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Risk management measures for REACH registered intermediate substances in pulp mill

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ABSTRACT

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The aim of this thesis work is to provide risk management measures for five intermediate substances processed in Stora Enso Imatra mills. The intermediate substances are black liquor, green liquor, white liquor, sodium bisulphite and sodium sulphite. These substances have already been registered into ECHA. The risk management measures must be provided to ECHA.

In the beginning of this thesis work the essential regulations and authorities which control the manufacture and use of chemicals in European Union are presented. Then information about registration criteria for chemicals is presented and the focus is in intermediate substances. In the end of thesis the risk management measures for each intermediate substance is provided. The risk management measures includes technical means of rigorous containment and minimization technologies, procedural and control technologies, management means and training of personnel and transportation of intermediates. To support understanding, physic-chemical properties and brief process descriptions for each substance are also presented in this thesis.

CONTENTS

Contents

ABBREVIATIONS AND SYMBOLS

Acronyms

AEO	Authorised Economic Operator
CoC	Chain of Custody
CLP	Classification, Labeling, Packaging
CW	Controlled Wood
ISO	International Organization for Standardization
OHSAS	Occupational Health and Safety Advisory Services
PEFC	Programme for the Endorsement of Forest Certification schemes
REACH	Registration, Evaluation, Authorization of Chemicals
SFS	Finnish Standards Association
VAK	Transport of dangerous goods

1 INTRODUCTION

The essential authorities controlling the use of chemicals are European chemicals agency ECHA and Finnish safety and chemicals agency TUKES. Essential regulations are Reach (Registration, Evaluation, Authorization and Restriction of Chemicals) and CLP (classification, labeling, packaging). Reach is the European Parliament and Council Regulation No 1907/2006 and it has entered into force on the 1st of June 2007.

According to REACH-regulation industrial companies must register their chemicals. In this thesis the registration has been limited to intermediate substances. In another words they are chemical substances which are manufactured to be transformed into other chemical substances. There are reduced registration requirements for chemical substances that are used as intermediate substance if the manufacturer or user of the substance can justify that the chemicals are used or manufactured in strictly controlled conditions.

This thesis work is made for Stora Enso Imatra mills. It has already registered their intermediate substances in the ECHA. The registration dossier is delivered to ECHA and one part of registration dossier is the risk management measures for each intermediate substance.

The aim of this thesis is to compile description of risk management measures for five intermediate substances which are manufactured and used in kraft pulping in Stora Enso Imatra mills. The substances are black liquor, green liquor, white liquor, sodium bisulphite and sodium sulphite. These chemical substances have been registered separately. Risk management measures includes information about identified risks, technical means of rigorous containment and minimization technologies, procedural and control technologies and management and training measures. Brief process descriptions for each substance are also provided to support understanding.

1.1 Stora Enso Imatra mills

Imatra mills comprise two production unit which are Kaukopää and Tainionkoski. The whole mill employs around 1000 people. The annual production of mill is over a million tonnes of board and paper. About 90 % of production goes for export and the most important market is Europe but also a significant share goes also to Southeast Asia.

Imatra mills product packaging and graphic board and paper. Typical end products of liquid packaging board include milk and juice cartons. End products of food service boards are paper cups and various food packages. Packaging boards are produced for the food, tobacco and sweet packages. Graphic boards are used for book covers, cards and luxury packaging. Also high-quality packaging papers are made in Imatra Mills. (Stora Enso, 2013)

2 EUROPEAN CHEMICALS AGENCY ECHA, REACH AND CLP

Essential authorities and regulations concerning the chemical legislation are presented in this chapter.

2.1 ECHA, European Chemical Agency

ECHA is a driving force among the chemical legislation in European Union. It helps companies to comply with the legislation, advances safe use of chemicals, gives information about chemicals and addresses chemicals that causes harm. Organization of ECHA consists of management board, executive director, member state committee, risk assessment committee, committee for socio-economic analyses, forum, secretariat and board of appeal. The registration dossiers are submitted to ECHA and they are also reviewed in there. (ECHA, 2013h.)

2.2 REACH regulation

REACH is the European Parliament and Council Regulation No 1907/2006. REACH has entered into force on the 1st of June 2007. The term REACH includes the words: Registration, Evaluation, Authorization and Restriction of Chemicals. Its aim is to protect human health and the environment from the hazards caused by chemical substances. Its aim is also to improve competitiveness, and it improves the methods that are used for evaluation of hazards. REACH gives the responsibility to industry to manage and control the risks from chemicals that are manufactured and marketed inside EU. They have to prove that substances are used safely. REACH will harmonize European chemical legislation. (ECHA, 2013a.)

2.2.1 The registration requirements

The companies must register their chemical substances which they produce or import to European Union. The registration dossiers must include information about the hazards and risks concerning the use of chemical and information about risk management. The authorities and scientific comities of chemical agency will evaluate if the risks concerning the substances are manageable. If it's necessary they can restrict the use of chemical substances of which hazards aren't manageable. (ECHA, 2013a.)

2.2.2 Phase-in substances

There is a special system for substances which were in the markets before REACH entered into force. They are called phase-in registered substances. Companies can benefit from this system if they have pre-registered their substances by 1 December 2008. Pre-registration allows registrants of the same phase-in substance to get together and submit a registration dossier jointly. In phase-in system the registration is divided to three phases. (ECHA, 2013b). The REACH time line and the three phases are presented in figure 1.

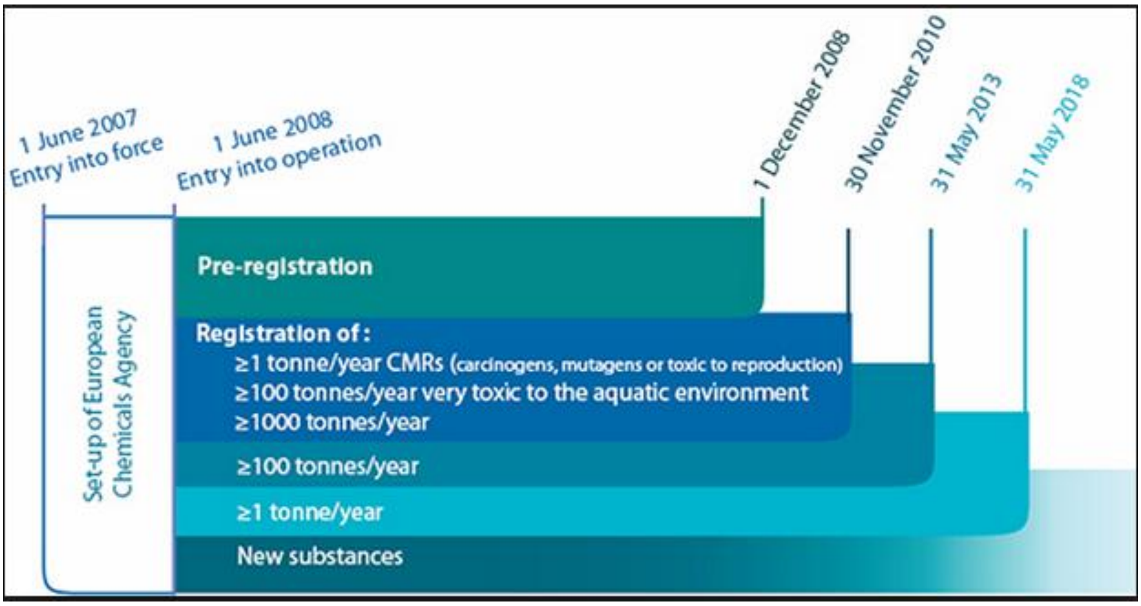

Figure 1. REACH time line. (Clariant, 2012)

2.2.3 Data sharing

The data sharing in registration means that only one set of registration documents is provided concerning one substance. "Substance information exchange forum" SIEF is the mechanism for data sharing for pre-registered phase-in substances. Companies which are registering the same substance must join to same SIEF. Joining to this exchange forums is a statutory duty. One of the SIEF-members is the lead registrant. It acts with the agreement of the other co-registrants and submit the lead registration dossier of the joint submission. (ECHA, 2013c.) Stora Enso Oyj. is a member of several SIEFs because there's own SIEF for every substance. Imatra mills is part of Stora Enso Oyj.. It has registered the intermediate substances which are processed in liquor cycle. (Lipeäkierron välituotteiden rekisteröinti, 2013.)

2.3 CLP regulation

CLP regulation is a regulation concerning classification, labeling and packaging of chemical substances and mixtures. The regulation is ordered by European parliament. CLP-regulation came into effect in January 2009. The regulation ensures that hazards concerning chemical substances are informed to employees and consumers inside EU. CLP includes standard statements and pictograms on labels and safety data sheets. (ECHA, 2013d.)

2.3.1 Structure of CLP regulation

CLP-regulation consists of 62 articles and seven appendixes. The appendixes include information and instructions about the classification and labeling. The appendixes are

- Appendix I: labeling and classification in accordance with health-, environmental- and physical hazard features.
- Appendix II: packaging regulations for substances
- Appendix III: list of hazard phrases
- Appendix IV: list of precautionary statements
- Appendix V: list of warning signs
- Appendix VI: list of dangerous substances
- Appendix VII: conversion chart from recessive classification to CLP

In addition, ECHA will maintain a classification and labeling inventory which includes industry's notifications about classification and labeling of dangerous substances. CLP Regulation will bring change especially to the label and terminology used. For example the old symbols will be changed in new pictograms. Old R as "risk"- and S as "safety"-phrases will be changed into H as "hazard" and P as "precautionary" statements. Signal words "danger" and "warning" will be applied on the label. There are more danger classes and categories in CLP regulation than in the old one. (Tukes, 2010)

2.3.2 **Duties concerning the suppliers**

The suppliers have one or more of following roles: manufacturer, importer, producer, downstream user or distributor. (ECHA, 2013g.) The suppliers need to decide on the classification of a substance or mixture. This is self-classification. The manufacturers and importers must also classify substances which aren't released into markets. These kinds of substances are isolated and transported isolated substances, for example the intermediate substances in liquor cycle. (ECHA, 2013e.) Guidance on intermediates is deal with in chapter four.

To classify substance the supplier must

- Collect available information concerning the substance
- Evaluate the adequacy and reliability of information
- Review of information based on the classification criteria
- Decision on classification

2.3.3 **Labeling and packaging**

Suppliers have to label a substance which is contained in packaging according to CLP before releasing it to markets when it's classified as dangerous. CLP defines the content of labeling and order of labeling elements. Substances and mixtures classified as hazardous shall be packed and stored in the packaging according to CLP regulation. Packaging must not leak or loosen. The packaging materials must not react with the contents. Containers with replaceable fastening devices must be able to close the container again without leaking. The shape of a package including hazardous substance or mixture may not be attractive to children or misleading to consumers. It mustn't refer to the food, feed, medicine or cosmetics. (TUKES, 2009.) Warning signs are presented in figure 2.

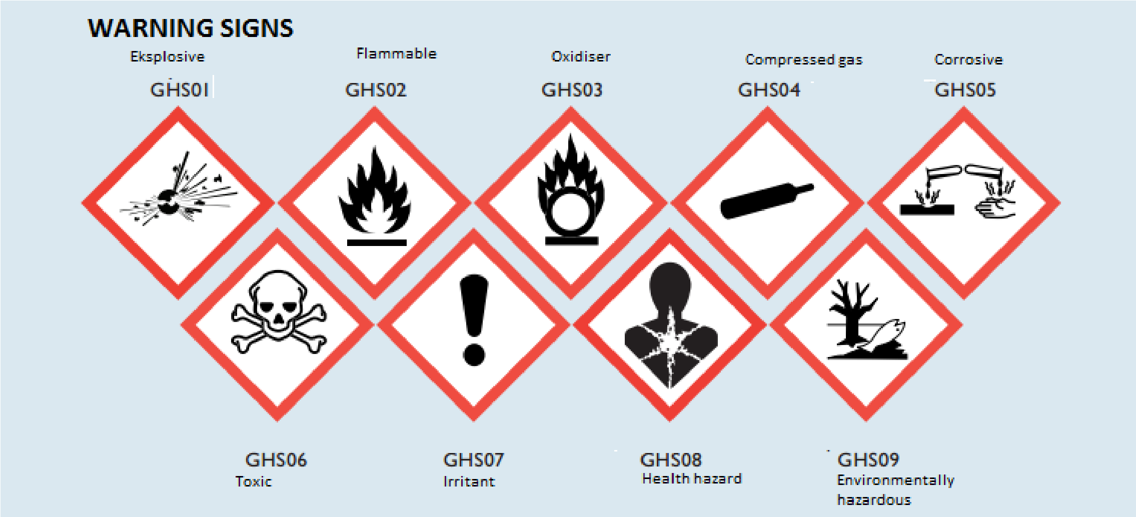

Figure 2. The Warning signs.

3 TUKES AND TRANSPORTATION OF DANGEROUS GOODS

In this chapter general information about TUKES and transportation of dangerous goods is presented.

3.1 TUKES, Finnish Safety and Chemicals Agency

TUKES controls and advances technical safety, conformity and consumer and chemical safety in Finland. Its aim is safe, reliable and ecologically sustainable community. Branches that TUKES effects on are metals, handling of chemical substances and gases, consumer safety, measurement equipment, explosives, electricity, construction products, chemicals and biocides, mining and pressure equipment. The products, services and production systems which are included in branches mentioned before are supervised by TUKES. The purpose of operation is to protect people, property and environment. (TUKES, 2012.)

3.2 Transportation of dangerous goods-VAK

Tanks and packaging used in the transport of dangerous goods must meet the chemical-specific technical requirements to ensure that their contents don’t pose a risk to people, property or the environment, including in the event of an accident. Tukes monitors the conformity of packaging and tanks used for transport in Finland. (TUKES, 2012.)

Here are the legislation and regulations concerning tanks and packages.

-Act on Transport of Dangerous Goods (719/1994)

-Government Decree on the Transport of Dangerous Goods by Road (194/2002)

-Decree of the Ministry of Transport and Communications on the Transport of Dangerous Goods by Road (171/2009)

-Directive 2010/35/EU of the European Parliament and of the Council on transportable pressure equipment (TUKES, 2012.)

4 GUIDANCE ON INTERMEDIATES

Intermediates are a class of substances for which specific provisions have been laid down under REACH for reasons of workability and because of their special nature. Especially the intermediates benefits from reduced registration requirements. (European chemicals agency (ECHA), 2010, s. 2.)

4.1 The definition of intermediates

REACH defines an intermediate as a substance which is manufactured for or used for chemical processing in order to be transformed into another substance. There are three different types of intermediates which are defined under REACH. These types are non-isolated intermediates, on site isolated intermediates and transported isolated intermediates. (European chemicals agency (ECHA), 2010, s. 2.)

A non-isolated intermediate is an intermediate that during synthesis is not intentionally removed from the equipment in which the synthesis takes place. (European chemicals agency (ECHA), 2010, s. 2.) On-site isolated intermediate is an intermediate which is first isolated before being used for chemical processing to be transformed into another substance. The chemical processing of substance happens at a later date and it must happen at same location as the isolation. A transported isolated intermediate is also an isolated substance and transported between or supplied to other sites. As for on-site isolated intermediates, transported isolated intermediates are first isolated before being used for chemical processing to be transformed into another substance. (European chemicals agency (ECHA), 2010, s. 33)

4.2 The Registration of isolated intermediates

The first task for the registrant is to determine if the on-site isolated or transported isolated substance under investigation is an isolated intermediate manufactured and used under strictly controlled conditions. Registrant must provide registration dossier to fulfill his obligations. In case of strictly controlled conditions it's possible to use reduced registration requirements. (European chemicals agency (ECHA), 2010, s. 8.)

If the manufacturer or importer of a substance manufactures or imports the substance for other purposes than only the use as an intermediate, or if the manufacture can't demonstrate that substance is manufactured or imported under strictly controlled conditions, then the manufacturer or importer needs to submit a standard registration dossier. (European chemicals agency (ECHA), 2010, s. 8.)

4.3 The definition of strictly controlled conditions

"Strictly controlled conditions should be seen as a combination of technical measures that are underpinned by operating procedures and management systems." Strictly controlled conditions must be achieved without taking into account the use of personal protective equipment. (European chemicals agency (ECHA), 2010, s. 9-11.) To prove intermediate is manufactured and used under strictly controlled conditions during its whole lifecycle, the registrant should include following risk management measures to the registration dossier.

- Technical means of rigorous containment
- Procedural and control technologies to minimize emissions
- Training and authorization of personnel
- Special procedures in cases of maintenance work
- Documentation and supervising of procedures
- Physic-chemical properties of intermediate substance (European chemicals agency (ECHA), 2010, s. 9-11.)

5 DESCRIPTION OF LIQUOR CYCLE IN IMATRA MILLS

In Imatra mills the intermediate substances of liquor cycle are processed in liquor recovery plant. The liquor recovery plant consists of two evaporation plants, two recovery boilers and causticization plant. The recovery plant is in continuous operation. (Stora Enso Oyj., 2006a.)

Weak black liquor comes from pulp digester to storage tanks and from there to evaporation. In evaporation the solids content of black liquor increases from 16 % to 70 %. The high concentrate liquor from evaporation is called strong black liquor. Black liquor consists of organic ingredient which is called lignin and non-organic cooking chemical. (Stora Enso Oyj., 2006a.)

After evaporation strong black liquor is pumped to storage tank and from there to the recovery boiler. The intention of recovery boiler is to recover the cooking chemical and burn the organic lignin. Burning the lignin also produces energy to pulp and board mill integrate. The melted mixture of sodium sulphide (Na_2S), sodium carbonate ($Na_2CO_{3)}$ and sodium sulphate (Na_2SO_4) is then poured into dissolving tank where it's mixed with weak white liquor from causticization plant. (Stora Enso Oyj., 2006a.)

Now the mixture is called green liquor. From the tank green liquor is pumped to the causticization where burned lime is added to green liquor and after the reactions sodium carbonate becomes sodium hydroxide (NAOH) Together the sodium hydroxide and sodium sulphide are called white liquor and this mixture is used again in kraft pulping. The material flows are presented in figure 3. (Stora Enso Oyj., 2006a.)

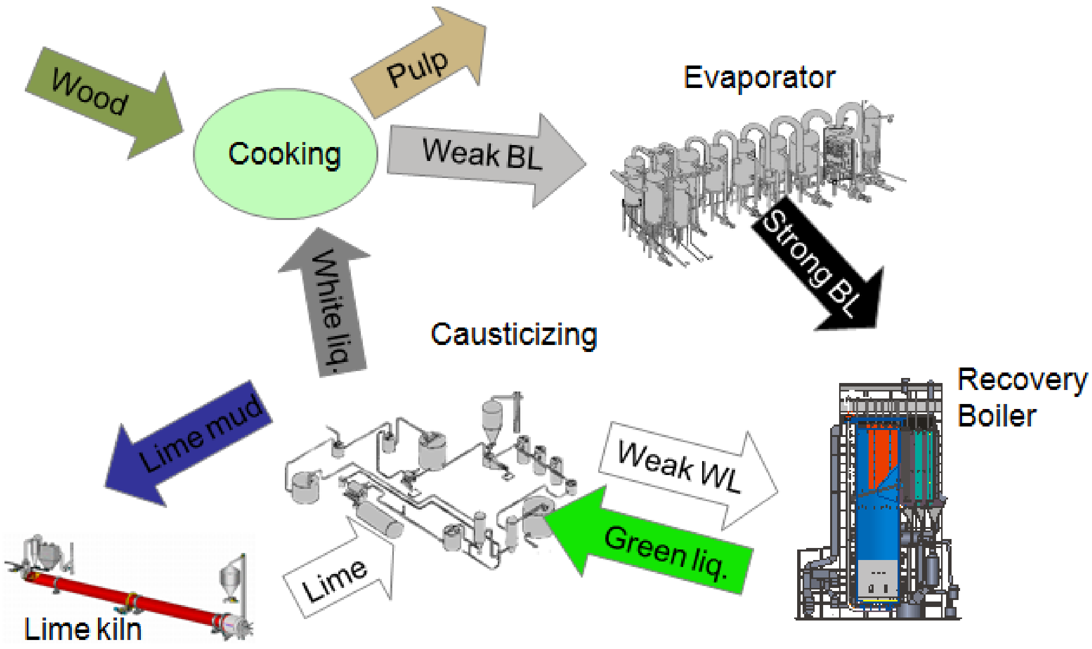

Figure 3. The material flows in liquor cycle. (Vakkilainen 2007a.)

White liquor from the recovery plant is used in kraft pulping. The kraft pulping plant in Imatra mills consist of three fiber lines. The fiber lines are in continuous operation. The chips are absorbed with black liquor in absorption tower. The black liquor for absorption is taken from the cooking zone. After absorption the chips are fed to digester for cooking with white liquor. After cooking, pulp goes through several washing stages where black liquor is separated from the pulp. From the digester black liquor is pumped to storage tanks and so on to evaporation plant. The washed pulp goes to oxygen delignification, screening and bleaching. (Stora Enso Oyj., 2006b,c.)

6 BLACK LIQUOR

In this chapter the information for risk management measures of black liquor, is provided. In Imatra mills black liquor is registered as a transported isolated intermediate.

6.1 The properties of black liquor

Its IUPAC name is "used liquor from alkaline sulphite or the sulphate process, and bleaching, which include inorganic chemical substances and dissolved organic materials of cellulose raw materials". Black liquor is UVCB material having a variable composition. For this reason, its physical and chemical properties will change. (Stora Enso Oyj., 2011a.)

Black liquor consists of conifer and deciduous tree, and sodium hydroxide. It consists about 30 - 55 % of non-organic material and 45 - 70 % of organic material. Black liquor is a tacky liquid in normal temperature and pressure conditions. Its concentration varies as it goes through the evaporating process. The composition of black liquor in solids content of 33 % is presented at table 1. Black liquor's concentrations in different phases of process are presented at table 2. (Stora Enso Oyj., 2011a.)

Table 1. Composition of black liquor. (VTT expert services Ltd, 2010.)

Black liquor	Method		Concentration
Dry substance	SCAN-N 22:77	[%]	33
In dry matter		[%]	
pH 13,1			13,1
inorg./org.-ratio	KCL 61:83		0,48
lignin content	UV-spektrometer	[%]	29,4
sodium Na	SCAN-N 37:98	[%]	19,1
potassium K	SCAN-N 37:98	[%]	2,5
sulphur S	SCAN-N 37:98	[%]	5,7
carbonate $CO_3^{=}$	SCAN-N 32:98	[%]	4
sulphate $SO_4^{=}$	KCL 71:81	[%]	2,2
sulphide $S^{=}$	SACN-N 31:94	[%]	3,5
residual alkali NaOH	SACN-N 33:94	[%]	4,8
polysaccharides	HPAEC-PAD	[%]	3,2
sum of hydroxy acids	CE	[g/kg]	71
acetic acid	CE	[g/kg]	39
formic acid	CE	[g/kg]	24
Sodium carbonate Na_2CO_3	calculated	[g/kg]	66
Sodium hydroxide NaOH	calculated	[g/kg]	3,6
Sodium sulphide Na_2S	calculated	[g/kg]	79,4
Sodium sulphate Na_2SO_4	calculated	[g/kg]	29,9
Potassium hydroxide KOH	calculated	[g/kg]	0,4
Potassium carbonate K_2CO_3	calculated	[g/kg]	6,7
Potassium sulphide	calculated	[g/kg]	8,8

Table 2. Concentrations in different types of black liquors. (Stora Enso Oyj., 2005a.)

Chemical name	Systematic name	CAS number	Concentration
Weak black liquor (includes evaporation plant and hill containers)	Sodium hydroxide	1310-73-2	0,2-0,5 %
	Sodium sulphide	1313-82-2	0,5-2 %
	Sodium carbonate	497-19-8	1-3 %
	Sodium sulphate	7767-82-6	0,2-1,5 %
Intermediate black liquor (includes evaporation plant)	Sodium hydroxide	1310-73-2	0,3-0,6 %
	Sodium sulphide	1313-82-2	3-6 %
	Sodium carbonate	497-19-8	2-5 %
	Sodium sulphate	7767-82-6	1-2,5 %
Strong black liquor (includes evaporation plant)	Sodium hydroxide	1310-73-2	< 0,5 %
	Sodium sulphide	1313-82-2	6-8 %
	Sodium carbonate	497-19-8	2-8 %
	Sodium sulphate	7767-82-6	3-11 %
Strong black liquor (Recovery boilers)	Sodium hydroxide	1310-73-2A	< 0,5 %
	Sodium sulphide	1313-82-2	6-8 %
	Sodium carbonate	497-19-8	2-8 %
	Sodium sulphate	7767-82-6	3-11 %
	Hydrogen sulphide	4.6.7783	
	Methyl mercaptan	79-93-1	
	Dimethyl sulphide	75-18-3	
	Dimethyl sulphide	624-92-0	
	Lignin	9005-53-2	19-29 %
Combustion liquor (Recovery boilers)	Sodium hydroxide	1310-73-2A	< 0,5 %
	Sodium sululphide	1313-82-2	6-8 %
	Sodium carbonate	497-19-8	2-8 %
	Sodium sulphate	7767-82-6	3-11 %
	Hydrogen sulphide	4.6.7783	
	Methyl mercaptan	79-93-1	
	Dimethyl sulphide	75-18-3	
	Dimethyl sulphide	624-92-0	
	Lignin	9005-53-2	19-29 %

The smell is characteristic for compounds which includes sulphur. Black liquor is highly alkaline as it’s presented in table 1. Black liquor starts boiling in 109 ℃ - 120℃ It doesn't have flaming point under 200 ℃. Black liquor isn't self-igniting, highly flammable or explosive when it's in touch with water. Combustibility experiments have been done in accordance with EU-method A.10, A.12 and A.13. This substance is stable in normal conditions.

The substance releases very toxic and highly flammable hydrogen sulphide when it's in contact with acids. If the content of hydrogen sulphide (H_2S) in the air is 4 - 46 %, it forms an explosive gas mixture. Hydrogen sulphide is heavier than air so it will accrue to the bottoms of tanks. (Stora Enso Oyj., 2011a.)

Black liquor is corrosive to respiratory, skin and eyes. It’s is harmful to aquatic organisms and has long-term effects to environment. It's not easily degradable. The danger and safety phrases considering black liquor, are presented in table 3. (Stora Enso Oyj., 2011a.)

Table 3. Classification of black liquore according the CLP-regulation. (Stora Enso Oyj., 2006d)

Substan-ce	Danger classes	Explanation for danger class	Danger Phrase	Explanation for risk phrase	Safe phrase	Explanation for safe phrase
Black liquor	1B	corrosive to skin	H314	highly corrosive to skin and harmful to eyes	P260	Don't breathe dust, smoke gas, fog ,steam or spray
	kat. 1	dangerous to waterenvironment	H290	corrosive to some metals	P264	Wash hands carefully after treatment
	kat. 3	chronical danger	H412	harmful to aquatic organisms, long term effects on water systems	P270	Eating, drinking and smoking is forbidden when handling the chemical
			EUH032	toxic gas is developed when being in touch with acids	P271	The use only outside or in premises with good air conditioning
			EUH071	harmful to respiratory	P273	Avoid releasing the chemical into environment
					P280	depending a task, use protection gloves, protective clothes, glasses and mask

6.2 Process description

Black liquor from kraft pulping is stored in weak black liquor tank where solids content of black liquor liquor increases from 16 to 18 %. The weak black liquor tank is usually kept full. From the tank weak black liquor is fed to evaporation plant. The liquor goes through 6 -7 evaporation phases and after that it’s stored in intermediate liquor tank in solids content of 27 %. The soap is separated in the intermediate liquor tank by pouring it into soap collecting tank. From the intermediate tank black liquor is pumped into next evaporator phases where the solids content rises to 68 %. After that the liquor is pumped into expansion tank where the solids content rises to 70 %. Now the substance is called strong black liquor and it's pumped into strong black liquor tanks. After strong black liquor tanks strong black liquor is pumped to mixing tank before it's fed to recovery boiler. (Stora Enso Oyj., 2012.)

In recovery boilers the inorganic part of liquor is reduced in furnace. The reduction happens when the chemicals are in touch with carbon in high temperature and in reductive atmosphere. The organic lignin is burned at same time in the furnace. The following reactions are the most important ones. The smelt poured out from the boiler consists mainly of end product of following reactions, sodium sulphide and then sodium carbonate. (Stora Enso Oyj., 2011c.)

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$$

$$Na_2SO_4 + 4CO \rightarrow Na_2S + 4CO_2$$

The smelt is poured to dissolving tank where it’s mixed with weak white liquor. The mixture is called green liquor. Black liquor is an intermediate substance in pulp mill’s recovery cycle and it’ll be transformed into green liquor.

6.3 Risks identified at evaporation plant and recovery boilers

Next hazardous situations have been identified in evaporation plant, where black liquor is processed in different concentrations and solids contents,:

- breaking or flange leak of a pipe line
- breaking of black liquor tanks
- breaking of evaporation units
- breaking of pumps or other process equipment
- breaking of odorous gas handling equipment and stripping colonna

In cases of these malfunctions chemical spills to process premises and environment are possible. It might cause a danger to personnel. The odorous gases might consist of toxic hydrogen sulphide. (Stora Enso Oyj., 2006f.)

The next malfunctions have been identified in recovery boiler.

- breakage or flange leak and black liquor pipelines
- breakage of strong black liquor tanks
- molten smelt explosion of furnace
- liquor spatters from smelt chutes
- breakage or over flow of salt mixing tank or strong liquor tank

In cases of these malfunctions chemical spills to environment or process premises are possible. It may cause a danger to personnel. (Stora Enso Oyj., 2006e.)

6.4 Technical means of rigorous containment and minimization technologies

Black liquor is processed in evaporation plants and recovery boilers plant. The malfunctions that cause danger to human health or environment have been taken account of in technical planning. The process is closed and in normal operation liquor stays inside the process equipment.

Spills are controlled by technical means. Liquor spills in evaporation plants and recovery boilers are collected to leak liquor swells. The swells are equipped with continuous conductivity measurements with alarms. In upper limit of measurement the pump starts pumping liquor to leak liquor tank. The clean over flow of the swell goes to process sewer which goes to waste water treatment plant. (Stora Enso Oyj., 2011e.)

In table 4 it's presented that all black liquor tanks are in safety basins of which sewers lead to waste water treatment plant. The sewers of process premises also lead to waste water treatment plant. These sewers are equipped with conductivity measurement and pH-measurement with alarms. Cooling and rain water sewers are also equipped with pH- and conductivity measurements. Possible spills are immediately detected in control room. There're also sewer sealing mats in recovery plant area to block chemical spills to sewer system in case of incidents. The liquor spills in the safety basins and mill yard are collected with vacuum trucks and then they are returned back to process. If the spilled liquor gets contaminated it'll be delivered to hazardous waste treatment. In normal operation waste isn't generated. (Stora Enso Oyj., 2011e.)

All black liquor tanks are equipped with level measurements. The over flow chutes are equipped with temperature measurements. Increase of temperature causes alarm in control room. Recovery boilers are equipped with automated safety lock system. The system will bring the boiler process to safe state in cases of large failure even if the boiler plant is without electricity. (Mustonen, 2013.)

The gaseous emissions are controlled by technical means. The process premises of evaporation plant and recovery boilers are equipped with fixed hydrogen sulphide measurements. They cause alarm in control rooms when they sense hydrogen sulphide in the air. (Stora Enso Oyj., 2006g.) There occur smelling sulphurous gases called TRS-substances in evaporation plant's vacuum pump, fouled condensate tank and stripping colonna. These gases are lead to water seal of methanol distillery and so on to odorous gas boilers. (Stora Enso Oyj., 2011b.)

All sewers to waste water treatment are equipped with continuous measurements of flow, conductivity and pH-value. If the conductivity rises over the alarm level, the waste waters are pumped to weak black liquor storage tanks to prevent malfunctions in the waste water treatment plant. There're numerous continuous measurements in waste water treatment for monitoring and optimizing the treatment process. In case of large chemical spill to waste water treatment, there's an emergency basin which can take the whole capacity of mill's waste waters for eight hours. (Stora Enso, 2007a.)

Table 4. Information about black liquor storage. (Stora Enso Oyj. 2004.)

Tank name and location	Contents	Volume [m3]	Leak control
Pesulipeäsäiliö, Tasa	Weak black liquor	1500	Safety basin, leaks to the canal and so on to waste water treatment plant
Pesulipeäsäiliö, HO6	Weak black liquor	4900	Combined safety basin 30%. Sewer to HO6 leak liquor swell, from which the leaks are pumped to HO6 leak liquor tank or to feed liquor storage tank. Over flow of leak liquor swell goes to waste water treatment plant
Syöttölipeäsäiliö, HO5	Weak black liquor	3000	HO5 shared safety basin 60%. Sewer to waste water treatment plant
Vuotolipeäsäiliö, HO5	Weak black liquor	1080	HO5 shared safety basin 60%. Sewer to waste water treatment plant
Vuotolipeäsäiliö, HO6	Weak black liquor	1500	Shared safety basin 90%. Sewer to HO6 leak liquor swell, from which it is pumped to leak liquor tank Over flow of a swell to process sewer (to waste water treatment)
Syöttölipeäsäiliö, HO6	Weak black liquor	4000	Shared safety basin, 1400 m^3. Sewer to HO6 leak liquor swell, from which it is pumped to leak liquor tank Over flow of a swell to process sewer (to waste water treatment)
Syöttölipeäsäiliö, HO6	Weak black liquor	7000	
Syöttölipeäsäiliön varastosäiliö 1, HO6	Weak black liquor	20 000	Shared ground rampart basin 100%. There is a sewer swell, where are shut-off valves. From the swell the rain water is lead to check pond
Syöttölipeäsäiliön varastosäiliö 4, HO6	Weak black liquor	20 000	
Välilipeäsäiliö, HO5	Intermediate black liquor	2100	HO5 Shared safety basin, 20%. Process sewer to waste water treatment.
Välilipeäsäiliö, HO6	Intermediate black liquor	3000	Shared safety basin, 50%. Sewer to HO6 leak liquor swell, from which it is pumped to leak liquor tank Over flow of a swell to process sewer (to waste water treatment)
Vahvalipeäsäiliöt 1+2, SK6	Strong black liquor	2·1000	Outside shared safety basin. 20%. Process sewer to waste water treatment.
Vahvalipeäsäiliö 2	Strong black liquor	1000	HO5 Shared safety basin, 60%. Process sewer to waste water treatment.
Vahvalipeäsäiliö 1	Strong black liquor	1000	Outside in shared safety basin. 20%. Process sewer to waste water treatment.

7 GREEN LIQUOR

In this chapter the information for risk management measures of green liquor, is provided. In Imatra mills green liquor is registered as transported isolated intermediate.

7.1 Properties of green liquor

Green liquor is an aqueous alkaline solution of sodium salts produced by dissolving smelt from incineration of spent liquor from sodium based pulping processes. It's used as an intermediate. Green liquor consists of aquatic inorganic ingredients like hydroxides, carbonates, sulphides, sulphites, sulphates and their alkali metal salts. The main components are sodium sulphide, sodium carbonate and sodium hydroxide. Typical water content is 75 %. (Stora Enso Oyj., 2013a.)

In normal temperature and pressure green liquor is stable, bright and greenish fluid. It smells like sulphurous substances. It's fully water-soluble. It's not an explosive or easily flammable substance based on its chemical composition. Very toxic and flammable gas, hydrogen sulphide, is developed when the substance reacts with acids or its pH-value decreases below seven. Because of green liquor's corrosive properties it must be stored in tank which has proper inner liner. Composition of green liquor is presented in table 5. (Stora Enso Oyj., 2013a.)

Table 5. Composition of green liquor. (VTT Expert services Ltd, 2010.)

Green liquor	Method		Concentration
pH			>12
sodium Na	SCAN-N 38:10 modif	[g/l]	89
potassium K	SCAN-N 38:10 modif	[g/l]	12
sulfur S	SCAN-N 38:10 modif	[g/l]	27
Thiosulfate	KCL 70:83 modif	[g/l]	3,7
Effective alkali	SCAN-N 30:85	[g/l]	46
Active alkali	SCAN-N 30:85	[g/l]	71
Total alkali	SCAN-N 30:85	[g/l]	150
Sodium sulfide Na_2S	calculated	[g/l]	45,9
Sodium carbonate Na_2CO_3	calculated	[g/l]	99,1
Sodium hydroxide NaOH	calculated	[g/l]	2,1
Sodium thiosulfate $Na_2S_2O_3$	calculated	[g/l]	4,8
Potassium hydroxide KOH	calculated	[g/l]	2,1
Potassium carbonate K_2CO_3	calculated	[g/l]	10,1
Potassium sulfide K_2S	calculated	[g/l]	5,1
Potassium thiosulfate $K_2S_2O_3$	calculated	[g/l]	0,5

The properties of green liquor are defined in accordance with (EY) regulation number 1272/2008. Green liquor is highly corrosive to skin and respiratory and also damaging to eyes. It’s not classified as carcinogenic substance. It’s non-likely that toxic amount of substance is got to fetus and male or female reproductive organs. Any ingredient of green liquor isn’t classified dangerous to reproduction according to EY. The substance is not classified as damaging to environment although it might have an effect on water system's pH value and be damaging to aquatic organisms. Green liquor is non-organic substance and it’s not bio-degradable. Microbes can’t use it as a source of carbon and energy. Bioaccumulation is not important considering the ingredients if green liquor. Movement of substance in soil is high and its absorption to soil is relatively low. Identification of danger in accordance with CLP-regulation is presented in table 6. (Stora Enso Oyj., 2013a.)

Table 6. Safety and danger phrases for green liquor. (Stora Enso Oyj., 2013.)

Substance	Danger classes	Explanation for danger class	Danger Phrase	Explanation for risk phrase	Safety phrase	Explanation for safe phrase
Green liquor	1B	corrosive to skin	H314	highly corrosive to skin and eyes	P260	Don't breathe dust, smoke gas, fog ,steam or spray
	kat. 1	dangerous to water environment	H290	corrosive to some metals	P264	Wash hands carefully after treatment
			EUH032	toxic gas is developed when in contact with acids	P270	Eating, drinking and smoking is forbidden when handling the chemical
			EUH071	hazardous to respiratory	P273	Avoid releasing the chemical into environment
					P280	Based on danger evaluation of a task, use protective gloves, clothes, glasses

7.2 Process description

Green liquor system consists of smelt chute, dissolving tank, fume scrubber, green liquor pumps, pipelines and weak white liquor pipe lines. The smelt from the recovery boiler furnace is poured into dissolving tank. The tank is filled with weak white liquor from the causticization plant. The chemical substances in the smelt are dissolved into weak white liquor and together they form a mixture which is an aqueous solution of sodium sulphide and sodium bicarbonate. The process is simply described in figure 4. From the dissolving tank green liquor is pumped into the causticization plant via pipe line. (Stora Enso Oyj., 2009.) In the causticization green liquor goes first to stabilization tanks of which aim is to stabilize the concentration, temperature or flowing differences. From the stabilization tanks green liquor is pumped into clarifiers to separate sediment from the green liquor. After clarification green liquor goes through the causticization process and after that it’s transformed into white liquor. (Stora Enso Oyj., 2003.)

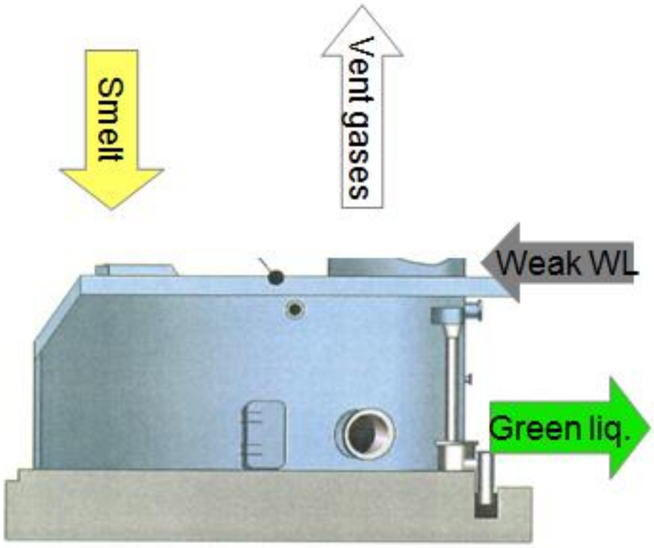

Figure 4. Dissolving tank after recovery boiler. (Vakkilainen 2007c.)

7.3 Risks identified for processing green liquor

Breakage of pipe fitting of clarifier or stabilization tank has been identified as risks concerning green liquor in the causticization process. Also the breakage of truck loading equipment is possible. (Stora Enso Oyj., 2006f.) In recovery boilers breakage of green liquor pipe line or breakage of dissolving tank, flange leak of pipe line or over flow of dissolving tank is possible (Stora Enso Oyj., 2006e).

In all these cases green liquor can leak to safety basin, process sewers, cooling water sewers or rain water sewers. It may cause a danger to process personnel and it can be released to environment. (Stora Enso Oyj., 2006e,f.)

7.4 Technical means of rigorous containment and minimization technologies

The green liquor process is closed and in normal operation the liquor stays inside the process equipment. The green liquor tanks are located in safety basin. The drain valves of the basins are held closed. In case of spills to basin, it's emptied to leak liquor swell by vacuum truck.

In causticization plant spills are collected to leak liquor swell and they're pumped to green liquor equalization tank. The swell is equipped with conductivity measurement. The fumes are washed with fume scrubbers. There're level measurements in green liquor tanks. In pipe lines there are flow measurements so that the leaks can be observed in control room. The information about green liquor tanks is presented in table 7. (Stora Enso Oyj., 2011)

In recovery boilers the smelt chutes are monitored with cameras. There're safety lock system which will bring the boiler process to safe state in case of large failure even if the boiler plant is without electricity. This will happen though the automated control system crash. During normal operation a significant amount of green liquor waste isn't created. Instead, green liquor dregs, which are filtered out of the chemical cycle, is the largest landfilled waste fraction in the mill (Stora Enso Oyj., 2009)

Table 7. The green liquor storage. (Stora Enso Oyj. 2004.)

Tank name	Location	Content	Volume [m^3]	Leak control
Tiheyden tasaussäiliö	KS3	Green liquor	500 m3	Tanks are in combined safety pool, 1500 m3
Selkeytin 1+2	KS3	Green liquor	2·5400 m3	

8 WHITE LIQUOR

In this chapter the risk management measures for white liquor are presented. In Imatra mills white liquor is registered as transported isolated intermediate.

8.1 Physical and chemical properties

White liquor is an intermediate to chemical synthesis. It's used for pulp production. The substance is used in closed continuous process where random exposure is occurred. The substance is an alkaline aqueous solution of the inorganic cooking chemicals in sulphate pulp production. (Stora Enso Oyj., 2011f)

White liquor consists of sodium salts from green liquor and calcium oxide. Sulphur compound's sulphide and thiosulphate content varies depending on the sulphide concentration of the plant and process' sulphide oxidation. In normal temperature and pressure white liquor is yellowish liquid. It smells like sulphurous substances. Its boiling point is 106,3 °C. White liquor isn't flammable or explosive. Composition of white liquor is presented in table 8. (Stora Enso Oyj., 2011f)

Table 8. Composition of white liquor.

White liquor	Method		Concentration
pH			>12
sodium Na	SCAN-N 38:10 modif	[g/l]	92
potassium K	SCAN-N 38:10 modif	[g/l]	12
sulphur S	SCAN-N 38:10 modif	[g/l]	28
Thiosulphate	KCL 70:83 modif	[g/l]	4,3
Effective alkali	SCAN-N 30:85	[g/l]	110
Active alkali	SCAN-N 30:85	[g/l]	140
Total alkali	SCAN-N 30:85	[g/l]	160
Sodium sulphide Na_2S	calculated	[g/l]	50,3
Sodium carbonate Na_2CO_3	calculated	[g/l]	23
Sodium hydroxide NaOH	calculated	[g/l]	79,8
Sodium thiosulphate $Na_2S_2O_3$	calculated	[g/l]	5,6
Potassium hydroxide KOH	calculated	[g/l]	8,7
Potassium carbonate K_2CO_3	calculated	[g/l]	2,3
Potassium sulphide K_2S	calculated	[g/l]	5,5
Potassium thiosulphate $K_2S_2O_3$	calculated	[g/l]	0,5

White liquor is classified as highly corrosive to skin and respiratory and also damaging to eyes. It isn't mutagenic. Immediately toxic and highly flammable hydrogen sulphide is developed when white liquor is in touch with acids. It isn't classified damaging to water systems although it might increase the pH-level of water. Pure substance isn't highly flammable or explosive. It's corrosive to materials like aluminum, magnesium, lead, zinc, tin and plastics. White liquor is acutely toxic to aquatic organisms. During normal use significant amounts of waste isn't created. If waste is created it'll be disposed as hazardous waste. The safety and danger phrases are presented in table 9. (Stora Enso Oyj., 2011f)

Table 9. Safety and danger phrases concerning white liquor.

Substance	Danger classes	Explanation for danger class	Danger Phrase	Explanation for risk phrase	Safety phrase	Explanation for safe phrase
White liquor	1B	corrosive to skin	H314	highly corrosive to skin and harful to eyes	P260	Don't breathe dust, smoke gas, fog ,steam or spray
	kat. 1	dangerous to water environment	H290	corrosive to some metals	P264	Wash hands carefully after treatment
			EUH032	toxic gas is developed when being in touch with acids	P270	Eating, drinking and smoking is forbidden when handling the chemical
			EUH071	harmful to respiratory	P273	Avoid releasing the chemical into environment
					P280	Based on danger evaluation of a task, use protective gloves, clothes, glasses and mask

8.2 Process description

Cooking white liquor is produced from green liquor by adding slaked lime (CaO) which produces sodium hydroxide and calcium carbonate ($CaCO_3$) called lime mud. Green liquor is fed to lime slaker where the causticization process begin. Dregs are filtered out of green liquor in the slaker. After that process continues in causticization tanks. Lime mud is then fed into lime kiln to produce slaked lime. The main reactions in causticization plant go as follows.

$$CaO + H_2O \quad \rightarrow \quad Ca(OH)_2$$

$$Na_2CO_3 + Ca(OH)_2 \rightarrow \quad 2NaOH + CaCO_3$$

The final product from causticization system is white liquor of which main components are sodium sulphide formed in recovery boiler and sodium hydroxide. White liquor comes out of causticization tanks to white liquor filters where lime mud is separated from white liquor. After filtration white liquor is stored in tanks and then it’s pumped back to kraft pulping. In kraft pulping white liquor is again transformed into black liquor. The process is simply presented in figure 5.

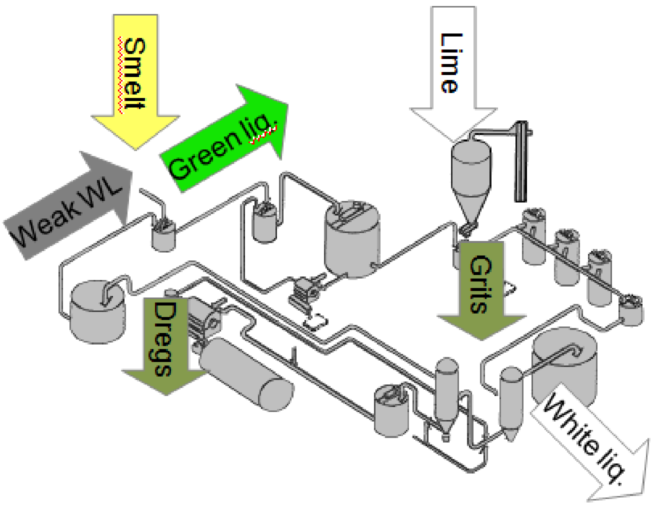

Figure 5. Causticization process. (Vakkilainen, 2007b.)

8.3 Risks identified concerning white liquor

In causticization plant the breakage of pipe fitting, tank or pipe line is possible. In case of large spills it's possible that white liquor gets to mill site and clean water sewers. Also the breakage of pumps or truck loading equipment can cause a leak to environment. They might also cause danger to process personnel. (Stora Enso Oyj., 2011f.) In fiber lines, there have been identified breakage of process equipment and also small spills from the functioning process are possible (Stora Enso Oyj., 2006h).

8.4 Technical means of rigorous containment and minimization technologies

The process is closed and in normal operation white liquor stays inside the process equipment. The white liquor tanks are located in safety basins of which drains lead to process sewer. Tanks are equipped with level measurement and there are flow measurements in pipelines. The liquor spills of causticization plant are collected to leak liquor swell from which they're pumped to green liquor equalization tank. The swell is equipped with conductivity measurement of which upper limit alarm starts the leak liquor pump. The clean over flow of swell is pumped to waste water treatment plant. At the beginning the leaks are probably small and they can be detected before any harm occurs. There're security cameras filming the causticization plant. (Stora Enso Oyj., 2006f.) Equipment in fiber lines are equipped with technical safety lock system, which take the process to safe state without electricity. Information about white liquor storage is provided in table 10.

Table 10. White liquor storage. (Stora Enso Oyj. 2004.)

Substance	Location	Tank name	Tank volume [m^3]	Spill control
White liquor	Tasa	White liquor tank	2200	Safety pool 20 %. Liquor leaked into pool is recovered with suction truck
	KS3	White liquor tank 1	6200	In combined safety pool of which sewer leads to waste water treatment
	KS3	White liquor tank 2	6200	

9 SODIUM BISULFITE

In this chapter the risk management measures for sodium bisulphite are presented. In Imatra mills sodium bisulphite is registered as transported isolated intermediate.

9.1 Properties

Sodium bisulphite is also called sodium hydrogen sulphite. Its chemical formula is $NaHSO_3$. Its concentration in water solution is 8 – 22 %. In normal temperature and pressure sodium bisulphite is pale yellow water solution. It's not highly flammable or explosive. Sodium bisulphite is a reducing agent. The chemical composition of the substance is presented in table 11. (Stora Enso Oyj., 2011g.)

Table 11. Chemical composition of sodium bisulphite.

Sodium bisulphite	Method		Concentration
pH	SFS 3021:79		6,5
Na:s ratio	EDXA	[mol/mol]	1.60:1
$NaHSO_3$	titrimetric method	[g/l]	n.d
Na_2SO_3	SCAN-N 4:78 modif	[g/l]	15
Na_2SO_4	SCAN-N 6:85 modif	[g/l]	0,02
SO_2			
$NaHCO_3$	wet digestion + ICP measurement	[mg/l]	<0,4
Na_2CO_3	wet digestion + ICP measurement	[mg/l]	<1
Chloride Cl^-	wet digestion + ICP measurement	[mg/l]	<1,6
Other impurities**	wet digestion + ICP measurement	[mg/l]	<1,6

**) Hg, Cd, Cr, Pb, As, Sb, Se, Ba, Al, Ca, Cu, Fe, Mg, Mn, Si, Co, Ni, P, Ti, V and Zn

Sodium bisulphite solution of concentration 8 – 22 % isn't classified immediately toxic in accordance with CLP-regulation. If swallowed, the sodium bisulphite solution of higher concentration is immediately toxic. The solution isn't considered irritating to skin, respiratory or eyes. Neither is it carcinogenic, mutagenic or harmful to human reproduction. In acidic conditions and in fire, toxic sulphur dioxide might be formed. Sodium bisulphite isn't bio accumulative because it dissociates easily in water solution. It's not bio degradable because it's inorganic. It's hazardous to aquatic organisms only in large concentration. (Stora Enso Oyj., 2011g.)

9.2 Process description

In Imatra mills sodium bisulphite is used mainly to produce sodium sulphite. Though, small amount of substance is used in the fume scrubber of fiber lines. (Mustonen, 2013.) Sodium bisulphite is manufactured from exhaust gases of odorous gas boilers. The process takes place in the scrubbers of the boilers. In the scrubbers sulphur dioxide (SO_2) molecules are absorbed with sodium hydroxide's (NAOH) water solution. The reaction produces sodium bisulphite water solution. Bisulphite water solution is pumped to sodium bisulphite storage container. The process is controlled by pH and density measurements in the pipe line between scrubbers and storage tank. If the measurement values don't satisfy the control system sodium bisulphite will be pumped to weak white liquor tank. From the bisulphite tank it goes to tube mixer, where bisulphite mixes with sodium hydroxide and transforms into sodium sulphite. (Stora Enso Oyj., 2002a.)

9.3 Risks identified concerning sodium bisulphite

Sodium bisulphite is manufactured in the scrubbers of odorous gas boilers. The next risks have been identified in there.

- Breakage of pipe lines or tank
- Breakage of scrubber
- Breakage of tube mixer

In case of these malfunctions Sodium bisulphite may cause danger to personnel and it can be released into environment. Toxic gases are processed in the odorous gas boilers so in case of malfunctions gas releases may also be possible. (Stora Enso Oyj., 1996)

9.4 Technical means of rigorous containment and minimization technologies

The system is closed and substance stays inside the process in normal operation. There're continuous pH and density measurements in the pipeline from scrubbers to storage tank. If the chemical isn't within the preset limits, it's pumped to weak white liquor tank and thus returned to pulping chemical circulation. There're level measurements in scrubbers of odorous gas boilers and in sodium bisulphite storage tank.

(Stora Enso Oyj., 2002a.) The sodium bisulphite tanks are in safety basins. The spills to process premises go to process sewers. The process sewers inside the odorous gas boiler process premises lead to waste water treatment plant. These sewers are equipped with conductivity measurements. If there occur large spills to sewers, conductivity will get high and the spills will be recovered back to process. All measurements include alarms in control room so the malfunctions will be immediately detected. It's unlikely that the substance is released to environment. (Stora Enso Oyj., 2011j.)

The odorous gas boilers are equipped with safety system, which will automatically take the process to safe state if malfunctions occur in the boilers. The safety system will stop the process, protect the process equipment and ventilate the process system. (Stora Enso Oyj., 1996.)

10 SODIUM SULPHITE

In this chapter the risk management measures for sodium sulphite are presented. Sodium sulphite isn't transported from Imatra mills.

10.1 Properties of sodium sulphite

Sodium sulphite's chemical formula is Na_2SO_3. It's soluble in water and its concentration varies between 6 and 22 %. The water solution also consists 2- 5 % of sodium hydroxide for the pH-control. Sodium sulphite isn't classified dangerous to environment. Sodium hydroxide, which is included in the mixture, has an effect on water's pH level. Sulphite substances are highly oxidant so it's unlikely that they accrue to the sediment. The substance isn't bio accumulative or bio degradable. It's inorganic so it isn't highly flammable or explosive. In acidic conditions toxic sulfur oxide might be formed. When the mixture reacts with some metals, like aluminum, zinc or other light metals, explosive hydrogen gas might be formed. Touching to acids and oxidants must be avoided. In high temperatures toxic gases, steams and smokes are formed. Chemical composition of sodium sulphite is presented in table 12. (Stora Enso Oyj., 2011h.)

Table 12. Chemical composition of sodium sulphite.

Sodium sulphite	**Method**		**Concentration**
Na_2SO_3	titrimetric method	[g/l]	160
$NaHSO_3$	titrimetric method	[g/l]	n.d
$Na_2S_2O_3$	titrimetric method	[g/l]	n.d
Na_2SO_4	SCAN-N 4:78 modif	[g/l]	15
Cl^-	SCAN-N 6:85 modif	[g/l]	0,02
pH	SFS 3021:79		11,4
Cr	wet digestion + ICP measurement	[mg/l]	<0,4
As	wet digestion + ICP measurement	[mg/l]	<1
Se	wet digestion + ICP measurement	[mg/l]	<1,6
Sb	wet digestion + ICP measurement	[mg/l]	<1,6
Ba	wet digestion + ICP measurement	[mg/l]	<0,4
Al	wet digestion + ICP measurement	[mg/l]	<2
Ca	wet digestion + ICP measurement	[mg/l]	3,7
Cu	wet digestion + ICP measurement	[mg/l]	<0,4
Fe	wet digestion + ICP measurement	[mg/l]	<2
Mg	wet digestion + ICP measurement	[mg/l]	1,3
Mn	wet digestion + ICP measurement	[mg/l]	<0,2
Si	wet digestion + ICP measurement	[mg/l]	<5
Co	wet digestion + ICP measurement	[mg/l]	<0,4
Ni	wet digestion + ICP measurement	[mg/l]	<0,4
P	wet digestion + ICP measurement	[mg/l]	<4
Ti	wet digestion + ICP measurement	[mg/l]	<0,4
V	wet digestion + ICP measurement	[mg/l]	<0,4
Zn	wet digestion + ICP measurement	[mg/l]	<0,4

Sodium sulphite isn’t classified as dangerous to health. The hazardous substance in the mixture is sodium hydroxide. The mixture is classified corrosive to skin and damaging to eyes because it consist sodium hydroxide. Sodium sulphite has no carcinogenic properties or effects to human reproduction and it isn’t mutagenic or harmful to respiratory. The risk and safety phrases are presented in table 13. (Stora Enso Oyj., 2011h.)

Table 13. Risk and safety phrases to sodium sulphite.

Substance	Risk Phrase	Explanation for risk phrase	Safety phrase	Explanation for safe phrase
Sodium sulphide	H314	corrosive to skin	P260	Don't breath dust, smoke, gas, fog, steam or spray
			P264	Wash hands after handling the substance
			P280	Use protective gloves, clothes, gogles, mask

10.2 Process description

Sodium sulphite is manufactured of sodium bisulphite solution by adding sodium hydroxide's water solution to sodium bisulphite solution. The manufacture of sulphite solution takes place in the odorous gas boilers inside a tube mixer in the pipe line between the bisulphite tank and sulphite tank. The manufacturing process is controlled by pH and density measurements in the pipe line. From sodium sulphite container it's pumped to storage container in VKA and so on to chemi-thermo-mechanical pulping (CTMP). Sodium sulphite solution is used as impregnation solution in CTMP-plant. (Stora Enso Oyj., 2002a.)

10.3 Risks identified concerning sodium sulphite

In odorous gas boilers, where sodium sulphite is manufactured, next risks have been identified.

- Breakage of pipe lines or tank
- Breakage of scrubber
- Breakage of tube mixer

The next risks and malfunctions have been identified in VKA, where sodium sulphite is stored, and CTMP-plant, where it's used.

- Breakage of process equipment
- Flange leak
- Breakage of pipelines or storage tanks

In case of these malfunctions Sodium sulphite may cause danger to personnel and it can be released to ground, rain water sewers and to lake nearby. (Stora Enso Oyj.,2006h.) Very toxic gases are processed in the odorous gas boilers so in case of malfunctions gas releases may also be possible (Stora Enso Oyj., 1996).

10.4 Technical means of rigorous containment and minimization technologies

The process is closed and sodium sulphite stays inside the process equipment in normal operation. The adding of sodium bisulphite is controlled by mass flow measurement. The pipe lines are also equipped with flow measurements, pH measurements and density measurements. The containers are equipped with level measurements. The manufacture of sodium sulphite is automatically discontinued when the level of storage container in VKA gets too high. (Stora Enso Oyj., 2002b.)

The sodium sulphite tanks are in safety basins. The spills to process premises go to process sewers which lead to waste water treatment plant. These sewers are equipped with conductivity measurements. If there occur large spills to sewers, conductivity will get high and the spills are recovered back to process. All measurements include alarms in control room so the malfunctions will be immediately detected. It’s unlikely that the substance is released to environment. (Stora Enso Oyj., 2011j.)

The odorous gas boilers are equipped with safety system, which will automatically take the process to safe state if malfunctions occur in the boilers. The safety system will stop the process, protect the process equipment and ventilate the process system. (Stora Enso Oyj., 1996.)

11 PROCEDURAL AND CONTROL TECHNOLOGIES IN RECOVERY PLANT AREA

In this chapter the procedural and control technologies concerning all five intermediate substances are presented.

11.1 Organization and process monitoring

In liquor recovery plant the evaporation and recovery boiler process is monitored in one control room. A typical amount of process personnel is 4 – 5 persons. There're two control room operators. One of them operates recovery boiler 5 and causticization, the other one operates recovery boiler 6 and evaporation plants. Moreover there's one site operator in recovery boilers and other in causticization and evaporation plants. Usually there's also one spare man in the shift. Every shift has its own supervisor and moreover there's one operation supervisor for recovery boilers and one for causticization and evaporation plant. The whole plant is supervised by power plant manager.

The process is operated using Metso DNA automation system (Stora Enso Oyj., 2007b). Regular inspection tours are made in the plant. The process premises are equipped with monitoring cameras. This way the possible spills to environment and process premises or malfunctions of process equipment can be detected quickly. The control room is continuously occupied and the working happens in three shifts. (Stora Enso Oyj., 2006e.)

11.2 Inspections

All pressure vessels are subject to periodic inspections with proper documentation. Pipe lines are in accordance with SFS standards. A document is made of every storage tank. The process equipment is maintained regularly. During maintenance work condition monitoring of vessels, pipelines and containers is done by personnel. The measurement sensors are calibrated as required. Possible malfunctions of sensors can be detected in control rooms. (Stora Enso Oyj., 2006g.)

A comprehensive safety and rescue plan have been made in recovery plant and it's kept up to date (Mustonen, 2013).

The comprehensive safety report consists of

- emergency routines for process units
- quick stop instructions for process units
- identified hazards concerning evaporation and recovery boilers
- documents of personal protective equipment and lifesaving aid
- lists of process chemicals
- risk and danger assessment for the use of black liquor
- fire protection instruction
- lists of safety places in the mill area
  (Stora Enso Oyj., 2006k.)

In the risk and danger assessment of this comprehensive report personal safety, environmental effects and economic effects have been taken account of. Probabilities of hazardous situations and seriousness of situation have also been assessed. (Stora Enso Oyj., 2006e,g.)

Several other assessments have been made in recovery plant and they are kept up to date regularly.

- a task-specific risk assessment
- a risk and danger assessment for pressure vessels
- risk assessment for personal safety (Mustonen, 2013.)
- environmental risk and hazard assessment, where probabilities of malfunctions, amount of residues and their effect on environment have been assessed (Stora Enso Oyj., 2012b).

12 MANAGEMENT MEANS AND TRAINING OF PERSONNEL

Imatra mills have next certified management systems

- AEO company safety system
- ISO 9001 Quality system
- ISO 14001 Environmental system
- ISO 22000 Product safety system since
- CoC (Chain of Custody) PEFC CoC system and FSC CoC and FSC CW (Controlled Wood) systems
- OHSAS 18001 Occupational health and safety system (Klemetti, 2013)

The process control manuals are well documented in line with above mentioned standards. There are also more detailed user manuals for process equipment in control room. The safety reports, instructions and safety data sheets concerning black liquor are available in Imatra mill's intranet and in the common hard disc of mill's computer system. The operating staff is orientated through the special training programme before they can take responsibility of their duty. The shift supervisor decides when the employee can take responsibility of the duty. In addition to professional training, occupational safety cards and first fire extinguishing cards are required.

12.1 Safety audits

Regular safety audits are made quarterly by mill's executive team. There are also small-group safety audits in recovery plant. They are made by group which includes process personnel, shift supervisor, operations supervisor and power plant manager. (Mustonen, 2013.)

12.2 Routines for personnel from external companies

There're strict procedures for external companies in the mill area. Every subcontractor working in the mill site must complete mill's safety info and a unit-specific safety info which is kept by unit operation supervisor. A registry of every safety info participants is kept up to date. In the info the subcontractors are provided information about risks concerning tasks, contact information of operation supervisors and control rooms and safety assembly areas. Special safety info is given in case of large maintenance shutdowns. Contents of the special info is mainly same as in the normal info but in addition there's provided information about definite storage areas and traffic and parking restrictions. In recovery plant the employees of external companies must not go to process premises without informed that to control room. (Mustonen, 2013.)

12.3 Special procedures applied before cleaning and maintenance

There're special procedures for cleaning and maintenance work. There are container work instructions for the maintenance work inside the containers. Instructions have been made for each tank separately. In the instructions there is information how personnel ensures that system is in zero energy state before any cleaning and maintenance can be done. Safety switches of electricity equipment are turned to zero and then the switches are locked. Valves are closed and locked or equipped with "Don't close" or "Don't open" signs. Measures of dangerous gases are performed in process premises. The equipment is cleaned before any maintenance work. Written permission from the operation supervisor is required before maintenance work can start. A special license for the work inside the containers is required. (Stora Enso Oyj., 2013b.)

12.4 Emergency routines and exits

There're procedures for process personnel in emergency situations. People in danger must be rescued first. In cases of fire the first extinguish and limiting the fire is done by the personnel. The hazardous situations are notified to mill's fire department. In case of gas accidents there are definite gas safety places in recovery plant's control room and in power plant's control room. Then air conditioning is switched off and the control rooms' doors and windows are tightly closed. In case of fire the assembly area is the parking lot of recovery plant. There're also emergency showers in evaporation plant and recovery boiler plant. Pulling the handle of shower causes an alarm in control rooms. Operation supervisor is responsible to test the showers once a week. All process premises in recovery plant are equipped with clearly marked emergency exit routes. (Stora Enso Oyj., 2006d.)

There's general danger alarm system in Imatra mills. It includes sirens, high-performance speakers on the roof of recovery boiler 6, emergency GSM-messages and PcAlarm- emergency messages to computers. It's possible to give voice messages and situation-specific instructions via sirens and speakers. The alarm equipment is tested regularly. (Stora Enso Oyj., 2013c.)

There's own fire department in Imatra mills. Fire department is trained regularly so that they are ready for red alert. Personnel in fire department have a special training concerning hazardous substances and chemical spills. Personnel of fire department are trained and instructed for recovery boiler explosion. In serious emergency situations special rescue service team is in command. (Stora Enso Oyj., 2012c.)

After accidents the spills to environment are limited as low as possible. The leaks blocked and spreading of extinguishing and cleaning water is limited to as small area as possible. It's possible to lead the leaks to waste water treatment plant and operation of plant is observed continuously. There're instructions of handling the hazardous substances like black liquor after accident. (Stora Enso, 2011i.)

12.5 Personal protective equipment

Personnel are ordered to use helmet, protective gloves and safety glasses when they move in the field. In case of accidents there are several compressed air breathing equipment and filter gas masks in recovery plant area. They're distributed in different places of recovery plant so that they are closer to personnel when accident happens. In addition there're helmets, flashlights, rescue ropes, firefighting suits, boots, first aid kits and stretchers in control rooms. A task-specific personal protective equipment list has been made in recovery plant. Mill's fire department is in charge of annual inspection of respirators. Respirators are inspected every third year. (Stora Enso Oyj., 2005b.)

12.6 Transportation of intermediates

White liquor, green liquor, black liquor and sodium bisulphite are registered as transported isolated intermediates. Sodium sulfite isn't transported from Imatra mills. A transport instruction card has been made all of transported intermediates. In the card there are instructions concerning

- classification for VAK transportation
- information about the chemical
- quality of risk
- personal protective equipment
- actions in case of accidents
- actions in case of any leaks
- first aid

The drivers must have a VAK license and a tanker-truck must be VAK classified.) The transportation classes for intermediates are in table 14.

Table 14. Transportation classes.

Chemical name	VAK transport class
Black liquor	8, Corrosive substances (formic acid, sulphuric acid, sodium hydroxide)
White liquor	8, Corrosive substances (formic acid, sulphuric acid, sodium hydroxide)
Green liquor	8, Corrosive substances (formic acid, sulphuric acid, sodium hydroxide)
Sodium bisulfite	8, Corrosive substances (formic acid, sulphuric acid, sodium hydroxide)

In the loading areas there are also protection and truck labeling instructions. There're also prescribed routes for chemical transportations in the mill area. The white liquor loading place is equipped with emergency shut-off valve. The floors of all loading places are inclined at process sewer which lead to waste water treatment plant. (Tietoa kandidaatin työhön, 2013.)

13 SUMMARY

This Bachelor thesis has been made for Stora Enso Imatra mills. In Imatra mills the liquor recovery plant recovers the cooking chemical for kraft pulping. The process is called liquor cycle. In this thesis separate risk management measures were provided for intermediate substances which are processed in liquor cycle. The substances are black liquor, green liquor, white liquor, sodium bisulphite and sodium sulphite. The risk management measures are part of the registration procedure to ECHA.

In the beginning of this thesis the essential authorities and regulations relevant to this thesis were also presented. REACH is the regulation which requires that companies register their chemical substances. The classification and labeling must be done in accordance with CLP regulation. Both these regulations are controlled by ECHA.

The risk management measures provide information which indicate that the all five intermediate substances are manufactured and used safely in strictly controlled conditions. In the recovery plant technical means of rigorous containment are used to keep the substances in the process and in cases of malfunctions there are minimization technologies to minimize the possible spills to environment. In addition procedural and control technologies, like risk assessments, ensure that the safety is continuously kept up to date and the process is also monitored continuously by trained personnel.

Imatra mills have certified management systems. There're strict procedures and instructions for external companies, maintenance work and emergency situations in the liquor recovery plant. The intermediate substances are transported in accordance with the regulation of VAK "Transport of dangerous goods". Also all five substances meet the condition of intermediate substance that they are manufactured to be transformed into another substance.

14 REFERENCES

Clariant, [Clariant WWW- sivuilla]. Päivitetty 2012. [Viitattu 15.4.2013] Saatavissa http://www.clariant.com/C12576720021BF8F/vwWebPagesByID/DC6BB862C275200FC12577990010C00D

European chemicals agency (ECHA), 2010. *Guidance on intermediates.* Helsinki: European Chemicals Agency.

European chemicals agency, ECHA, [ECHA WWW-sivuilla] [Viitattu 14.03.2013a] Saatavissa http://echa.europa.eu/web/guest/regulations/reach/understanding-reach

European chemicals agency, ECHA, [ECHA WWW-sivuilla] [Viitattu 14.03.2013b] Saatavissa http://echa.europa.eu/fi/regulations/reach/substance-registration/substances-to-be-registered

European chemicals agency, ECHA, [ECHA WWW-sivuilla] [Viitattu 14.03.2013c] Saatavissa http://echa.europa.eu/fi/regulations/reach/substance-registration/data-sharing

European chemicals agency, ECHA, [ECHA WWW-sivuilla] [Viitattu 14.03.2013c] Saatavissa http://echa.europa.eu/fi/regulations/reach/registration

European chemicals agency, ECHA, [ECHA WWW-sivuilla] [Viitattu 14.03.2013d] Saatavissa http://echa.europa.eu/fi/regulations/clp/understanding-clp

European chemicals agency, ECHA, [ECHA WWW-sivuilla] [Viitattu 14.03.2013e] Saatavissa http://echa.europa.eu/regulations/clp/classification

European chemicals agency, ECHA, [ECHA WWW-sivuilla] [Viitattu 14.03.2013f] Saatavissa http://echa.europa.eu/regulations/clp/labelling

European chemicals agency, ECHA, [ECHA WWW-sivuilla] [Viitattu 14.03.2013g] Saatavissa http://echa.europa.eu/regulations/clp/clps-effect-on-companies

European chemicals agency, ECHA, [ECHA WWW-sivuilla] [Viitattu 14.03.2013h] Saatavissa http://echa.europa.eu/fi/about-us/who-we-are/mission

Stora Enso Oyj., 1995. HO5 työturvallisuus. Imatra: Stora Enso.

Stora Enso Oyj., 1996. HK1 turvallisuustoimenpiteet.

Stora Enso Oyj., 2002a. Käyttöohje HK2, hajukaasujen pesu ja imeytysliuoksen valmistus. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2002b. Käyttöohje HK2, pesurin käynnistys ja imeytysliuoksen valmistus. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2003. Käyttöohje: KS3 viherlipeän käsittely. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2004. Prosessikemikaalienkäyttö. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2005a. Turvallisuusselvitys, Kemikaaliluettelo VO/HO. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2005b. Turvallisuussuunnitelma työsuojelu: voimalaitoksen suoja- ja pelastusvälineet. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2006a. Turvallisuussuunnitelma työpaikkasuojelu, Kuvaus voimalaitoksen toiminnasta ja riskikohteista. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2006b. Turvallisuusselvitys työpaikkasuojlu, kuvaus kuitulinja 3 toiminnasta. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2006c. Turvallisuusselvitys työsuojelu, kuvaus kuitulinja 2 toiminnasta. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2006d. Linjan/osaston toimenpideohjeet vaara tai onnettomuustilanteessa. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2006e. Turvallisuusselvitys: Vaaranarviointi ja riskikartoitus VO/SK5, SK6. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2006f. Turvallisuusselvitys: Vaaran arviointi ja riskikartoitus VO/kaustisointilaitos. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2006g. Turvallisuusselvitys: Vaaranarviointi ja riskikartoitus VO/HO6. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2006h. Turvallisuusselvitys, vaaranarviointi ja riskikartoitus, KL3. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2006i. Turvallisuus suunnitelma, työpaikkasuojelu, Kuitulinja 3 suojavälineet. Imatra: Stora Enso.

Stora Enso Oyj., 2006j. Turvallisuussuunnitelma, työpaikkasuojelu: Kuitulinja 2 suojavälineet. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2006k. VO turvallisuussuunnitelma, sisällysluettelo. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2007a. Turvallisuussuunnitelma, Suuri lipeävuoto lipeäsäiliön- tai putkiston rikkoutuessa. Imatra: Stora Enso.

Stora Enso Oyj., 2007b. HO5 valvonta. Imatra: Stora Enso.

Stora Enso Oyj. 2009. SK5 viherlipeäjärjestelmä. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2011a. Käyttöturvallisuustiedote: mustalipeä. Imatra: Stora Enso.

Stora Enso Oyj., 2011b. HO5 ympäristön suojelu, ilman maaperän ja vesien suojelu. Imatra: Stora Enso.

Stora Enso Oyj., 2011c. Käyttöohje, SK5 prosessiselostus. Imatra: Stora Enso oyj.

Stora Enso Oyj., 2011d. KS3 ympäristönsuojelu, ilman, maaperän ja vesien suojelu. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2011e. LI viemärit ja jätevesipumppaamo toimintakuvaus. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2011f. Käyttöturvallisuustiedote: valkolipeä. Imatra: Stora Enso.

Stora Enso Oyj., 2011g. Käyttöturvallisuustiedote: natriumbisulfiitti. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2011h. Käyttöturvallisuustiedote: natriumsulfiitti. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2011i. Onnettomuuden jälkien ja ympäristön puhdistus. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2011j. HK2 ympäristönsuojelu, ilman, maaperän ja vesien suojelu. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2012a. HO5 ja biolietteen käsittely, toimintakuvaus, johdanto ja prosessikuvaus. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2012b. Ympäristönäkökohtien arviointi, päästöt, raka-aineiden ja energian kulutus, HO5 ja 6, KS3, SK5 ja 6, HK1 ja 2 ja MÖ. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2012c. Palokunnan toimintaohje. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2013a. Käyttöturvallisuustiedote, Viherlipeä. Helsinki: Käyttöturvallisuustiedote: Viherlipeä.

Stora Enso Oyj., 2013b. Liiketoimintajärjestelmä, voimalaitos, lipeä, säiliötyöohjeet. Imatra: Stora Enso Oyj.

Stora Enso Oyj., 2013c. Yleisen vaaramerkin hälyttimet. Imatra: Stora Enso Oyj.

Hannu Mustonen. 2013. Päivämestari, lipeäkierto, Stora Enso Oyj. Imatra mills. Tapaaminen 12.3.2013 Imatra.

Hannu Mustonen, 2013.Tietoa kandidaatin työhön. Sähköpostiviesti tekijälle

4.3.2013.

Jouni Kumpulainen, 2013. Lipeäkierron välituotteiden rekisteröinti. Sähköpostiviesti tekijälle 22.3.2013.

Stora Enso, [Stora Enson WWW-sivuilla], päivitetty 2013. [Viitattu 21.3.2013] Saatavissa http://www.storaenso.com/about-us/mills/finland/imatra-mills/Pages/tervetuloa-imatran-tehtaille.aspx

Tukes. (12. 04 2010). *Reach ja Clp neuvontapalvelu*. Haettu 17. 02 2013 osoitteesta http://www.reachneuvonta.fi/REACH/reach.nsf/sp3?open&cid=content40D56F&leftnavi2nf=FI\Sis%C3%A4lt%C3%B6\CLP\content40B3A2\content40D56F&leftnavi2nfa=o&size=#6

Tukes, [Reach ja clp neuvontapalvelu WWW-sivuilla]. Päivitetty 25.05.2009. [Viitattu 14.3.2013] Saatavissa http://www.reachneuvonta.fi/REACH/reach.nsf/sp3?open&cid=ContentD2B5D&leftnavi2nf=FI\Sis%C3%A4lt%C3%B6\CLP\ContentD2B5D&leftnavi2nfa=o&size=

TUKES [TUKES WWW-sivuilla]. Päivitetty 12.11.2012. [Viitattu 14.3.2013] Saatavissa http://www.tukes.fi/en/

Vakkilainen, E., 2007a. Pulp mill energy and recovery process, Lecture 1: Introduction to chemical recovery. Helsinki.

Vakkilainen, E., 2007b. Pulp mill energy and recovery process, Lecture 10: White liquor preparation. Helsinki.

Vakkilainen, Esa, 2007c. Pulp mill energy and recovery process, Lecture 4: Recovery boiler. Helsinki.