rahoituksesta.

### 2.3.1. Vaihtoehto 1: CEWIC-hanke

Projektin rahoitus.

| | |
|---|---|
| Soodakattilayhdistys + Pohjois-Pohjanmaalla toimiva yritys (esim. Stora Enso) | 15 500 e |
| CEWIC | 7750 e |
| | Yhteensä: 23 250 e |

Budjetti kuukausittain.

| | Kesäkuu | Heinäkuu | Elokuu | Syyskuu |
|---|---|---|---|---|
| **Palkka** | 2200 | 2200 | 2200 | 2200 |
| **Henkilösivukulut + lomaraha** | 600 | 600 | 600 | 600 |
| **Yleiskulut** | 600 | 600 | 600 | 600 |
| **Analyysit** | 2500 | 2500 | 2250 | - |
| **Muut kustannukset** | 600 | 600 | 600 | 600 |
| | 6000 | 6000 | 6000 | 6000 |

**Yhteensä: 23 250 e**

### 2.3.2. Vaihtoehto 2: Kemian laitoksen hallinnoima hanke

Projektin rahoitus.

| | |
|---|---|
| Soodakattilayhdistys | 23 000 e |
| | Yhteensä: 23 000 e |

Budjetti kuukausittain.

| | Kesäkuu | Heinäkuu | Elokuu | Syyskuu |
|---|---|---|---|---|
| **Palkka** | 2200 | 2200 | 2200 | 2200 |
| **Henkilösivukulut + lomaraha** | 600 | 600 | 600 | 600 |
| **Yleiskulut** | 600 | 600 | 600 | 600 |
| **Analyysit** | 2500 | 2500 | 2000 | - |
| **Muut kustannukset** | 600 | 600 | 600 | 600 |
| | 6000 | 6000 | 6000 | 6000 |

**Yhteensä: 23 000 e**