LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
LUT School of Energy Systems
LUT Mechanical Engineering

Ville Ahokas

Systematic approach to cell room piping material selection in chlor-alkali process

Examiners: Docent Harri Eskelinen
Professor Juha Varis
M.Sc. Janne Tynninen

TIIVISTELMÄ

Lappeenrannan teknillinen yliopisto
LUT School of Energy Systems
LUT Kone

Ville Ahokas

Systemaattisen lähestymistavan soveltaminen kennosalin putkiston materiaalinvalintaan kloori-alkali prosessissa

Diplomityö

2017

136 sivua, 39 kuvaa, 21 taulukkoa ja 7 liitettä

Tarkastajat: Dosentti Harri Eskelinen
Professori Juha Varis
DI Janne Tynninen

Hakusanat: materiaalinvalinta, kloori-alkali, putkistot, FMEA, LCC, LCA, Eko-idikaattorit, korroosio

Joutsenon kloori-alkalitehtaan kennosalin tuottamat väli- ja lopputuotteet aiheuttavat putkistoille korroosioympäristön. Kennosalin putkistoissa esiintyy korroosiovaurioita, jotka toistuvat tietyllä tiheydellä putkiuusinnoista. Näiden putkistojen vauriomekanismeja ja -tiheyttä eivät ole määritelty tarkasti. Joutsenon kloori-alkalitehtaalla ei ole tällä hetkellä käytössä putkistomateriaalin valintastrategiaa.

Tämän diplomityön tavoittena on selvittää miksi nykyiset putkistomateriaalit eivät kestä kennosalin putkistoissa vaikuttavia olosuhteita; löytyykö markkinoilta kloori-alkaliteollisuudessa entuudestaan käyttämättömiä putkistomateriaaleja, joita voidaan käyttää kennosalin putkistoissa sekä luoda prosessi putkistomateriaalien optimaaliseen valintaan. Putkistomateriaalin valintastrategialla pyritään minimoimaan elinkaarikustannukset, parantamaan prosessiturvallisuutta ja minimoimaan ympäristölle aiheutuvat vahingot putkimateriaalin valmistuksen ja käytön aikana.

Työ suoritettiin pääosin kirjallisuustutkimuksena käyttäen hyödyksi tieteellistä lähdemateriaalia ja Joutsenon tehtaan SAP PM tietokantaa. Tulosten oikeellisuus pyrittiin varmistamaan käyttämällä triangulaatiota. Tuloksiksi saatiin putkistomateriaalin valintastrategia, optimaaliset materiaalit kaikille väliaineille ja löydettiin useita laajalti käyttämättömiä putkistomateriaaleja. Optimaalisen putkistomateriaalin valinta on aina tapauskohtainen prosessi, jossa on noudatettava kemikaaliputkistoja koskevaa kohdemaan lainsäädäntöä. Löydettiin myös useita tutkimuksen aihepiiriin liittyviä jatkotutkimusaiheita.

ABSTRACT

Lappeenranta University of Technology
LUT School of Energy Systems
LUT Mechanical Engineering

Ville Ahokas

Systematic approach to cell room piping material selection in chlor-alkali process

Master's thesis

2017

136 pages, 39 figures, 21 tables and 7 appendices

Examiners: Docent Harri Eskelinen
Professor Juha Varis
M.Sc. Janne Tynninen

Keywords: material selection, chlor-alkali, piping, FMEA, LCC, LCA, Eco-indicators, corrosion

The intermediate and end-products of Joutseno chlor-alkali plant's cell room subject the pipelines to a corrosive environment. There are distinguishable corrosion failures that repeat at a certain frequency from pipeline renewal. The failure mechanisms and failure rates of these pipelines have not been determined in detail. There is a lack of a systematic pipeline material selection strategy at Joutseno plant.

The aim of this Master's thesis is to examine why the pipeline materials currently in use do not withstand the corrosion atmosphere in the cell room, to find previously unused piping materials that are not in widespread use in chlor-alkali process industry that could be used for cell room process piping and to create a systematic approach to piping material selection for Joutseno chlor-alkali plant's cell room. The material selection strategy aims to find the optimal pipeline materials for different chemical mediums with lowest possible lifecycle costs, taking into consideration also the health and safety hazards and to minimize the damage caused to the environment by pipeline material production and use.

The work was mainly conducted as a literary review using scientific articles and Joutseno plant's SAP PM Database. The validity of results was improved by using triangulation method. The following results were gathered: a systematic approach to piping material selection was developed, the optimal materials for all cell room media were selected and previously unused pipeline materials were found. Material selection for chemical pipelines is always a case-by-case process where the legislation concerning the country in question applies. Multiple subjects linked to the subject of the thesis that need further research were found.

FOREWORDS

The workload needed to finish this Master’s thesis exceeded my expectations significantly. Therefore, I have to thank all of the people involved in the success of finishing my work. I’d like to thank Kemira Chemicals Oy for giving me the opportunity to work on this thesis. Especially I want to give my deepest thanks to Janne Tynninen, Christian Lindgren and all the people from Joutseno site that made this thesis possible. Other special regards go to my examiner Harri Eskelinen for taking his time for holding meetings with me on a regular basis and in giving invaluable insights on material selection strategies. I’d like to thank my whole family for giving me the free time needed for accomplishing this task. I’d also like to thank the material and process experts I have interviewed regarding this thesis. To name a few in question; Juha Hujanen, Mikko Esko and Risto Salakka.

Ville Ahokas
Ville Ahokas
Punkaharju 31.8.2017

APPENDICES

LIST OF SYMBOLS AND ABBREVIATIONS

AC	material procurement cost
E°	the standard electrode potential
E_a	activation potential
E_b	critical pitting potential
E_{cor}	corrosion potential
E_s	open circuit potential
F	Faraday constant
i	interest rate
IC	manufacturing and installation costs
LCC	lifecycle costs
LP	shutdown losses
MI	Material Input
$MIPS$	Material Input Per Service unit
N	designed lifecycle of piping
n	years of usage
OC	usage and maintenance costs
Pt	Eco-indicator point
RC	recycling costs including possible refunds
S	Service unit
S_d	detectability factor
S_t	occurrence factor
$wRPN$	weighted risk priority number
X	numerical value of material attribute
Z	standardized value

z	number of electrons in a reaction
ζ	polarization
μ	mean value
σ	standard deviation
ΔG	the standard free energy of reaction
Δt	temperature gradient

AKD	AlkylKetene Dimer
AR-glass	Alkali Resistant glass
B_2O_3	Boron Trioxide
C-glass	Chemical resistant glass
CC	Cover-Coat
CED	Cumulative Energy Demand
CP	Chemically pure
CPI	Chemical Process Industry
CPT	Critical Pitting Temperature
CPVC	Chlorinated Polyvinyl Chloride
DC	Direct Current
D-glass	glass with Dielectric properties
DN	Nominal pipe size, Diametre Nominal
EAC	Environmentally Assisted Cracking
ECM	Ecodesign Checklist Method
ECR-glass	Electrical/Chemical resistant glass
ECTFE	Ethylene ChloroTriFluoroEthylene
EI95	Eco-Indicator 95
EI99	Eco-Indicator 99

EN	Electroless Nickel
ESC	Environmental Stress Cracking
FEP	Fluorinated Ethylene Propylene
FMEA	Failure Modes and Effects Analysis
FRP	Fibre Reinforced Plastic
GC	Ground-Coat
HAZOP	Hazard and Operability study
HCl	Hydrochloric Acid
HCR	Hardness Rockwell C
HOCl	Hypochlorous Acid
IPPD	Integrated Product and Process Development
KCl	Potassium Chloride
KGL	Kodak-Guidelines
LCA	LifeCycle Analysis
LCC	LifeCycle Cost
MADM	Multiple-Attribute Decision-Making
MIPS	Material Input per Service unit
NaCl	Sodium Chloride, table salt
NaClO	Sodium Hypochlorite
Na_2O	Sodium Oxide
NaOH	Sodium Hydroxide, caustic soda
NDT	Non-Destructive Testing
OCP	Open Circuit Potential
PFA	PerFluoroalkoxy Alkane
PN	Pressure Nominal
PP	PolyPropylene

PV	Present Value method
PVC	Polyvinyl Chloride
PREN	Pitting Resistance Equivalent Number
PTFE	PolyTetraFluoroEthylene
PVDF	PolyVinyliDene Fluoride
RFID	Radio Frequency Identification
R-glass	Reinforcement glass
RPN	Risk Priority Number
SCC	Stress Corrosion Cracking
S-glass	high Strength glass
SHE	Standard Hydrogen Electrode
SiO_2	Silicon Dioxide
SSC	Sulfide Stress Cracking
TF-E	TetraFluoroEthylene
TiO	Titanium Monoxide
TiO_2	Titanium Dioxide
Ti_2O_3	Titanium(III) Oxide
UV	UltraViolet
VE	Vinyl Ester
wRPN	weighted Risk Priority Number

1 INTRODUCTION

Kemira Chemicals Oy Joutseno site produces chemicals for the pulp and paper industry and is a part of global chemistry company Kemira Oyj. Joutseno site produces sodium chlorate, sodium hydroxide, sodium hypochlorite, hydrochloric acid, alkylketene dimer (AKD), hydrogen and green power. Joutseno site consists of a sodium chlorate plant, chlor-alkali plant and a hydrogen power plant which are depicted in figure 1.

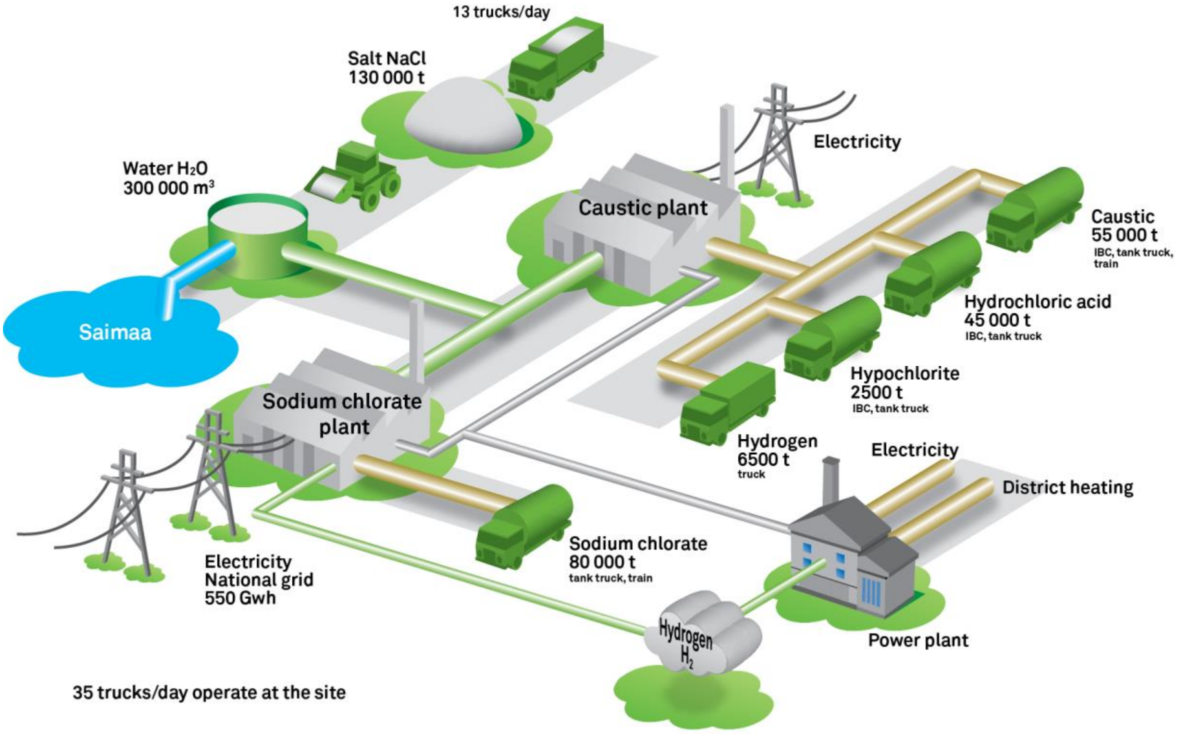


Figure 1. Process diagram of Joutseno site’s materials and end-products (Kemira Chemicals Oy, 2013).

This thesis work focuses on the chlor-alkali plant which produces sodium hydroxide (caustic soda), hydrochloric acid, hydrogen and sodium hypochlorite from table salt (NaCl). These chemicals are produced with an electrolysis process. Due to the various corrosion factors caused by different chemicals and the use of electricity in the process, corrosion control plays a key role in the maintenance of the factories. Corrosion can be seen as damage caused by the environment which the structure can’t sustain while still performing its function.

There are different kinds of chemical, electro-chemical and mechanical corrosion mechanisms that will be discussed.

To combat the negative effects of corrosion it is essential to choose the optimal materials for piping. There are several factors why this is important. The chemicals contained in the piping may be hazardous to human health and the process is very sensitive to pressure changes caused by leaking pipes. Also, unplanned downtime of plant due to pipeline leakage is one possible factor leading to production losses and decline in customer satisfaction.

Systematic material selection is one of the solutions to prevent or maintain corrosion at sustainable levels. Systematic material selection has a profound effect on pipeline lifecycle, process safety and lifecycle costs (LCC) because many of the total lifecycle costs can be eliminated or cut down at an early stage of the usage period.

1.1 Research problem

The main motivation for making this thesis is to find out why materials currently in use do not withstand the chemical and electrochemical stress factors caused by process chemicals, mainly wet chlorine and caustic soda. The Ethylene ChloroTriFluoroEthylene/Vinyl Esther-glass fiber reinforced (ECTFE/VE) piping used in chlorine header pipe lasts approximately five years before it needs to be replaced. The destruction mechanism is not clear and needs to be researched. Also, the wet chlorine piping sections made from titanium are susceptible to corrosion.

There is a lack of a systematic approach in choosing the construction materials for process piping at Joutseno plant. Most of the piping material selection is based on known best practice, but it isn’t always the most cost-effective way, taking into consideration the total lifecycle costs and different process variations in comparison to other chlor-alkali plants.

1.2 Goal

The goal of this study is to form a systematic material selection process that can be utilized in similar circumstances as this study, for example piping material selection for investment projects. Study also aims to find the optimal materials for different chemical media so that the risk of failure decreases to a level of 50 % from current situation if the total lifecycle costs are also at a minimum.

1.3 Research questions

The research questions are formulated from the findings of current problems and improvement possibilities and are stated as:

- Why current piping materials do not withstand the chemical, electro-chemical and mechanical stress factors?
- Can piping materials that are not in widespread use in chlor-alkali process industry that could be used in process piping with a plausible lifecycle for each medium at minimal lifecycle costs taking into consideration also the health and safety hazards be found?
- What are the main differences between a material selection strategy that fits the needs of chlor-alkali manufacturing process compared to universally applicable material selection strategies?

1.4 Research methods

The main research method used is triangulation. The triangulation method is based on a literary review, expert interviews and experimental failure mechanism analysis of damaged pipelines together with information from SAP PM maintenance database. This triangulation of information ensures the validity of results. The literary review is conducted mostly by an Internet database research but books and other publications are also used. Additional data about the failure timeframe and mechanisms is gathered from Joutseno SAP PM database. There are also parts of replaced process piping that are dismantled and visually examined for the failure mechanism analysis. Experts in the field of study are also interviewed for this thesis work.

1.5 Framework

This study focuses on the process piping of chlor-alkali plant's cell room, excluding the adjacent process piping like hydrochloric acid (HCl) and sodium hypochlorite (NaClO). Other auxiliary process lines like cooling water and condense piping are also excluded. Gasket materials and other process equipment (valves et cetera) are excluded from the scope of material selection. The chemistry of materials is taken into consideration but detailed process chemistry and corrosion protection through process parameter changes are excluded from this study. A detailed analysis of possible electrical or chemical corrosion protection systems will not be conducted. Material selection will not be extended to take into consideration the manufacturing process costs and techniques. Pipeline prices will be approximated as a “turnkey” delivery of piping flange-to-flange. Turnkey installation includes the manufacturing of pipes, piping material procurement, installation and declaration of conformity. The declaration of conformity ensures that pipelines are manufactured using the industry approved processes, pipelines are in accordance to laws and regulations, pipeline pressure tests are conducted, material composition is confirmed et cetera.

1.5.1 Viewpoint

Only the cell room main process pipelines are taken into consideration in this thesis. The work includes the following pipelines of the plant:

- Caustic soda: From the membrane cells to NaOH circulating tanks and back
- Hydrogen: From membrane cells to HCl burners
- Saturated brine: From saturated brine heater to membrane cells
- Depleted brine: From membrane cells to brine pH adjustment tank
- Chlorine: From membrane cells to chlorine cooler.

All other pipelines of the plant be excluded from the scope of this thesis.

1.6 Contribution of the thesis

Kemira Chemicals Oy Joutseno site will get a method of systematic construction material selection for chemical piping. Lifecycle costs will be taken into consideration and the lowest total lifecycle cost will be included in the ranking of the materials ensuring that there is a cost saving advantage compared to the current state of piping renewal. Safety will be considered and process safety will increase with optimal material selection. The environmental aspects of process pipeline materials will be considered in the LCA section of the thesis. This thesis also gives Joutseno site an informational package on corrosion and pipeline material selection.

2 RESEARCH METHODS

To understand the optimization of material selection process for chlor-alkali cell room piping, the chemical media contained in the piping systems must be examined. Joutseno chlor-alkali plant produces sodium hydroxide, hydrochloric acid and sodium hypochlorite from table salt, water and electricity. The chlor-alkali factory is divided into three sub processes, depicted in figure 2:

1. feed material processing
2. electrolysis
3. intermediate and end-product refining.

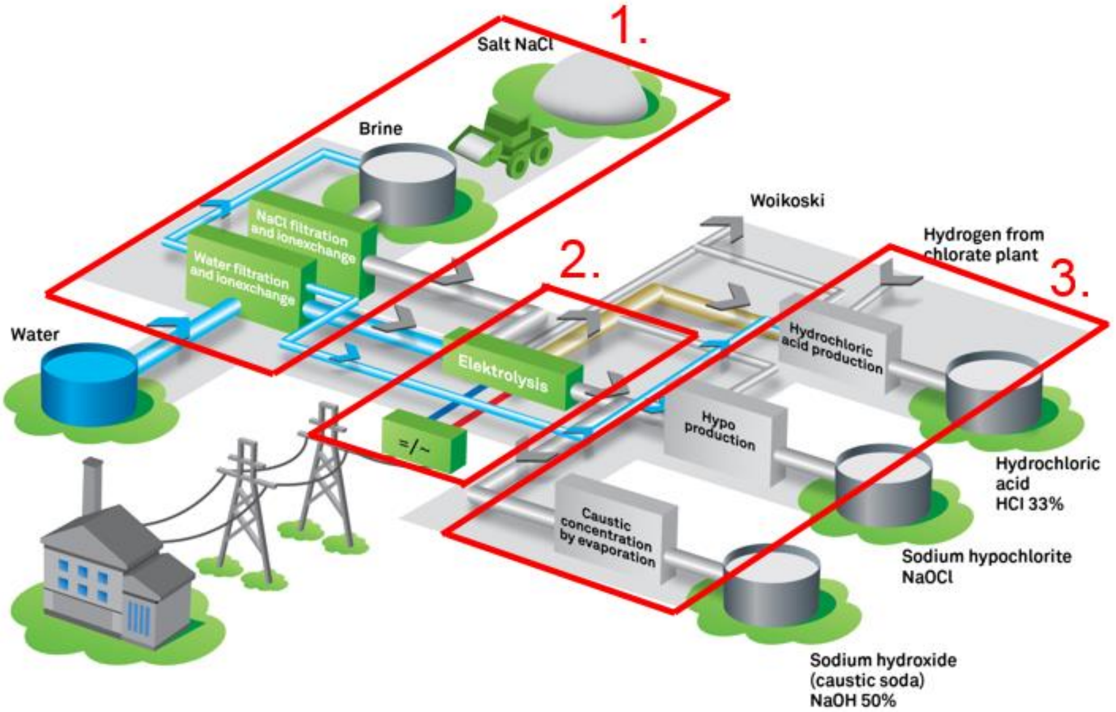


Figure 2. Process diagram of Joutseno chlor-alkali plant. This thesis focuses on the pipeline material selection for the electrolysis section of the process. (modified, Kemira Chemicals Oy, 2013.)

This thesis focuses on the section 2. of the process, electrolysis. The electrolysis process is based on electrical current (direct current, DC) which is used to separate chlorine and sodium ions from brine and hydrogen and hydroxide ions from water. The process uses a membrane cell for ion-exchange. The saturated brine (feed brine) is fed to the cell anolyte compartment. Negatively charged chloride ions are oxidized at the positive anode and they combine to form chlorine gas. The positively charged sodium ions pass through the ion exchange membrane to the catholyte side. A water solution of sodium hydroxide is fed to the catholyte side. At the negatively charged cathode the positive hydrogen ions from water react to form hydrogen gas, simultaneously releasing hydroxide ions. The sodium from anode is transported through the ion-selective membrane to the catholyte side. The positive sodium ions and negative hydroxide ions combine to form sodium hydroxide. The membrane cell process and chemical media involved in it is depicted in figure 3. (Paidar, et al., 2016, p. 740.)

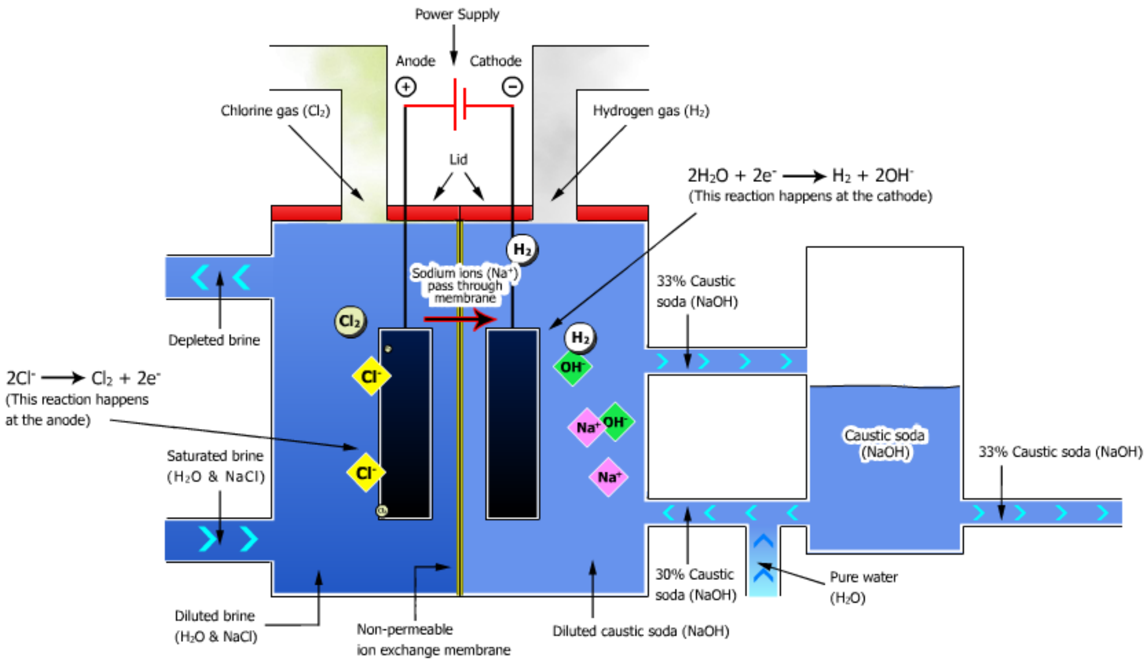


Figure 3. Membrane cell electrolysis diagram, depicting the chemical mediums produced in a chlor-alkali cell (Euro Chlor, 2015).

Because the process depends on electricity (monopolar electrolysis cells) and contains aqueous solutions and gases, these notions must be taken into consideration when defining the optimal material selection strategy. The corrosion characteristics are highly dependable on the chemical composition of the media contained in different sections of piping.

A literary review for the theory of corrosion mechanisms, failure mechanisms, failure rates, possible construction materials and the optimal material selection strategy will be conducted with a database search of Internet databases for books and scientific articles. The search will be conducted as a keyword-based search using building block strategic method and Boolean operators. This large data group will be reduced by using successive facets strategy by conducting multiple searches mixing different search terms. Field of search is limited to chemical and mechanical engineering databases. Parts of used ECTFE/VE chlorine header pipes will be dissected and visually analyzed to find out the failure mechanism. Experts in the field of study will also be interviewed.

Databases used in this study are:

- CRC Handbook of Chemistry and Physics
- Emerald Journals
- IEEE Xplore
- ISI Web of Science
- LUTPub/Doria
- ProQuest
- SFS-Standards
- Springer eBooks
- Scopus
- Wiley Online Library.

Books and other publications will be searched by using different search engines including LUT Finna and Google Scholar. Some commercial data and informational materials from pipeline manufacturers will be used in comparison with the data gathered from the literary review.

2.1 Systematic material selection process

In material selection for pipelines the optimal material aims to fulfill all the various demands dictated by the atmospheric conditions, legislation and end users. There is usually no superior material that excels in every category, but material optimization is always a tradeoff from one aspect to the other. The visualization 4 shows different considerations that must be taken into account when choosing optimal piping materials.

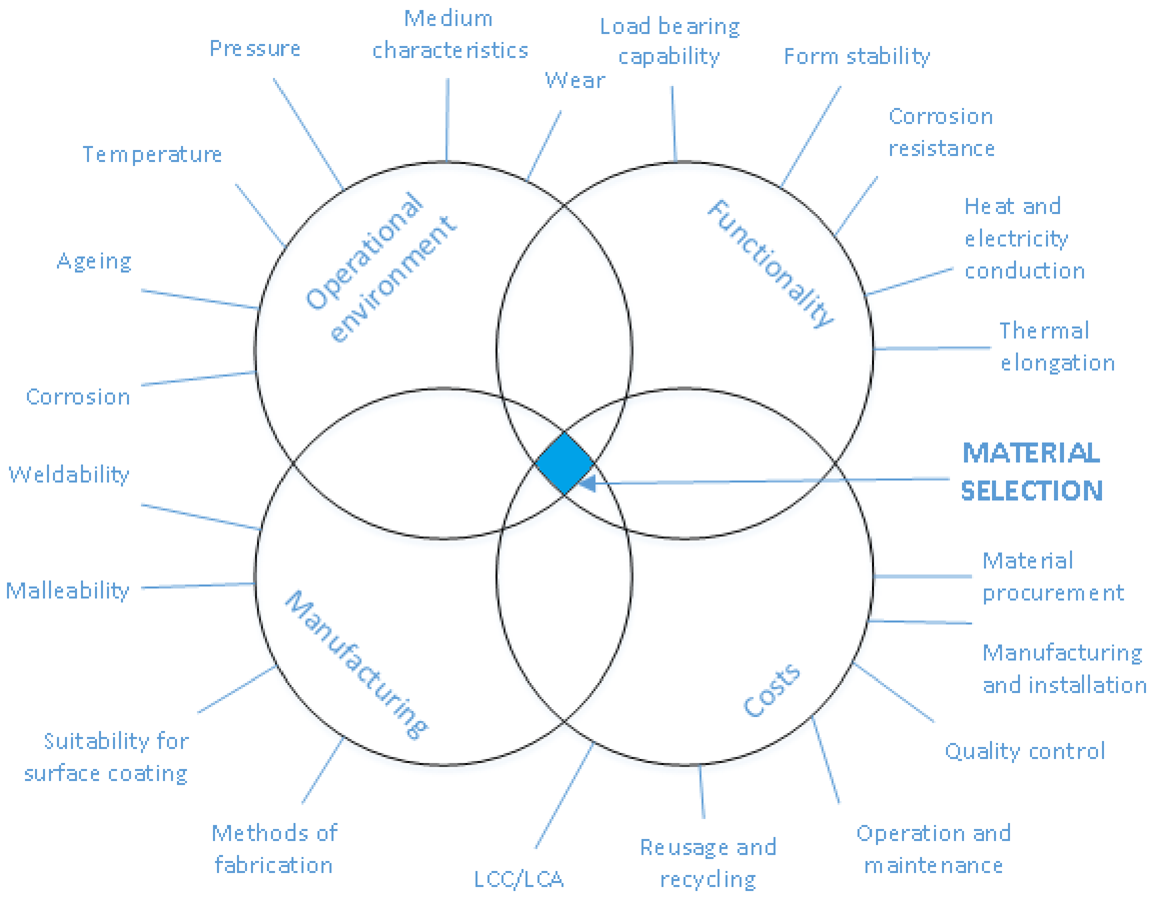


Figure 4. Material selection considerations for piping material selection (modified, Eskelinen & Karsikas, 2013, p. 37).

Material selection process is constructed of complex tasks involving a vast amount of information of material properties. Opposite of exact sciences, material selection requires the consideration of conflicting advantages and limitations. This results in multiple satisfactory solutions. There is often a necessity of trade-offs and compromises that must be made when choosing the optimal material. (Ali & Edwards, 2013, pp. 31-34.)

Most of the material selection literature available focuses on the material selection for new products. That is why current literature focuses on material selection strategies that include many nontechnical factors e.g. customer satisfaction based on the look and feel of the material. (D´Errico, 2015, p. 4.) Modern material selection strategies usually emphasize on the economic and environmental aspects of materials (Ali & Edwards, 2013, p. 2). In this thesis, the end user/customer is Kemira Chemicals Oy Joutseno site, so no marketing aspect is needed to be taken into consideration and this thesis will focus solely on the technical, economic, social and environmental aspects of piping materials. There still needs to be a clear material selection strategy that balances these aspects so that the optimal materials can be chosen.

In general, a material selection strategy includes the following steps in chronological order (modified, D´Errico, 2015, p. 6):

1. Translating the user needs influenced by material features into technical and nontechnical requirements
2. Formulation of performance metrics to measure how well a material matches a set of requirements
3. Material selection methods to:
    a. explore a solution space
    b. identify suitable materials that meet the constraints
    c. rank materials by their ability to meet the requirements and wishes.

It is important that no possible material groups get discarded in the early stages of material selection process before their limitations are checked. For example, assumptions like the unsuitability of glass as a material for piping because of its brittleness can be made, overlooking the fact that glass can be used as a thin enamel coating for steel pipes. In the case of piping material selection this can be achieved through out sorting chemical compatibility charts and finding out the possible constructions from literature and piping manufacturers.

The screening of unsuitable materials will be conducted by using fixed and flexible extermination of materials from further study. The fixed extermination takes into account the material attributes that exceed a set requirement, e.g. the usable limit temperature limit of a material with a known medium. The flexible extermination takes into account the variable limits of materials in the environment they are in. There is a limit of variable constraints that the material properties will be examined in. E.g. iso-corrosion rates of materials in different predetermined temperatures. The accepted iso-corrosion rate is not a set value, but determined by the end-user. (Ali & Edwards, 2013, p. 7.)

Failure modes and effects data analysis (FMEA) must also be taken into consideration when choosing a material for process industry piping. It is a valuable tool for giving insight on the material’s attributes needed for reliable usage. (Ali & Edwards, 2013, p. 5.) FMEA must always be considered and the magnitude of the possible failures must be identified. This way the material selection process can include the potential critical failures (e.g. fractures) in the foreseeable working conditions and adjust the material key features according to counteract them. (D´Errico, 2015, p. 80.) Especially in chemical piping containing hazardous chemical media these catastrophic failures of the structure cannot be allowed at any circumstances and must be taken into consideration.

2.1.1 Failure mechanism data analysis

A risk priority number (RPN) based classification method will be used to determine the effects of possible pipeline failures for different media, piping materials and pipeline sections. The failure-consequence analysis will be performed with assessing the risk priority number for the possible risks involved in different sections of piping. RPN takes into consideration the probability, severity and the detectability of the failure. Because of the nature of RPN analysis, the FMEA combines both qualitative and quantitative analysis and relies on expert knowledge. (Pillay & Wang, 2003, pp. 69-70.) The process is illustrated in figure 5.

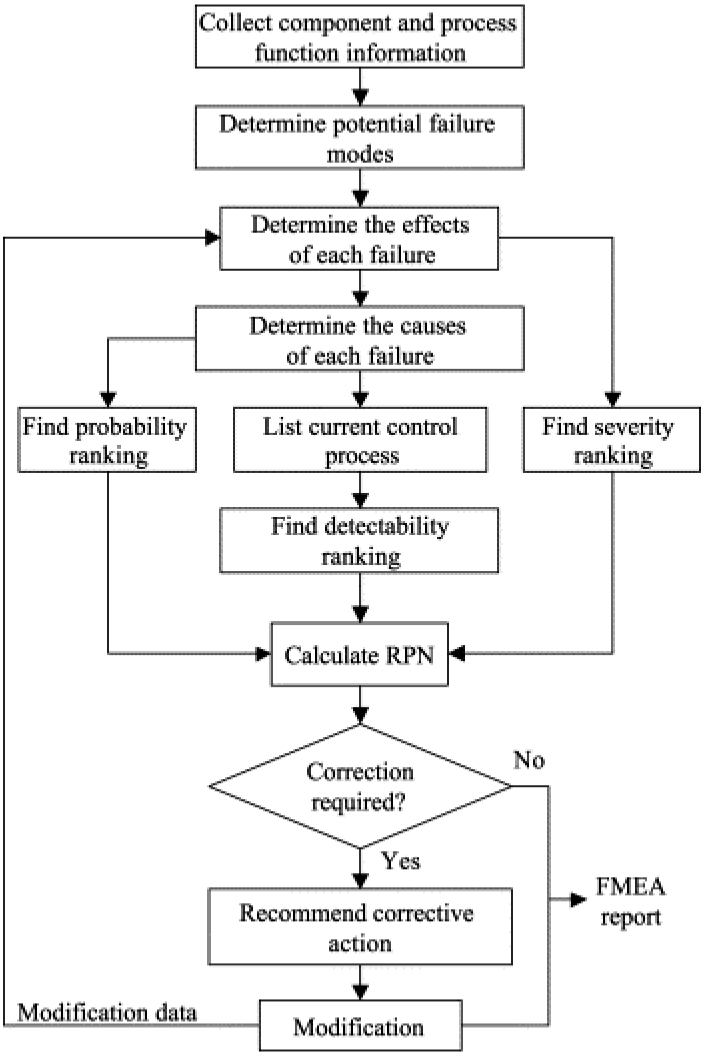


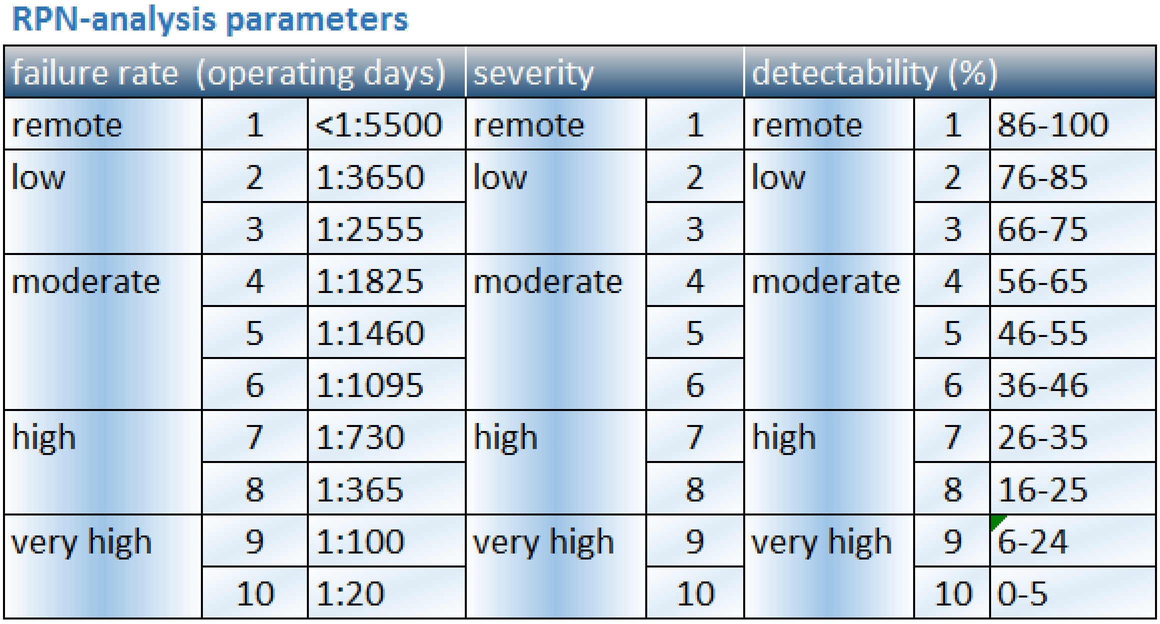
Figure 5. The process of FMEA in material selection for process piping (Pillay & Wang, 2003, p. 70).

The RPN number is calculated with the following equation (Pillay & Wang, 2003, p. 71):

$$RPN = S_t \times S \times S_d \qquad (1)$$

where S_t is the occurrence factor of failures in days, S is the severity of failure to the process and humans in a scale from 1 to 10 and S_d is the detectability factor of not detecting the failure in percent from. (Pillay & Wang, 2003, p. 71.) The scoring system used for the calculation of different parameters is shown in table 1.

Table 1. RPN parameter scales for occurrence, severity and detectability.



RPN-analysis parameters

failure rate (operating days)			severity		detectability (%)		
remote	1	<1:5500	remote	1	remote	1	86-100
low	2	1:3650	low	2	low	2	76-85
	3	1:2555		3		3	66-75
moderate	4	1:1825	moderate	4	moderate	4	56-65
	5	1:1460		5		5	46-55
	6	1:1095		6		6	36-46
high	7	1:730	high	7	high	7	26-35
	8	1:365		8		8	16-25
very high	9	1:100	very high	9	very high	9	6-24
	10	1:20		10		10	0-5

Because this method of RPN valuation does not take into account the fluctuations of factors in accordance to each other, the possible outcomes must also be compared and the criticality factors of different RPN values determined. Expert knowledge and the evaluation of consequences must be utilized for optimal results. (Pillay & Wang, 2003, pp. 71-72.) For example two different materials *a* and *b* in the same pipeline could have values of $S_{t,a}$ = 4, S_a = 9, $S_{d,a}$ = 2 and $S_{t,b}$ = 9 ; S_b = 1, $S_{d,b}$ = 8. Therefore, the RPN values will be identical (RNP$_a$ = 72; RPN$_b$= 72) but material *b* shows qualities of frequent low severity failures that are easily detected and *a* shows rare high severity failures that cannot be easily detected before the failure occurs. In this case, material *a* must be more frequently checked (e.g. with non-destructive testing methods) to ensure that the failure is contained. (Pillay & Wang, 2003, pp. 71-72.) Because of this setback in determining the RPN values based on the severity of assumed failure (e.g. blistering in the barrier layer of dual layer piping compared to environmentally assisted cracking of a metallic pipe) special attention must be paid in the FMEA section of material selection process. This will also have cost effect on the LCC of material.

This setback in severity rating can be combatted by weighing the different chemical's parameters separately with direct weighting. For example, chlorine header pipe failures would get a higher weight on the failure severity compared to a single cell feed brine pipe failure. Therefore, the formula used to calculate weighted risk priority numbers (wRPN) values is:

$$wRPN_n = aS_t \times bS \times cS_d \tag{2}$$

where a, b and c are the weighting factors with a combined equal of 1. The subscript in wRPN is the timeframe of the analysis, e.g. wRPN_{10} means the FMEA was conducted for a timeframe of 10 years.

For the failure modes and effects analysis of piping there will be a database search utilizing Joutseno plant's SAP plant maintenance software. This search is conducted by using the existing functional location hierarchy and focused on the different parts of piping determined in the previous chapter. The timeline of searches is set from 28.3.2007 to 16.3.2017. The data material is classified to groups and everything but pipeline failures will be excluded from further study. This data is constructed for the different factors needed to calculate the wRNP values. The data gathered in this section will be shown in appendices VII-VIII.

Older data than 28.3.2007 will be gathered for comparison purposes only. Data prior to 2007 will be gathered with interviews and by researching the paper database of Joutseno plant, but findings will not be implemented to the theory section of this thesis because of scarcity of information, possible false memories of people and the high error rate of results caused by these factors. This older data will be used for CASE-examples in the discussion section. There will be a visualization of pipe failures from 2007 to 2017 for the analyzation of the failure rates of different piping systems.

2.1.2 Lifecycle costs -analysis

In many cases the decision making of material selection is guided by the initial investment procurement, manufacturing and installation costs, while the largest LCC costs may in fact be generated during the usage period. LCC analysis focuses also on the hidden costs not easily foreseen in the design period. These hidden future costs include the likes of; investment capital costs, usage costs (for example energy consumption), maintenance costs (planned, unplanned), unplanned or planned shutdown costs, production losses during shutdowns and material recycling costs. (Lokka & Hänninen, 1994, pp. 4-5.)

The lifecycle costs of piping materials will be calculated using the present value method (PV). In this method, every yearly future costs or revenues will be discounted to represent their value at present time. Due to the interest rate affecting revenues periodically the capital invested in the future will always have a lesser value than capital invested today. The following formula will be used in the approximation of LCC (Lokka & Hänninen, 1994, pp. 4-15.):

$$\mathrm{LCC} = AC + IC + \sum_{n=1}^{N} \frac{OC}{(1+i)^n} + \sum_{n=1}^{N} \frac{LP}{(1+i)^n} + \sum_{n=1}^{N} \frac{RC}{(1+i)^n} \tag{3}$$

where, LCC = lifecycle costs
AC = material procurement cost
IC = manufacturing and installation cost
OC = usage and maintenance costs
LP = shutdown losses
RC = recycling costs including possible refunds
N = designed lifecycle of piping
i = interest rate
n = years of usage.

Lifecycle costs will be approximated with the cost data of renewed piping sections found from Joutseno SAP PM database between dates 28.3.2007 and 16.3.2017 and with quotations of piping material costs from industry suppliers. Also, approximations of installed pipeline material cost ratios will be used. A software application will be constructed to help calculate LCC costs for different materials. Piping material costs and their environmental impacts will be examined with a reference pipe section that is 1 m long, has a nominal pipe size of DN150, has end flanges but no pipe joints.

In the case of piping renewal, the terms AC and IC will be combined to accommodate for the “turnkey” piping installation costs. The term LP will get a numerical value of 0 in all cases because the risk management of Joutseno plant is set so that there can be no pipeline failure caused unplanned shutdowns that start to accumulate shutdown losses (intermediate storage size etc.). The designed lifecycle of piping will be set to 10 years of service life. The interest rate used is the real investment rate of a risk-free investment and will be set at 8 %.

2.1.3 Analysis of the ecological and social impacts of material selection

Sustainable development is a term that incorporates multiple different elements that measure the nature's ability to provide natural resources and ecosystem services to meet the demands of human consumption. It can be divided into four distinct categories according to Eskelinen & Karsikas (2013, pp. 10-11.):

- ecological
- economical
- social
- cultural.

Sustainable material selection incorporates the whole cradle to the grave lifecycle of the product. It includes the following aspects; saving energy, water and soil material in material processing, saving energy during the lifecycle of the material, using as little material as possible and recycling and reusing materials. (Eskelinen & Karsikas, 2013, p. 15.) The Institute of Chemical Engineers published in 2002 a diagram to highlight the key metrics of process industry that measure the sustainability of operations (Singh, et al., 2012, p. 285). They divided the operations into three key categories shown in figure 6; environmental, economic and social.

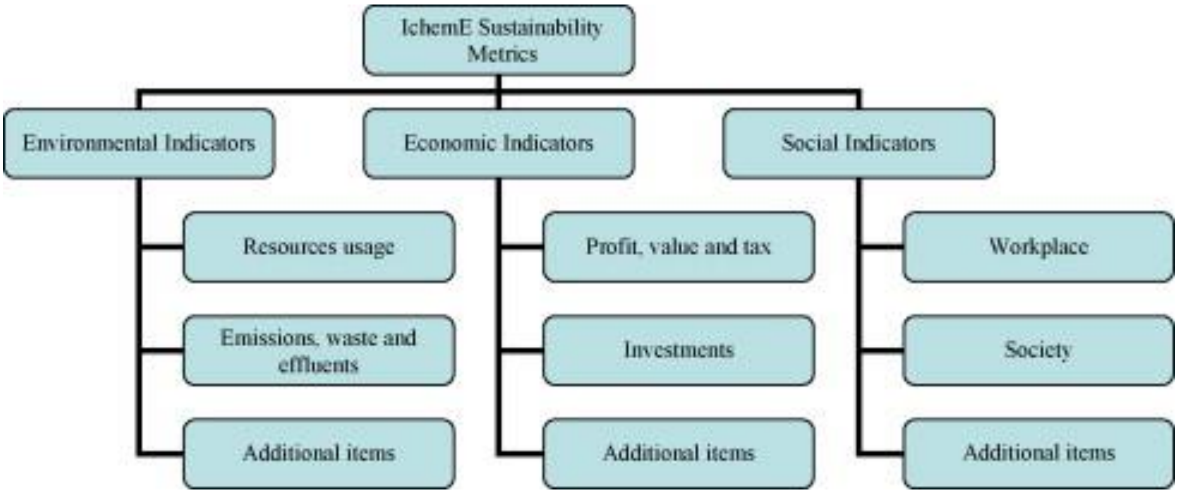
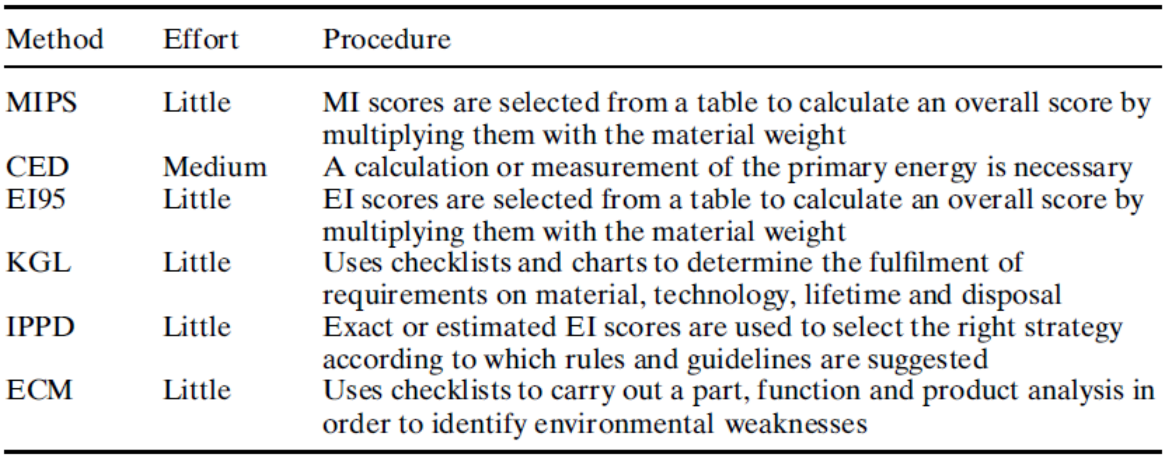


Figure 6. The sustainability metrics of process industry according to The Institute of Chemical Engineers (Singh, et al., 2012, p. 285).

In this thesis, the economic aspects will be analyzed in the LCC-analysis section. The ecological/environmental analyzation will be conducted with a limited lifecycle analysis (LCA) that emphasizes on quantitative parameters. The social and cultural aspects are a crucial part of publicly traded companies' operations but the amount of work to determine the impacts of piping material selection on a global scale is so vast that this section will be left out of the scope of this thesis. Kemira uses the Ethics & Compliance program to ensure that the principles of ethical business behavior are met (Kemira Oyj, 2017).

A comprehensive LCA analysis is a time demanding task. It can be so that on a project of a micro scale, LCA is left unperformed because of the low work-to-achievement factor. This is why methods that are easy and fast to perform have been developed. These methods can be either qualitative or quantitative. These easy-to-perform methods and according procedures weighed on the effort taken to perform them are depicted in table 2. (Ernzer & Wimmer, 2002, pp. 233-234.) Lifecycle assessment principles and framework is internationally standardized in ISO 14040:2006, but the standard does not describe the LCA techniques nor the methodology used for the individual phases of LCA (International Organization for Standardization, 2017). Thus, an environmental assessment procedure must be chosen for the material selection strategy. Different procedures for environmental assessment are depicted in table 2.

Table 2. Environmental assessment procedures overview (Ernzer & Wimmer, 2002, p. 238).



Method	Effort	Procedure
MIPS	Little	MI scores are selected from a table to calculate an overall score by multiplying them with the material weight
CED	Medium	A calculation or measurement of the primary energy is necessary
EI95	Little	EI scores are selected from a table to calculate an overall score by multiplying them with the material weight
KGL	Little	Uses checklists and charts to determine the fulfilment of requirements on material, technology, lifetime and disposal
IPPD	Little	Exact or estimated EI scores are used to select the right strategy according to which rules and guidelines are suggested
ECM	Little	Uses checklists to carry out a part, function and product analysis in order to identify environmental weaknesses

Out of these methods, Material Intensity per Service Unit (MIPS), Cumulative Energy Demand (CED) and EcoIndicator 95 (EI95) are quantitative and Kodak-Guidelines (KGL), Integrated Product and Process Development (IPPD) and Ecodesign Checklist Method (ECM) are qualitative methods (Ernzer & Wimmer, 2002, pp. 233-234). The MIPS values are used to quantitatively calculate the material footprint in the manufacturing phase of a product (Liedtke, et al., 2014). A quantitative method allows easy and numeric comparison of different materials' impact to the environment and is selected over the qualitative method.

MIPS and EI95 methods were selected for comparison of the environmental assessment procedure. The MIPS concept takes into consideration the fact that material consumption is finally converted into outputs and environmental impacts. The resources extracted for production are converted into end-products and can be back-traced to emissions and waste created in the production processes. MIPS follows the idea of matter-energy conservation law that states that there are quantitative equivalent inputs and outputs and estimates the outputs by following the formula (Liedtke, et al., 2014, pp. 547-548.):

$$MIPS = \frac{MI}{S} \tag{4}$$

,where *MIPS* is Material Input Per Service unit, *MI* is Material Input and *S* is Service unit. The material input is measured in kg or tonnes. It can be also called material intensity when related to material, energy or distance. The service unit is a dimensionless figure and must be defined in accordance to the service in question. (Liedtke, et al., 2014, p. 548.)

MIPS considers the whole lifecycle of the material from resource extraction, manufacturing, transport, packaging, re-use, re-cycling, and re-manufacturing to final waste disposal. There are up to five natural resource categories that are measured; abiotic raw material, biotic raw material, water, air, and earth movements in agriculture and forestry. The MIPS-values can be found from literature, mainly from the Wuppertal Institute. (Liedtke, et al., 2014, pp. 548-549.) There is limited data for pipeline materials available as MI numbers.

EI99 is a further development from EI95 method. Standard eco-indicators are numbers that show as a value the total environmental load of a product or process. With the use of these standard eco-indicators the environmental load of a kg of material can be determined as a dimensionless number. The scope of EI99 includes the following types of damage to the environment; human health, ecosystem quality and resources. Where human health includes the number and duration of diseases and lives lost because of the effects of environmental causes, ecosystem quality includes the effects on species diversity and resources include the energy needed for extracting raw minerals and fossil resources and the depletion of agricultural and bulk resources. (Ministry of Housing, Spatial planning and the Environment, 2013, pp. 6-7.)

The EI99 method is specifically developed to enable the designer to choose the most environmentally materials for a construction. The eco-indicator unit is Eco-indicator point (Pt). According to the Neatherlands' Ministry of Housing, Spatial planning and the Environment (2013, p. 9) "The scale is chosen in such way that the value of 1 Pt is representative for one thousand of the yearly environmental load of one average European inhabitant." For material comparison, it is sufficient to use only the raw material components eco-indicator value. (Ministry of Housing, Spatial planning and the Environment, 2013, pp. 9-14.)

The eco-indicator values are calculated by making an inventory of all relevant emissions, resource extractions and land use in all processes that form a lifecycle of a product. The next step is to calculate the damages these flows cause to human health, ecosystem quality and resources. Finally, the weighting of these three damage categories is carried out by a panel of experts and non-experts. (Ministry of Housing, Spatial planning and the Environment, 2013, pp. 23-24.)

Another development based on EI99 has been called the ReCiPe method, which has been developed in 2008 as a LCA method that comprises harmonized category indicators similar to EI99 at midpoint and endpoint levels. The Ecolizer 2.0 tables of eco-indicator numbers used for the LCA analysis in this thesis uses the principles of ReCiPe and weights the two levels into one single indicator of material environmental impact. (OVAM, 2009, p. 3.)

Because of the simplicity of the method and the better availability of material data from Ecolizer 2.0 tables the EI-method was chosen for the LCA section of the thesis over MIPS method.

2.1.4 The ranking of materials in material selection process for pipelines

The ranking of materials will be conducted with numerical attributes of materials (wRPN, LCC, LCA). The numerical attributes which all have different ranges will be standardized so they can be compared regarding to each other. The values of different parameters will be modified with the mean and the standard deviation where 0 is the neutral material. The formula used for standardization is:

$$Z = \frac{X - \mu}{\sigma} \tag{5}$$

where Z is the standardized value, X is the numerical value of material attribute, μ is the mean of attribute values and σ is the standard deviation of material attribute values.

The weighting will be conducted with a subjective method called direct weighting procedure where each attribute will be weighted using a weighting parameter. Each of the weighting parameters will add up to a combined total of 1. (Ali & Edwards, 2013, p. 51.)

To help to understand a material selection process, flow charts that show the individual steps have been created. A flow chart of a universal material selection procedure is depicted in figure 7. (Ali & Edwards, 2013, p. 69.)

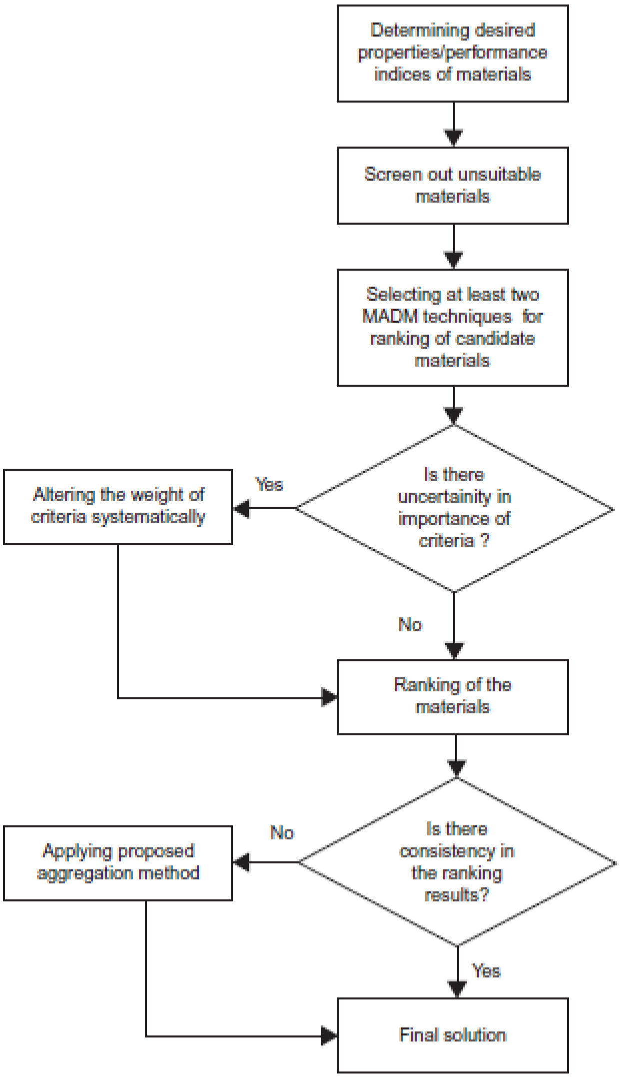


Figure 7. A universal material selection process flow chart (Ali & Edwards, 2013, p. 69).

The term MADM techniques in figure 5 refers to multiple-attribute decision-making. MADM is needed when there are two or more materials and two or more material attributes affecting the ranking of materials in consideration. (Ali & Edwards, 2013, p. 4.) This flow chart will be used as a basis for the piping material selection strategy.

2.2 Reliability, validity and sensitivity of the used methods

The reliability of results will be confirmed by using triangulation in the search procedure. The initial data is confirmed by using three different informational sources; scientific articles, books and expert interviews when possible. The data gathered from the literary review will be confirmed at least from two or more different sources. The newest possible research information and peer reviewed articles have the highest priority in references.

The margins of error will not be constituted when calculating LCC costs, because the approximation of errors caused by different vendors quotations, affluence of manufacturing technologies and installation times, the cost of NDT (non-destructive testing), the fluctuations of interest rate and cost of design is impossible to estimate.

The eco-indicator analysis doesn’t take into consideration the in-use, e.g. energy consumption and chemical production caused environmental effects. Also, the information of Ezolizer 2.0 calculations for every material are not available, so estimations of similar materials values have to be used. This lowers the sensitivity of LCA result.

3 THEORY OF CORROSION MECHANISMS OF DIFFERENT MATERIAL GROUPS WITH AQUEOUS AND GASEOUS SOLUTIONS

This section focuses on pipeline corrosion mechanisms. To understand the material attributes that are needed to perform the FMEA and extermination of materials in fixed and flexible extermination phases, the possible forms of corrosion damage in pipelines must first be determined to be able to counterbalance their effects with suitable material properties. Corrosion theory explains the physical phenomena and failure mechanisms involved in corrosion failures.

It is crucial to know the corrosive media contained in the piping to be able to perform the preliminary material scoping. Different chemical media have very different corrosive properties, for example some piping materials are considered in literature “acid tolerant” but most of them do not comply with strongly corrosive acids like hydrofluoric acid. In the later stages of material selection, the process parameters (pressure, temperature etc.) must be known to be able to exterminate non-suitable materials from further investigation. These parameters affect the corrosion speed and possible corrosion mechanisms, which must be also taken into consideration in the ranking stage of the suitable materials.

The piping examined in this thesis will be divided into different categories by the chemical media contained in the pipes. The piping is divided into the following categories by the media contained:

- Caustic soda: From the membrane cells to NaOH circulating tanks and back
- Hydrogen: From membrane cells to HCl burners
- Saturated brine: From saturated brine heater to membrane cells
- Depleted brine: From membrane cells to brine pH adjustment tank
- Chlorine: From membrane cells to chlorine cooler

The piping included in the scope of this thesis is depicted in bolded form as a schematic diagram in figure 8.

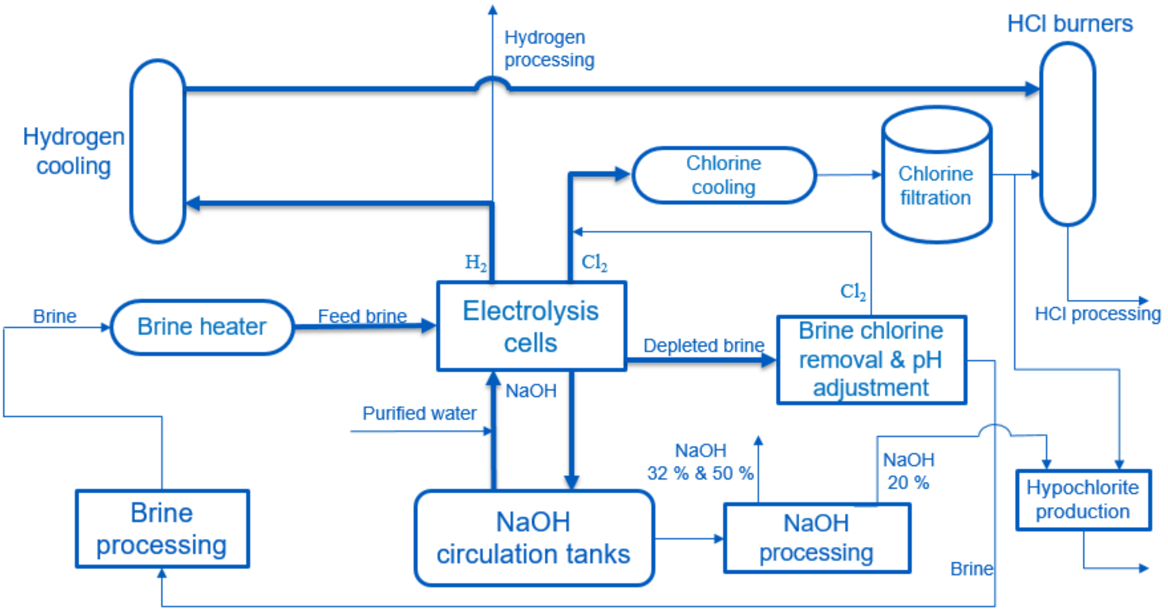


Figure 8. A simplified schematic diagram of Joutseno chlor-alkali plant's process and pipelines, highlighting the examined process piping in bolded form.

3.1 Forms of corrosion in researched process piping

To understand the forms of corrosion, the underlying physical phenomena of corrosion must be understood first. These phenomena vary greatly with the chemical composition of the material in question. Piping engineering materials can be divided into few key material classes which are (modified, Ali & Edwards, 2013, p. 2):

- metals
- polymers and elastomers
- glasses
- ceramics
- composites.

This thesis will focus on aqueous solutions and gases (chlorine and hydrogen) present in the cell room piping. High temperature dry corrosion will be left out of scope because of the nature of corrosive substances and plant operating parameters that are in normal working temperatures <100 °C. Excluded from deeper research are fields of wear, for example corrosive wear and erosion corrosion. The combined actions of corrosion and stresses are discussed and topics like stress corrosion cracking and hydrogen embrittlement will be researched. These topics are discussed because of their utmost importance for applied corrosion science in causing catastrophic destruction of structure. For example, the very little overall surface corrosion reactions causing a crack tip combined with static or dynamic stresses can cause a formation of a catastrophic failure crack. (Landolt, 2007, p. 12.)

The corrosion behavior of different materials inside material groups must be considered. For example, with different steel grades a normal unalloyed construction steel in certain atmosphere will show higher uniform corrosion rates annually than a highly alloyed steel. On the other hand, in some cases the highly alloyed steel could show qualities of localized corrosion that leads to a faster, uncontrolled destruction of the structure due to mechanisms like stress induced cracking. So, it is in many cases safer to choose the less noble material and monitor the corrosion periodically than let the structure fail uncontrolledly. (Aromaa, 2005, p. 102.)

The most crucial variables affecting the corrosive properties of the aqueous solutions according to Aromaa (modified, 2005, p.21) are:

- The solvent; the main component of the solution of which the other components are dissolved in
- pH, which is the acidity of the solution
- Redox-potential; the ability of the solution to oxidize affects the reaction speeds and passivation
- Temperature, which affects the reaction speeds
- Dissolved salts that affect the reactant layer formation and destruction
- The flow of the solution that affects the reaction speeds and the stability of the reactant layers.

3.2 Corrosion of metals

Metallic materials tend to return to the most thermodynamically stable state, mainly by forming oxides, sulfides and ores. Therefore, corrosion of metallic materials is always present in atmospheric conditions and can be only annihilated by an inert atmosphere or total vacuum. Aqueous metallic corrosion is always of an electro-chemical nature and thus follows the laws of thermodynamics. (Schweitzer, 2007c, pp. 1-2.) Thermodynamics predict whether reactions can or cannot occur, but it doesn’t predict the rate of these actions. The prediction of reaction rates is in the area of kinetics. (Marcus, 2003, p. 5.) Only the very noble metals like gold or platinum are immune to corrosion caused by atmospheric oxygen in normal operating conditions (Kaesche, 2003, p. 1).

The main physical principle in chemical equilibrium thermodynamics is the free reaction enthalpy, known also as Gibbs reaction energy. This is the driving force of thermodynamic reactions proceeding at approximately constant temperature and pressure. (Landolt, 2007, pp. 15-25.) Gibbs free energy determines whether a reaction occurs or not. The more negative the change of Gibbs free energy is the more likely the reaction is to occur. (Aromaa, 2005, p. 38.)

With the electrical cell potential equivalent to the free reaction enthalpy the Nernst equation is used to calculate the quantitative values of equilibrium potential as a function of concentration and temperature. With metal-solution systems the concept of electrode potential is of importance. This is usually measured as a reference electrode against the standard hydrogen electrode (SHE). (Landolt, 2007, pp. 25-30.)

The electrode potential (potential difference across the double layer) is one of the most important factors in aqueous corrosion situations to be taken into consideration when studying the electrified interface between the metallic electrode and aqueous electrolyte. (Protopopoff & Marcus, 2003, p. 8.) The standard electrode potential, $E°$ can be calculated by using the following formulas:

$$E° = \frac{\Delta G}{z * F} \quad \text{anodic reaction} \tag{6}$$

$$E° = -\frac{\Delta G}{z * F} \quad \text{cathodic reaction} \tag{7}$$

, where ΔG is the standard free energy of reaction, z is the number of electrons in the reaction and F is the Faraday constant (96500 C/mol). In standard electrode potential (p = 100 kPa, T = 25 °C and when the activity of reagents is 1) the metal is in a stable state of corrosion dynamics. So, a solid metal is in equilibrium with the ionic species of the same metal in the solution. The anodic and cathodic reactions counterbalance each other and the system is stable. These reactions are referenced to the standard hydrogen electrode (SHE) where $E° = 0$. (Aromaa, 2005, pp. 38-39.)

The corrosion potential E_{cor} refers to the potential of the electrode-electrolyte interface spontaneously produced. In single electrode situations, this potential is equal to $E°$. When potential equals $E°$ there is no current flowing through the electrode-electrolyte interface. When the potential differs from $E°$ there is an electric current flowing between the electrode and electrolyte. Polarization ζ can then be calculated for the electrode reaction by subtracting the corrosion potential from the potential of the electrode. A positive value of polarization equals to an anodic reaction and a negative value to a cathodic reaction. (Landolt, 2007, pp. 119-120.)

By using the Butler-Volmer equation the current intensity that is exponentially proportional to polarization can be determined (Landolt, 2007, p. 120). Then the current density can be calculated by using Faraday’s law. In determining the corrosion speeds, the current density acting on the electrode, density of material and the temperature must be taken into consideration. (Aromaa, 2005, pp. 42-47.)

When considering the corrosion resistance of metals, they are usually divided into two categories; passive metals and active metals. Passive metals develop a thin (typically 1-3 nm) oxide layer to protect them from the environment. Active metals do not develop an oxide layer and the metal dissolution is continuous in corrosive atmospheres. Most of the metals and alloys that withstand corrosive agents well are in a passive state. These metals include the likes of titanium, tantalum, stainless steel and nickel-chromium based superalloys. (Landolt, 2007, p. 227.)

3.3 Uniform corrosion of metals

An even rate of metal loss on the exposed surface is called uniform or general corrosion. Uniform corrosion can be seen as the loss of surface metal caused by chemical attack or dissolution of metal into metallic ions. (Schweitzer, 2007c, pp. 3-7.)

Metallic corrosion is (excluding tribocorrosion mechanisms) always caused by an irreversible oxidation-reduction reaction (redox). This oxidation reaction takes place between the metal and the oxidizing agent in the environment and follows the formula (Landolt, 2007, pp. 2-4.):

$$\text{metal} + \text{oxidizing agent} \rightarrow \text{oxidized metal} + \text{reducing agent} \qquad (7)$$

In aqueous corrosion, there are two principal oxidizing agents that are encountered in practice; solvated protons (e.g. H^+) and dissolved oxygen. In wet corrosion, there are also other agents that have to be taken into consideration. For example (Landolt, 2007, pp. 2-4.):

- Oxidizing metal cations; Cu^{2+}, Fe^{3+}
- Oxidizing anions NO^{2-}, CrO_4^{2-}, OCl^-
- Dissolved oxidizing gases O^3, Cl^2.

Redox reaction contains two partial reaction; partial oxidation reaction (anodic partial reaction) and partial reduction reaction (cathodic partial reaction) (Schweitzer, 2007c, p. 10). According to Protopopoff & Marcus (2003, p. 8) “Oxidation is the removal of electrons from atoms or groups of atoms, resulting in an increase in valence, and reduction is the addition of electrons to atoms or groups of atoms, resulting in a decrease in valence.” For example, the reaction of zinc and hydrogen (Schweitzer, 2007c, p. 10):

$$\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2 \qquad (8)$$

where anodic partial reaction is:

$$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e} \qquad (9)$$

and cathodic partial reaction is:

$$2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2. \qquad (10)$$

All corrosion reactions that imply a charge transfer between an electrodic conductor (electrode) and an ionic conductor (electrolyte) are referred as electrochemical reactions. (Schweitzer, 2007c, p. 10.) With metal-water solution equilibrium the concept of potential-pH (*E*-pH) diagrams (Pourbaix diagrams) are used to evaluate the protective metallic compounds’ stability. These diagrams show the regions of stability that can exist in the systems. (Marcus, 2003, p. 6.)

In uniform corrosion, the anodic and cathodic reactions take place on the same surface. In microscopical analysis it can be assumed that the surface is divided into anode and cathode areas of different sizes. These anode and cathode areas are constantly changing place so the corrosion seems uniform. On the surface of the metal the grains form microscopic corrosion cells driven by potential differences. (Aromaa, 2005, p. 65.) This mechanism is depicted in figure 9.

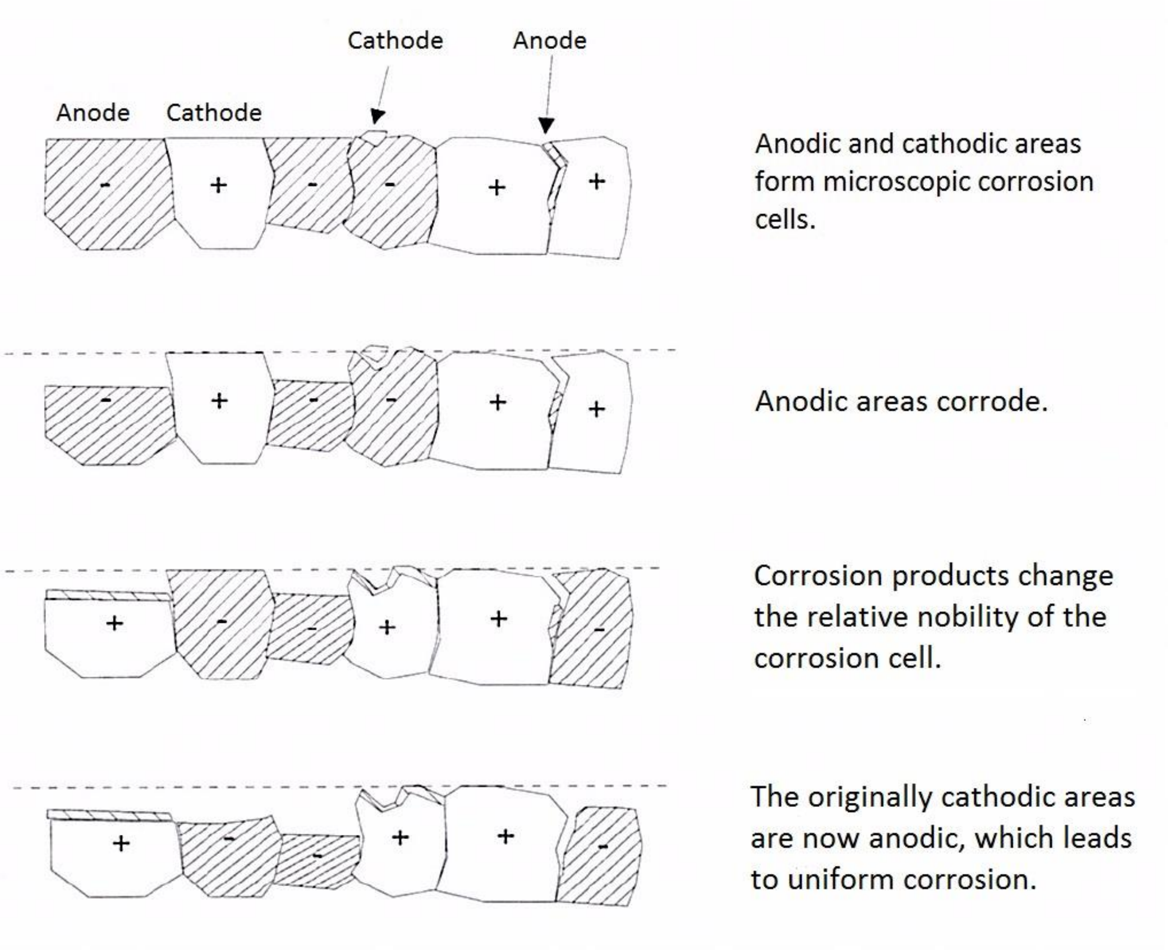


Figure 9. Progression of uniform corrosion in the metal surface layer (modified, Aromaa, 2005, p. 65).

Uniform corrosion rate can be measured in many ways, of which the most used are a mass loss per unit of surface and per unit of time and corroded depth per unit of time. (Landolt, 2007, p. 7.) In process industries, an acceptable corrosion rate is 0,01 mm/year. At this corrosion rate, it can be assumed that the metal does not go under harmful corrosion. A corrosion rate of 0,1 mm/year requires monitoring and the use of corrosion margins in thickness calculations. A corrosion rate of 1 mm/year deems the material unusable unless financial reasons do not make it viable. (Aromaa, 2005, p. 65.)

Normally metallic corrosion is always caused by an irreversible oxidation-reduction reaction (Landolt, 2007, p. 2). Tribocorrosion mechanisms like erosive wear makes an exception, because the combined effect of mechanical degradation and electrochemical mechanisms can cause a greatly increased corrosion rate. (Landolt, 2007, pp. 415-417.) At Joutseno plant’s parameters in the cell room pipelines, all of the media are fully dissolved so there are no abrasive particles contained in the solutions. Thus, the metallic corrosion is always of an electrochemical nature.

Tribocorrosion mechanisms like wear corrosion must only be considered if the media is containing abrasive particles impinging on the surface. Erosive wear (solid particles in the liquid) causes the metal to progressively lose volume due to mechanical degradation mechanisms on the metal-fluid film. This results in metallic particles in the media rather than solvated metallic ions. Erosive corrosion is the combined effect of erosive wear and corrosion. Erosive wear can affect the passive layer of the metal and greatly increase the corrosion rate. (Landolt, 2007, pp. 415-417.)

Erosion corrosion is dependent on the composition of the material (hardness, ductility, surface layer composition etc.), the composition of the solution (redox, particle size, pH etc.) and the flow speed of the liquid. The most important preventive measure for piping materials is the proper design of the liquid velocity. When a certain critical flow speed of a metal is exceeded, the corrosion rate increases substantially. Metals that have a passive oxide surface layer tend to withstand better than metals with active surface layer. (Aromaa, 2005, pp. 69-71.)

3.4 Local corrosion of metals

Local corrosion of metals has various forms of manifestation. Local corrosion mechanisms are usually harder to foresee than global corrosion and can cause catastrophic failure of the structure rapidly. Therefore, special attention to possible local corrosion mechanisms must be given and taken into account in material selection process.

3.4.1 Galvanic corrosion

Galvanic corrosion occurs in a situation where two metallic structures that have separable nobilities (standard electrode potentials) are connected and are affected by an electrolyte. This potential difference between the metals will exaggerate the dissolution of the less noble material and decrease the dissolution of the nobler one. Even nonmetallic materials like graphite can act as a cathode and increase the dissolution rate of metal. (Schweitzer, 2007c, pp. 8-10.)

Galvanic corrosion in dissimilar metallic joints can be prevented by selecting materials that are close to each other in the galvanic series. Tables of electrochemical series are readily available in literature. When joining two metals of different nobility, galvanic corrosion can be prevented by placing an insulator between them. (Schweitzer, 2007c, pp. 9-10.)

3.4.2 Environmentally assisted cracking (EAC)

The term environmentally assisted cracking contains many different aggressive media induced failure mechanisms. It is common in all EAC failures that the metal affected by both tensile stresses and aggressive media induced corrosion loses its ductility and this leads to cracking. (Rebak, 2006, p. 1.) There is no universally satisfactory theory to explain all the different mechanism of crack forming. There are many theories that explain a certain behavior mechanism. The subject is very complex and the understanding of these mechanisms is mostly phenomenological. (ASM International, 2003, pp. 345-346.) That is why this section of the thesis focuses on chloride induced cracking, caustic induced cracking and hydrogen induced cracking.

Stress corrosion cracking (SCC) is a phenomenon where the combined actions of continuous corrosion induced flaws and a critical value of stress concentration form a crack. This kind of corrosion process is called synergistic because neither one of the mechanisms is alone able to start crack formation. Precorrosion combined with a loading of the structure in inert atmosphere (no corrodents) will not sustain crack formation. The combined effect of chemical and mechanical forces will cause a crack formation that is time-dependent. Typically, SCC is seen in metallic alloys but it has been shown that even pure metals are susceptible to SCC. (ASM International, 2003, p. 347.)

In general, SCC is of great concern in corrosion-resistant alloys that depend on a passive layer for corrosion resistance in highly aggressive environments. Austenitic stainless steels show SCC in hot, concentrated chloride solutions, titanium alloys show SCC in hot aqueous halide ion containing solutions. (ASM International, 2003, p. 347.)

SCC is a slow process of crack formation from 10^{-9} to 10^{-6} m/s until the stresses in the remaining metallic ligament exceeds the fracture strength. There are numerous environmental and material properties that are known to influence the rate of crack growth in aqueous solutions. To name a few factors, there are: the temperature, pressure, pH, concentration and electrochemical potential of the solution; the magnitude of applied stress, the loading mode at the crack tip, alloy composition, and crack geometry in the material. Therefore, SCC rate is hard to approximate when comparing laboratory tests to real process environments. (ASM International, 2003, pp. 354-356.)

Hydrogen damage is a form of EAC that is caused by the combined effects of hydrogen and residual or applied tensile stress. Hydrogen damage has many forms and is specified to different alloys. Hydrogen damage can result in cracking, blistering, hydride formation and loss of tensile ductility. Hydrogen damage is not to be confused to hydrogen induced cracking (HIC), because many forms of failure do not demonstrate features of embrittlement. (ASM International, 2003, p. 367.)

Most of the hydrogen damage processes involving gaseous hydrogen need a high gas pressure, exceeding 200 bar and high temperatures of > 100 °C. This can be observed from appendix I. The only hydrogen damage process that occurs near atmospheric pressure and in low temperatures (< 100 °C) is hydrogen environment embrittlement. It affects alloys of steel, nickel and titanium. (ASM International, 2003, pp. 367-369.)

A kind of EAC mechanism found in alkaline solutions (e.g. $NaOH + H_2O$) is called sulfide stress cracking (SSC). Studies conducted on the matter discuss mostly of stainless steels and nickel based alloys because the allowable corrosion limit of carbon steels and mild steels is limited to approximately 66 °C at NaOH concentration of up to 50 %. There is also the contamination of solution by iron when considering the use of plain steels that cannot be allowed at Joutseno chlor-alkali plant. (Rebak, 2006, pp. 1-5.)

The suggested mechanisms of SSC are anodic dissolution, hydrogen effect and dealloying. Out of these hydrogen effect seems unlikely to be the root cause of SSC because there is plenty of corrosion activity on the surface of the metal that is protected by a passive oxide layer. Hydrogen effect takes place inside the metal after the protective layer is dissolved. The second proposed mechanism is dealloying in stainless steels and nickel based alloys. Alloying elements like Mo, Fe and Cr dissolve preferentially in caustic solutions, leaving behind a Ni rich layer. However, the unaffected base alloy under the dealloying layer does not suffer crack formation and thus dealloying layer formation does not seem a plausible explanation to crack formation. This leaves the anodic dissolution of preferentially dissolved elements as the main cause of crack propagation. Cracking occurs only in a specific window (200 mV wide) above the OCP (open circuit potential) in deaerated condition. (Rebak, 2006, pp. 6-8.)

Generally, the type of SCC fractures is transgranular in stainless steels and intergranular in nickel alloys. Transgranular cracking takes place on the grain boundaries and intergranular cracking happens through the grains. The type of cracking can vary according to the thermal treatments of alloys. (Rebak, 2006, p. 7.)

3.4.3 Leakage current corrosion

Leakage current can be defined as a current lost from the electrolysis cells via the pipelines connected to them and the electrolyte contained in the pipelines. The effects of leakage currents can be determined by the composition of the pipeline (conductive or non-conductive) and the nature of the current (anodic or cathodic). The magnitude of leakage currents is proportional to the number of cells connected in series, squared. (Riskin, 2008, pp. 41-42.)

The cells in the cell room are connected in series and form a set. This set is fed with direct current from a rectifier. The potentials on the rectifier's poles are equal to V/2 and –V/2 and in the middle of the set the potential is 0. Parallel systems of pipelines transporting the electrolyte to the cells and pipelines for tapping the electrolysis products exist in the cell room. Electrolysis current always branches off to these parallel pipelines from the electronic series. (Riskin, 2008, pp. 38-39.)

There are always limits of polarization in metal solution interfaces because there is a limit of the corrosive medium concentration affecting REDOX reactions and a limit of the operating temperature. The limiting factor in corrosion by an external current is the magnitude of the current. Thus, the effect of external currents on metallic corrosion can surpass the effects of corrosion by the solution significantly. (Riskin, 2008, pp. 19-20.) The operating currents at a chlor-alkali cell room can reach values higher than 120 kA and the solutions handled are always conductive.

By applying an external current to a metal, the potential of the metal and solution can be increased or decreased. This of course changes the corrosion characteristics of the metal in question. The behavior is affected by the nature of the metal; either active or passive. The areas of pipeline affected by leakage currents have been researched and a schematic has been created. This schematic showing the places and the nature of the current depending on the position of the electrolyzer in the set is depicted in figure 10. (Riskin, 2008, pp. 28-40.)

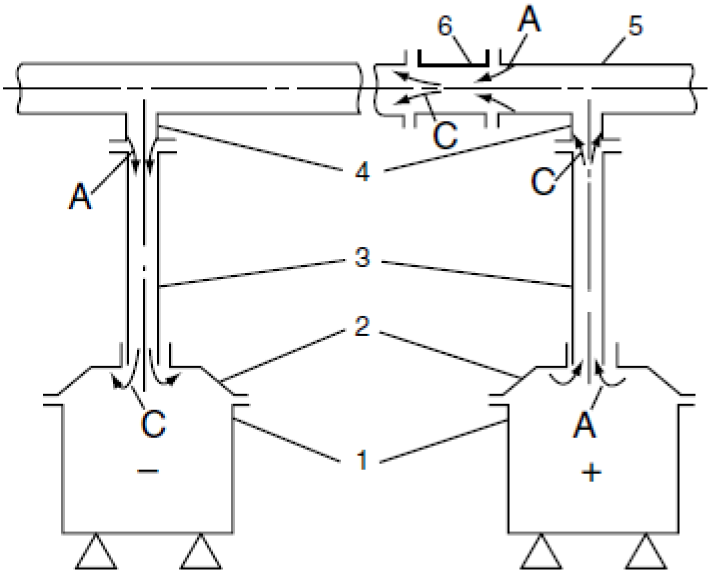


Figure 10. Areas of attack by leakage current in the pipelines connected to electrolytic cells (Riskin, 2008, p. 40).

In figure 10 the arrows depict the leakage current direction and symbol A depicts an anodic direction and C a cathodic direction. Symbol 1 depicts the electrolytic cells, 2 the metallic covers of the cells, 3 are tubes made from non-conductive material, 4 are the metallic pipe branches, 5 is the group header and 6 is an insulating insert.

To prevent corrosion by an external current, the open circuit potential E_s must be kept below the activation potential E_a, where the corrosion of the metal starts. To determine the corrosion characteristics both potentials must be determined in the according media. In pipelines, it is possible to calculate the potential distribution along the internal surface to verify whether the pipeline goes under harmful corrosion or not. The type of pipeline, diameter, the length of tubing and electrolyte resistivity influence the potential calculations from the current measurement from the flanges. The length is a parameter to consider, because not all the current is entering the pipeline wall. (Riskin, 2008, pp. 122-132.)

The calculations of leakage currents affecting corrosion in the pipelines are not viable using electric schemes because assumptions are necessary to simplify the calculations. In practice, the size of pipelines and the liquid and condensate levels in the pipeline vary affecting the resistance of the pipeline. Moreover, the polarization characteristics of metals vary depending on the value of the external current. The metal’s potential can shift to different areas where there are different types of electrochemical processes proceeding. (Riskin, 2008, pp. 41-47.)

Therefore, measurements of leakage current must be made to determine the possibility of effects on corrosion in the pipelines. The most straight-forward method is to measure the leakage current intensity with a millivoltammeter between the metallic pipes at a point where the leakage current is interrupted, e.g. from flanges where there is a non-conductive bellow in-between. This data must be confirmed by using a voltmeter-and-shut technique. In this technique, the dropdown of the voltage in the flange is measured. After this a shut is connected in parallel to the measurement device and a new value of the voltage drop is measured. Using Kirchhoff’s and Ohm’s laws the current value can be then calculated. (Riskin, 2008, p. 44.)

3.4.4 Pitting corrosion

In pitting corrosion, the passive surface layer of a metal is damaged or imperfect and thus in a more active state than the rest of the layer. Pitting corrosion process cannot start if even one of the following conditions is not met; sufficient aggressive ion concentration, sufficient temperature and surpassing a certain anodic potential difference. (Aromaa, 2005, p. 72.) Pitting requires the presence of aggressive anions and is mostly associated with halide ions like chlorides. Hypochlorites are considered to be very aggressive. (Schweitzer, 2007c, p. 14.)

Pits are small cavities which size varies from few micrometers to some millimeters. Pits can grow eventually to perforate the metal completely. Thus, a small area of corrosion can lead to a significant leakage. Pitting takes place when the critical pitting potential E_b is exceeded. The higher the pitting potential is, the better the metal withstands pitting corrosion. Examples of pitting potentials for austenitic stainless steel Fe18Cr-8Ni and titanium in 0.1 M NaCl solution at temperature of 25 °C, are $E_{b, Fe18Cr\text{-}8Ni} = 0.3$ V and $E_{b, titanium} = {\sim}10$ V. This shows the superior resistance of titanium to pitting corrosion in chloride-containing environments. Rise in temperature and rise in aggressive ion concentration both lower the pitting potential. (Landolt, 2007, pp. 312-316.)

Performance of steels in the area of pitting can be measured by utilizing the critical pitting temperature (CPT) and pitting resistance equivalent number (PREN). The higher the PREN, the better the pitting resistance. PREN values can be determined from the contents of chromium, molybdenum and nitrogen and it follows the next formula: PREN = %Cr + 3.3(%Mo) + 30(%N). (Schweitzer, 2007c, p. 14.) When the chromium content exceeds 40 %, pitting no longer occurs. (Landolt, 2007, p. 316).

3.4.5 Crevice corrosion

Crevice corrosion is resulted from local differences in oxygen concentration and stagnant liquid collection. Crevice corrosion is possible in any metals in any corrosive environment. Most susceptible are metals depending on passive oxide film especially with media containing chloride ions. Gaps can be formed inside flanged joints if the material used for gasketing is porous and allows absorption of liquid, for example polymers and elastomers. Definition of a crevice is usually a gap that is large enough to entrap liquid but too small to allow liquid flow. Width is in order from few thousands of a millimeter but not exceeding 3,18 mm. Normally crevice corrosion is formed in gaps in the range of 0,025…0,1 mm. (Eskelinen & Karsikas, 2013, p. 77 ; Schweitzer, 2007c, pp. 10-11.)

In neutral chloride solution, the anodic dissolution of metal is caused by the cathodic reaction of oxygen (Schweitzer, 2007c, p. 11):

anodic $\mathrm{M} \rightarrow \mathrm{M}^{n+} + n\mathrm{e}^-$ (11)

cathodic $\mathrm{O_2} + 2\mathrm{H_2O} + 4\mathrm{e}^- \rightarrow 4\mathrm{OH}^-$ (12)

As this reaction proceeds the dissolved oxygen in the crevice is consumed. But the anodic reaction is not halted in the crevice because the electrons reach outside of the crevice through the metal and interact with oxygen in the solution outside. When there are chloride ions present in the solution this reaction is further intensified. The negatively charged chloride anions are attracted from the bulk solution by the positively charged cations in the crevice. The metal chloride hydrolyzes to produce hydroxide and hydrochloric acid (Schweitzer, 2007c, pp. 10-11.):

$$\mathrm{MCl} + \mathrm{H_2O} \rightarrow \mathrm{MOH} + \mathrm{HCl} \tag{13}$$

The hydrochloric acid destroys the passive film protecting the metal and accelerates the rate of metal dissolution inside the crevice. The cathodically protected outside area of the crevice limits the cathodic reduction inside the crevice. (Schweitzer, 2007c, pp. 10-11.)

3.5 Corrosion of polymers and elastomers

Corrosion of polymers differs from the corrosion of metallic materials in the fact that corrosion rates of polymers cannot be accurately predicted. Polymers are either completely resistant to a corrodent at constant temperatures or they deteriorate rapidly. The deterioration process is caused by either chemical reactions or by solvation of the corrodent into the polymer structure. The attack mechanisms leading to polymeric corrosion can be listed as following (Schweitzer, 2007b, p. 16.):

- disintegration or degradation due to physical phenomena e.g. absorption, permeation
- oxidation, where chemical bonds are attacked
- hydrolysis, where ester linkages are attacked
- radiation
- thermal degradation leading to depolymerization and possibly repolymerization
- dehydration
- any combination of the above.

There is also a form of environmentally assisted cracking that can be observed in certain amorphous polymers like polycarbonate. This is caused by applied stress and environmental reactions and is called craze cracking. Craze cracking leads to coalesce microvoids in the polymer and forms small cracks in the polymer. Crazing does not cause a uniform crack growth and in fact increases the fracture strength of the polymer locally. (ASM International, 2003, p. 347.)

Polymers can be divided into three categories by their structure; thermoplastics, thermosets and elastomers. Thermoplastics can be repeatedly softened for remolding by heating or using a solvent. Thermosets cannot be plasticized by heat because their structure is cured by an irreversible chemical bonding. Elastomers show a high reversible deformation. The structure of a polymer can be linear, branched, cross-linked or networked. (Aromaa, 2005, p. 15.) The different structures are shown in figure 11.

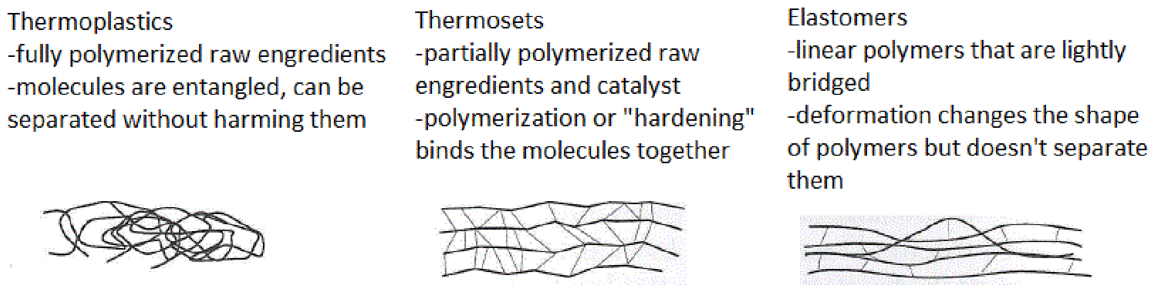


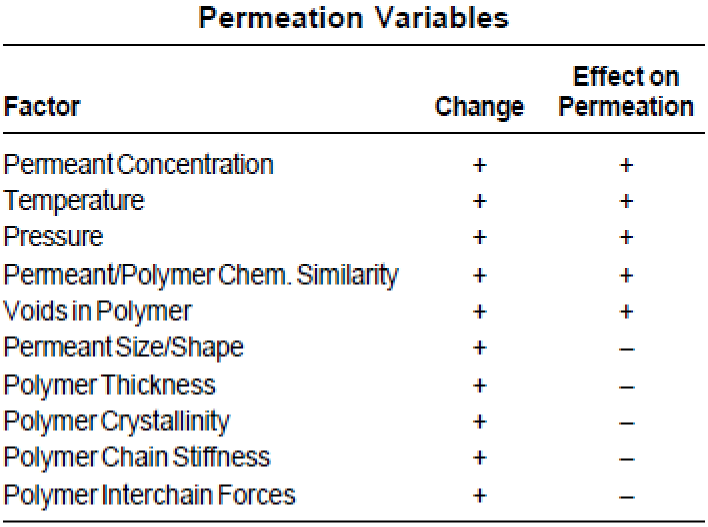
Figure 11. Different structures of polymers affecting their mechanical properties. All of the three polymer categories can be utilized as pipeline materials. The structure affects their manufacturability and operating temperature resistance. (modified, Aromaa, 2005, p. 14.)

Thermoplastics are usually a combination of perfect crystalline phase and an amorphous phase. They can be used between the glass transition temperature and the melting temperature. Below the glass transition temperature, the structure becomes hard and brittle because the polymeric chains cannot move. Above the melting temperature the polymeric structure becomes a viscose liquid leading to a loss of strength. Thermosets do not have a glass transition temperature or a melting temperature. When they are heated they start to become charred. (Aromaa, 2005, p. 15.)

3.5.1 Permeation in polymers

Permeation is a physical phenomenon of molecules migrating through a structure. Molecules in gaseous, liquid and vapor form will permeate polymers. In polymers, this phenomenon is exaggerated compared to other materials like metals due the microvoids or voids between polymers. Permeation causes no direct chemical damage to the polymer. (Schweitzer, 2007a, p. 290) Permeation rate is affected by the following physical and chemical factors shown in table 3. Table 3 also shows the change of factor and its effect on permeation.

Table 3. The change of physical and chemical factors and their effects on permeation rate of chemical media through polymers (DuPont, 2017, p. 2).



Permeation Variables

Factor	Change	Effect on Permeation
Permeant Concentration	+	+
Temperature	+	+
Pressure	+	+
Permeant/Polymer Chem. Similarity	+	+
Voids in Polymer	+	+
Permeant Size/Shape	+	–
Polymer Thickness	+	–
Polymer Crystallinity	+	–
Polymer Chain Stiffness	+	–
Polymer Interchain Forces	+	–

Raise of temperature will increase permeation with liquid permeants due to increase of solubility in the polymer and increased polymer chain movement. Permeability increase may not be linear if permeant is highly soluble in the polymer. This will decrease the diffusion because the concentration gradient will be reduced. With gaseous permeants, the partial pressure difference is the main driving force of diffusion. The permeation rate of many gases follows a linear increase with partial pressure difference. (Schweitzer, 2007b, pp. 9-11.)

The increase of polymer density affects permeation rates because with increased density there will be lesser and smaller voids that allow the bypass of molecules. Increase of thickness of polymer wall will decrease permeation to the power of square. (Schweitzer, 2007b, pp. 11-12.)

Permeation data as diffusion rate against the film thickness and the rate of permeation at different temperatures with a given film thickness for different polymeric materials is available, but careful interpretation of this data is needed for reliable results of material comparison. Usually the data is valid for only the permeant used for testing e.g. water vapor or gases like O_2 or N_2 at atmospheric pressures. Thin film data is typically misleading. Mixtures of gases and liquids can affect permeation rate because mixtures can permeate selectively or differently than pure gases or solutions. Thus, the laboratory data is recommended only for qualitative comparison of different polymer materials. (DuPont, 2017, pp. 3-4.)

In polymer lined pipelines permeation can cause failure of substrate due to corrosion, bond failure and blistering if substrate is less permeable than liner and collapse of liner if permeant vapors are entrapped between liner and substrate. Increasing the liner thickness to combat permeation can cause disadvantages like ascension of temperature difference across the layer. The rise of temperature difference can lead to a bond failure due to increase of thermally induced stress on the boundary. (Schweitzer, 2007b, p. 12.) The collapsing of liner could be a problem with perfluoropolymer linings, like PolyTetraFluoroEthylene (PTFE), that cannot be fusion bonded to the substrate.

3.5.2 Absorption in polymers and elastomers

When the polymeric structure absorbs liquid, it starts to swell. The molecules of the solution integrate between the polymers and force the macro molecules further apart. When the polymeric chains are separated the material becomes softer and more flexible. The absorption also lowers the glass transition temperature and might turn a strong material into weak and rubber-like. (Aromaa, 2005, p. 15.)

The mechanism of absorption relies on the changes in temperature and pressure. When the liner is subjected to higher pressure and temperature the absorption of liquid starts in the polymer. If the pressure drops the liquid can vaporize causing a micropore and eventually a blister. Absorption can be reduced by insulating the substrate which then decreases the temperature gradient across the pipe preventing condensation. Insulation also reduces the rate and magnitude of temperature changes. (Schweitzer, 2007b, p. 13.)

3.5.3 Radiation

The main degradation mechanism of polymers leading to a loss of mechanical performance, a change in appearance and a reduced impact resistance in outdoor application is ultraviolet (UV) radiation. UV light causes photochemical degradation via photons breaking chemical bonds. Short wave UV light is more harmful and a critical threshold for the maximum length of detrimental UV light for each material can be determined. UV-A (wavelengths 400-315 nm) and UV-B (wavelengths 315-200 nm) cause damage to polymers. The shorter UV-B radiation causes severe polymer damage but is absorbed by glass windows. (Schweitzer, 2007b, p. 17.)

Polymers can be coated with a protective paint layer to provide UV protection. This can adversely make a visual inspection of the substrate harder or impossible. (Schweitzer, 2007b, p. 15.)

3.6 Corrosion of ceramics

Ceramics can be divided into two distinct categories; traditional ceramics and modern ceramics. Traditional ceramics contain the likes of bricks, concrete and pottery. They are made out of clay based ingredients that are sintered to rock-like materials in high temperature burning processes. (Aromaa, 2005, pp. 12-13.) Modern ceramics consists of a crystalline compound of metallic and non-metallic elements. According to (Wang, 2012) “The metallic elements are usually aluminum, silicon, titanium, magnesium, and boron. While the non-metallic ones are oxygen, carbon or nitrogen.”

The structures of ceramics can be crystallized, partially crystallized or amorphous. Most modern ceramics are a combination of crystallized phases that are held together with an amorphous phase. (Aromaa, 2005, p. 13.)

Ceramics show high strength in compression, good strength at high temperatures, and excellent oxidation resistance. However, they show qualities like brittleness, low strength in tension, low resistance to thermal shock and to impact loads. These factors are caused by both the crystallized and amorphous phases. In the crystallized phase, the dislocations cannot perform plastic dislocation. The amorphous phases show the same qualities because the plastic deformations are not able to occur because of the non-organized structure.

Deformations take place by flow like in liquids. The chemical reactivity of ceramics depends on the chemical bonds of the substance. The corrosion of ceramics usually is caused by chemical dissolution of the weakest part of the structure. The grain boundaries are usually the easiest to dissolve. (Aromaa, 2005, p. 13.)

3.7 Corrosion characteristics of glass

Glass, otherwise known as porcelain enamel or industrial enamel, is a class of coatings that are fused to a metallic substrate, usually steel or cast iron, at high temperatures (above 425 °C). These enamels are vitreous in nature and can be distinguished from other ceramics as their own group of materials. (ASM International, 2003, p. 750.) Glass is differentiated from ceramics because it is amorphous or does not have a crystalline order (Wang, 2012, p. 216).

Usually an enamel surface contains two different layers; a ground-coat (GC) and a cover-coat (CC). The ground coat contains metallic oxides (cobalt oxide and/or nickel oxide) to improve the adherence to the substrate metal. The cover coat is used to improve the properties, for example corrosion resistance, of the enamel coating. (ASM International, 2003, p. 750.) The GC is porous to compensate for the miss-match of thermal and mechanical properties of substrate metal and the brittle CC. Pores also trap the hydrogen gas induced via the substrate. Figure 12 illustrates a typical cross section of a chemical-resistant glass coating on JIS SS400 carbon steel (bottom layer). (Murakami & Takemoto, 2005, pp. 215-216.)

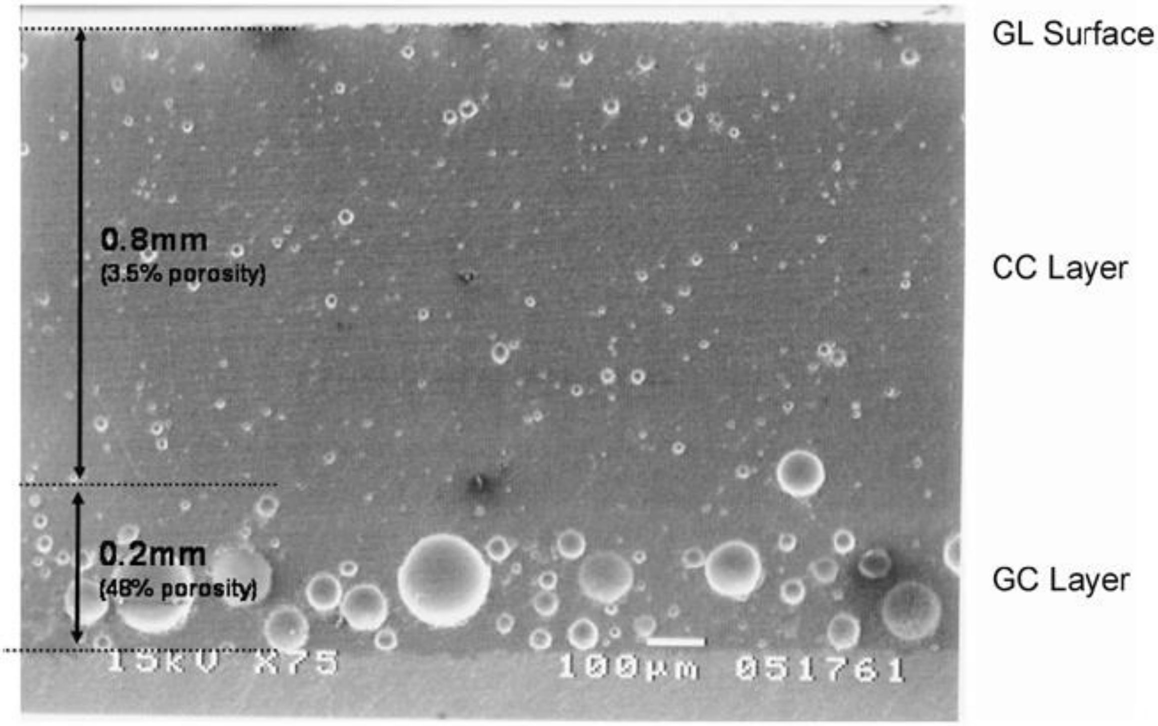


Figure 12. A laser microscope image of a 1 mm thick glass lining on carbon steel showing the porosity of CC and GC layers (Murakami & Takemoto, 2005, p. 216).

The chemical composition of glass lining varies depending on the final end-use application and the substrate material used. The frit (basic material of the porcelain-enamel coating) consists of smelted complex borosilicate glasses. Typical classes of frits are regular, alkali-resistant, acid-resistant and water-resistant. The main components of these frits are SiO_2, B_2O_3 and Na_2O. Their ratios and amounts of other constituents vary depending on the properties wanted from the coating. (ASM International, 2003, p. 751.)

Glasses are usually very corrosion resistant and are usually corroded by hydrofluoric acid and strong alkalis. The destruction of glasses is caused by the environment being able to dissolve the grid structure forming oxide. The structural integrity of glass is affected by the porosity and the micro cracks that lower their strength characteristics because stresses are concentrated on them. (Aromaa, 2005, p. 13). Glass suffers from same qualities as ceramics: brittleness, low strength in tension, low resistance to thermal shock and to impact loads.

3.8 Corrosion of composites

Composites consist of at least two different kinds of materials that are combined to maximize their good properties and minimize the weaknesses. They usually consist of a matrix that binds the reinforcements to form a united structure. The matrix and reinforcements can consist of metals, ceramics or polymers. (Aromaa, 2005, p. 15.) The reinforcements can be fiber or sets containing fiber, particles, foams or laminate materials like wood. Commonly used reinforcements in piping are of the fiber type. Nanofillers are also being studied (Biron, 2014, p. 312.)

The corrosion of composites is affected by the structure of the composite. Basically, all the metallic, ceramic and polymeric destruction mechanisms are possible depending on the composition of the composite. The destruction can be caused by damage to the matrix so the reinforcements are exposed and their destruction dismantles the composite structure. (Aromaa, 2005, p. 16.)

3.8.1 Fiber reinforced polymers

Fiber reinforced polymers or fiber reinforced plastics (FRP) are a widely used composite material for chemical piping. The structure consists of a polymer resin filled with glass, carbon or aramid fibers to ensure the efficient amount of stress handling capability. The resin gives the material its corrosion protective capability and the fibers give the needed mechanical properties. (Schweitzer, 2007b, pp. 19-20.)

The corrosion mechanism of the polymeric matrix follows the same principles as pure polymer materials, but laminates are usually cured in the case of thermoset resins. Improper or inefficient curing will have a detrimental effect on the corrosion resistance of the composite. (Schweitzer, 2007b, pp. 16-17.) The matrix structure is usually a thermoset or a thermoplastic polymer. In the matrix structure for pipes that need to withstand chemical stresses the most used resins are vinyl ester (VE) type. There are different grades of glass types used for FRP (modified, Biron, 2014, p. 319.):

- E-glass: the general-purpose grade that represents more than 90% of the reinforcement fibers
- R- or S-glass with high mechanical performances
- D-glass with high dielectric properties

- C- and ECR-glass with enhanced acid resistance
- AR-glass, alkali resistant, particularly intended
  for the reinforcement of concrete.

The corrosion of polymer composites can occur in the form of the action of the chemicals on the plastic composite, adsorption of the fluid in the plastic, attack on the reinforcement, reduction of the reinforcement/matrix binding, extraction by the fluid of some of the material component (e.g. plasticizers or antidegrants), pollution by the environment, environmental stress cracking (ESC) or electrolytic corrosion when in contact with an electrically conductive metal (Biron, 2014, pp. 435-436).

3.9 The usability of results from lifecycle and failure mechanism analysis

The information gathered in this section of the thesis can be used to evaluate the corrosion rates, recognize possible corrosion mechanisms and to calculate FMEA parameters needed to be able to perform the material selection strategy. It can also be used for improving the monitoring of in-use pipelines at Joutseno plant because the specific failure mechanisms can be determined.

4 RESULTS OF LIFECYCLE AND FAILURE MECHANISMS ANALYSIS OF PROCESS PIPING MATERIALS IN CHLOR-ALKALI PRODUCTION

The piping materials in use were determined from piping and instrumentation diagrams and confirmed with a visual inspection at the factory. Information on the materials currently in use can be used to perform the FMEA and to determine the possible failure rates of materials in real-world process situations. The failure rates will be determined from the data gathered from Joutseno plant's SAP PM data base.

For each chemical pipeline, there is firstly a short section that clarifies the different chemicals contained in the piping and their properties affecting corrosion and health and safety factors of possible leakage or emissions. The failure mechanisms, failure frequency and their impacts to the process and health and safety matters are discussed further in this section of the thesis.

4.1 Chlorine pipeline failure rates and failure types

Molecular chlorine is a strong oxidizing substance that is in ambient pressure and at room temperature in a gaseous form. Chlorine is situated in the halogen group in the periodic table. Chlorine is never found in its pure molecular form in the nature because of its predominantly reactive nature. Mostly chlorine is compounded with alkali metals and with them it forms salts such as NaCl and potassium chloride (KCl). These salts are called chlorides. (European Union, 2007, pp. 4-6.); (Horvath, 1992, p. 4.)

Chlorine is not in itself explosive but it can form explosive mixtures with hydrogen gas and can cause detonation combined with selected hydrocarbons. Chlorine is soluble in water and salt solutions and it partially hydrolyzes in aqueous solutions to form hydrochloric acid and hypochlorous acid. (European Union, 2007, pp. 4-5.)

Molecular chlorine is hazardous to human health and the environment. Chlorine gas causes respiratory system irritation, irritates eyes causing smarting and tearing and in high doses irritates the skin. Being exposed to 5-10 minutes to high doses (100-150 ppm) of chlorine gas can cause a life-threatening case of pulmonary edema. Exposure to extremely high doses

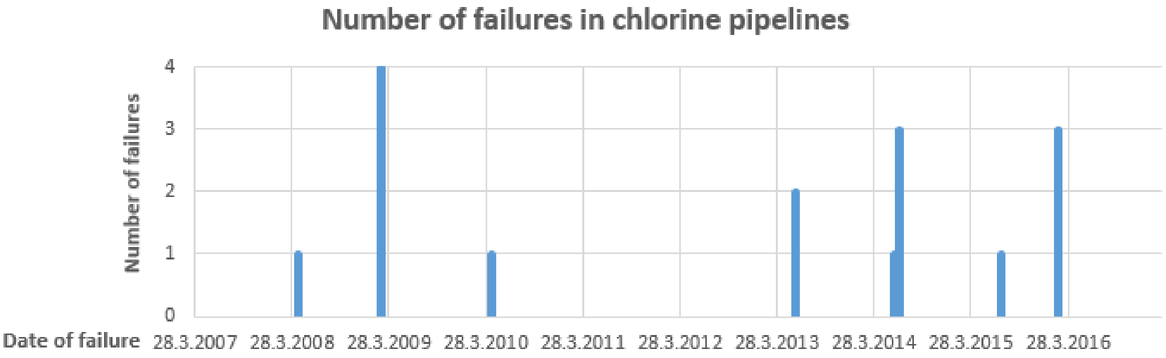
(1000 ppm) can cause mortality with few inhalations of the gas. Chlorine is also very toxic to water based life forms and chlorine can react with organic substances in water and form different kinds of organic chlorine compounds of which many are toxic, do not disintegrate well and accumulate in organisms. (Työterveyslaitos, 2016)

Chlorine is divided into three categories when considering its corrosive behavior. Liquid chlorine, dry chlorine gas and wet chlorine gas. Chlorine gas is considered to be dry when its water content is under 20 mg H_2O/kg Cl_2. (Euro Chlor, 1995, p. 5.) According to the European Union Risk Assessment Report on Chlorine (2007): “Dry chlorine reacts combustively with most metals depending on the temperature. Aluminum, arsenic, gold, mercury, selenium, tellurium, and tin react with dry Cl2 in gaseous or liquid form at ordinary temperatures; steel ignites at about 170°C depending on the physical shape; titanium reacts violently with dry chlorine. Wet chlorine is very reactive because of the hydrochloric acid and hypochlorous acid.”

For safety purposes considering titanium piping approximately 1% of water is required at room temperature (Schweitzer, 2007c, p. 536). With Joutseno plant’s normal operating parameters >0,45 % is considered to be safe according to appendix I (Wellington, 1992, p. 238). At Joutseno plant, the chlorine gas is saturated with water vapor at the cells and is always wet in the piping.

At this moment, the chlorine header pipes are constructed out of ECTFE/VE-glass fiber laminate. There is no secondary gelcoat-layer in the FPR structural layer used with fluoropolymer lining. The adjacent Y-section is made out of Titanium Grade 2 with the bottom section lined with Titanium Grade 7. The following single pipeline to chlorine cooler is constructed out of Titanium Grade 7 to the upward section after the bend and continues as Grade 2 from there on to the cooler. Pipes from cooler to Brink filtration and onwards to hypochlorite and HCl production are made from VE-glass fiber laminate. There is a gelcoat layer 2.5 mm thick in FRP pipelines.

The maintenance data gathered from SAP PM of Joutseno plant shows that there have been eight chlorine piping renewals between the dates 28.3.2007 and 15.3.2017. If the pipeline sections are differentiated, there have been a total of 17 separate piping failures. The majority, 15/17 have been non-destructive testing (visual testing) induced piping renewal. None of the failures have led to a catastrophic chlorine emission. The number of failures and the according dates are depicted in figure 13.



	28.3.2007	18.4.2008	27.2.2009	15.4.2010	1.6.2013	12.6.2014	30.6.2014	19.7.2015	18.2.2016	15.3.2017
■ number of failures	0	1	4	1	2	3	1	1	3	0

Figure 13. The total number of renewed chlorine piping sections at Joutseno chlor-alkali plant, implying a continuous failure rate. This means that individual pipeline sections must be renewed on a failure based time cycle.

From this figure, we can see that the need for chlorine piping renewal is continuous. Additional data of the renewal of pipeline sections can be found from appendix VI. The cycle between renewals is approximately 5 years for ECTFE/FRP piping and >10 years for titanium piping. All the piping failures recorded have been in the direct vicinity of the cell room (from cells to chlorine cooler). The pipeline failures have been limited to piping materials ECTFE/FRP and titanium Grade 2.

4.1.1 Corrosion of titanium in chlorinated environments

The titanium sections used in wet chlorine piping are made from titanium grade 2 and grade 7. Titanium grading according to ASTM go from grade 1 to 39. Grades 1 to 4 are commercially pure (CP) titanium and grades 5…39 are alloys or titanium with added impurities. (ASTM B265-15, 2015.)

The corrosion resistance of titanium is based on a protective oxide layer. This oxide layer forms instantly in the presence of oxygen or moisture. The oxide film of titanium is thin but very stable and it is not affected by erosion-corrosion easily. It has been tested that titanium can withstand sea water velocities up to 27 m/s without damage to its oxide film. (Schweitzer, 2007c, p. 528.)

At Joutseno plant titanium corrosion in piping flanges has been witnessed. According to Lindgren (2017) the chlorine header pipes' Y-jointed connection has suffered from flange leakage during start-ups after maintenance shutdowns. When the flanges have been inspected there have been worm like cavities in the sealing surface of the collar. The corrosion has been limited to the A-side flange of the electrolysis circuit. This points to the fact that electrolysis induced anodic currents have been a factor in the crevice corrosion inducing potential rise.

Laboratory and industrial tests have shown that chemically pure (CP) titanium withstands chloride (wet chlorine and chlorinated solutions) induced corrosion in temperatures up to 95 °C in neutral pH. With the presence of electrolysis induced stray currents titanium is susceptible to crevice corrosion. (Riskin, 2008, p. 80.)

Titanium's passive oxide layer can consist of TiO, Ti_2O_3 and TiO_2. In the presence of oxidizers and under anodic polarization a film of TiO_2 is formed. This oxide film acts a diode allowing cathodic current to flow through and preventing almost all anodic current to the metal. With no external stray currents, in chloride and sulphate solutions of all concentrations at temperatures up to 100 °C titanium potentials stay in the safe range of 1.5-2V. The pH value can go as low as 1.5 and titanium still stays in the passive region. (Riskin, 2008) This can be seen from figure 14.

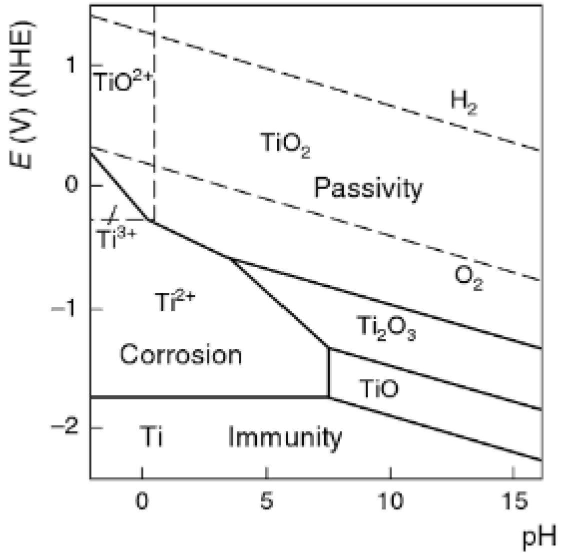


Figure 14. A simplified equilibrium potential – pH diagram of titanium in aqueous solutions at room temperature (Riskin, 2008, p. 80).

Chemically pure titanium (Grades 1-4) is susceptible to crevice corrosion in chloride containing environment. The mechanism behind this is, that when the oxidizing agents are restricted from a small volume area between the flange surface and seal, the metal there becomes more electronegative than the metal still in contact with oxygen from water vapor or condensate. This leads to an electrolytic cell, where the oxygen depleted titanium in the crevice acts as an anode and the bulk of the titanium acts as a cathode. Titanium dissolves at the anode and forms titanium chlorides which hydrolyze into HCl. Following the next reaction mechanisms:

$$\mathrm{Ti} + 2\mathrm{H_2O} \rightarrow \mathrm{TiO_2} + 2\mathrm{H_2} \tag{14}$$

$$\mathrm{Cl_2} + \mathrm{H_2} \rightarrow 2\mathrm{HCl} \tag{15}$$

This lowers the pH to as low as 1 and simultaneously speeds up corrosion as the potential reduces further. Crevice corrosion of titanium can be reduced by alloying titanium with elements like palladium, nickel and molybdenum. (Schweitzer, 2007c, p. 534.)

Titanium grade 7 is alloyed with 0.12-0.25 % palladium to reduce the crevice corrosion susceptibility of chemically pure titanium. Other titanium alloys specially designed to withstand crevice corrosion are grades 9, 11, 12 and 18. Grade 12 is specially created as a low-cost version of alloys 7 and 11 to withstand reducing acids and crevice corrosion. It is alloyed with Mo and Ni. (Schweitzer, 2007c, pp. 526-528.)

Comparing figures 15, 16 and 17. the effects on crevice corrosion range with alloying titanium with palladium or nickel and molybdenum can be seen. These visualizations show the crevice corrosion susceptibility depending on the pH and the temperature with a saturated NaCl solution.

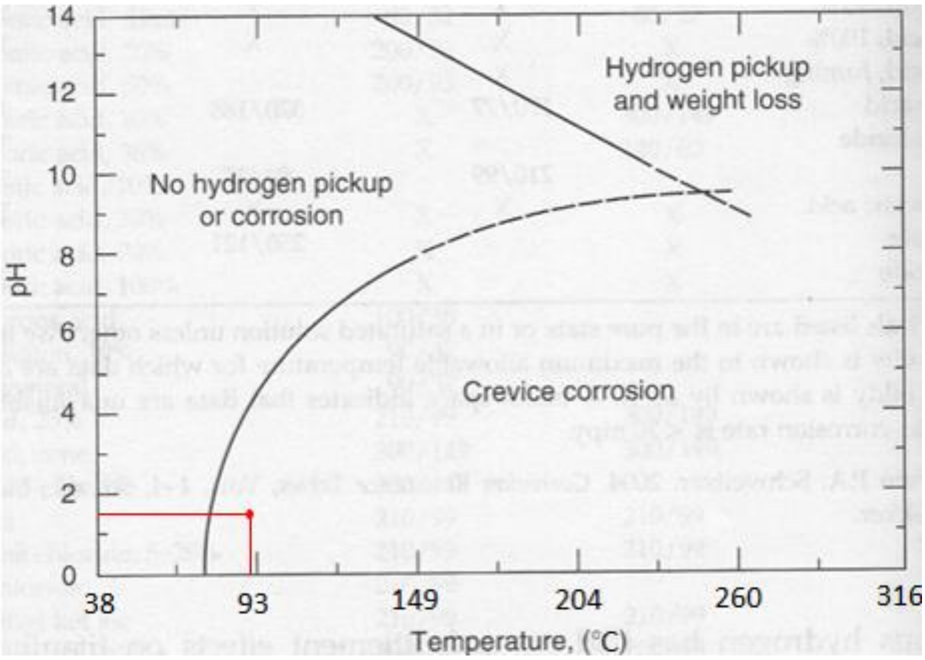


Figure 15. The susceptibility of crevice corrosion of grade 2 (commercially pure) titanium depending on the pH and temperature of NaCl solution with Joutseno plant's parameters marked (modified, Schweitzer, 2007c, p. 534).

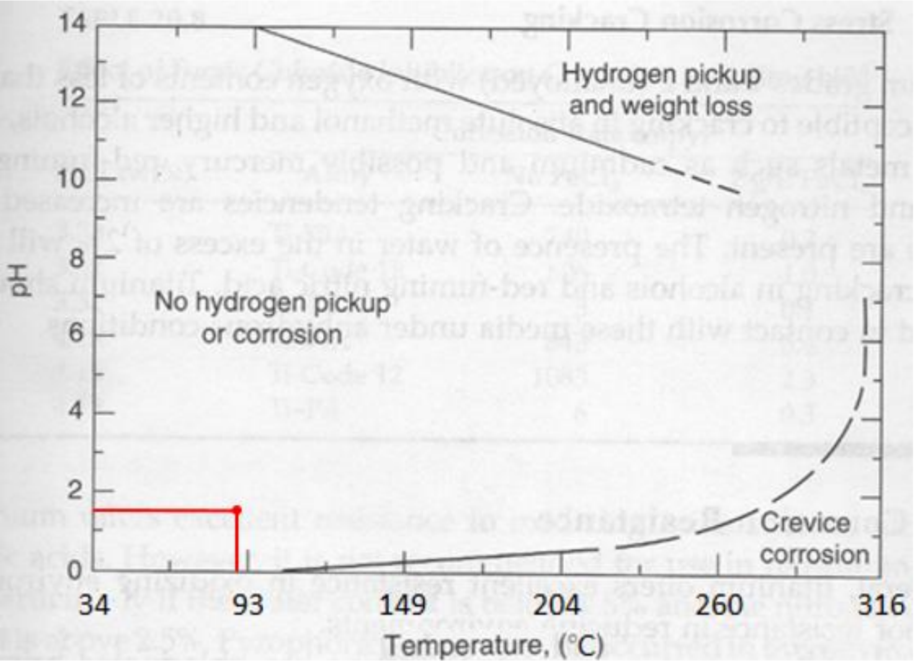


Figure 16. The susceptibility of crevice corrosion of grade 7 (Pd alloyed) titanium depending on the pH and temperature of NaCl solution with Joutseno plant's parameters marked. (modified, Schweitzer, 2007c, p. 535)

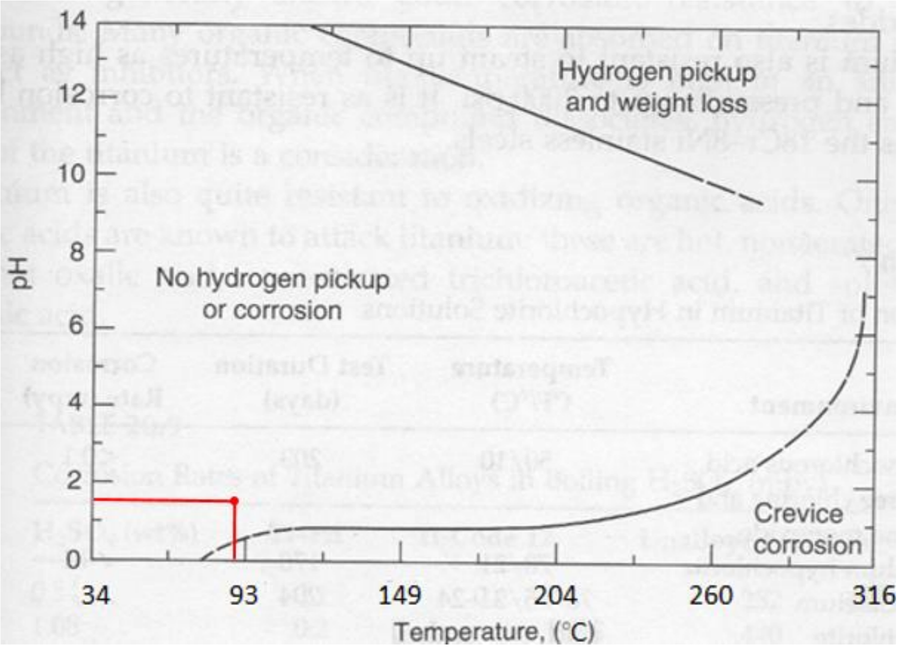


Figure 17. The susceptibility of crevice corrosion of grade 12 (Mo and Ni alloyed) titanium depending on the pH and temperature of NaCl solution with Joutseno plant's parameters marked (modified, Schweitzer, 2007c, p. 535).

The $wRPN_{15}$ value for chemically pure titanium piping used in wet chlorine service is 5,184 which can be considered severe compared to other plausible construction materials. When titanium is alloyed with crevice corrosion inhibiting elements the $wRNP_{15}$ value decreases to 0.288.

4.1.2 Polymer piping destruction mechanisms with wet chlorine gas

At Joutseno plant the piping material used in the cell room chlorine gas header is ECTFE lined VE/ECR-glass fiber (FRP) composite pipe. During regular maintenance inspections (visual inspection period of 2 years) it has been seen that the pipe lining suffers from blistering. The rate of permeation, approximated from SAP maintenance data, through the liner is approximately 4 years when the thickness of ECTFE lining is 2,3 mm. The rate of piping renewal is 5 years.

The permeating substance diffuses through the lining because of the temperature gradient Δt and partial pressure difference of chlorine between the medium and the substrate. The diffusion goes through the ECTFE-embedded glass-fiber mat and stops at the surface layer of FRP which has a higher density than the fluoropolymer. The osmotic pressure caused by the permeating medium starts to form deformations to the lining. The deformations bulge the liner inwards and take the shape of a blister that enlarges over time. Some of the blisters may intersect to form bigger blisters. The effect of permeation inside the lined piping wall is depicted in figure 18.

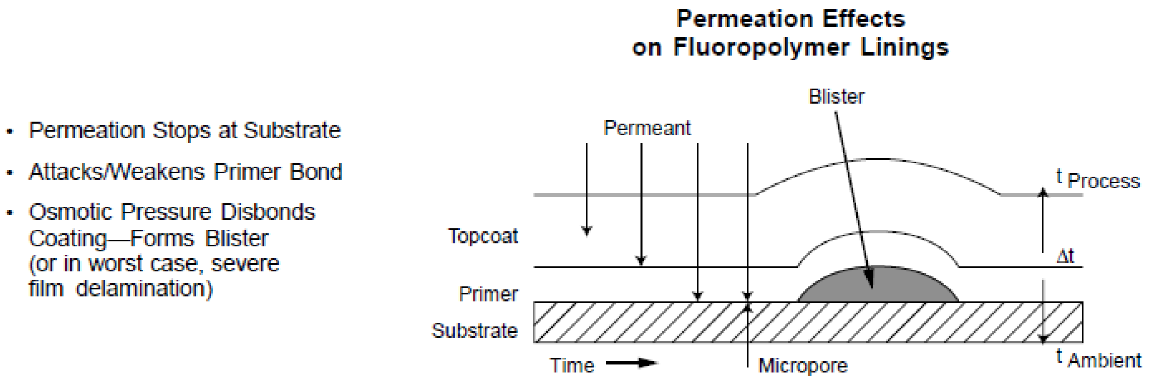


Figure 18. The effect of permeation on fluoropolymer linings to time leading to blistering of the lining (modified, DuPont, 2017, p. 7).

This effect can be seen from the cutouts of piping dismantled in 2016 from the chlorine gas header pipeline. In figure 19 all blisters bigger than 20 mm in diameter have been marked with an X, there are also smaller blisters marked with dots. From this image, we can see that the average count of blisters per meter is 12. The same average amount of blisters continues throughout the dissected pipe. The pipeline lining is also covered in smaller <10 mm blisters. The position of blisters is not affected by the incoming pipe joints from cells or their radial position in the tube. Thus, it is safe to assume that blistering occurs throughout the circumference of the pipe and is not limited to the condensate level in the pipe. Thus, assuring that the main mechanism of destruction is permeation of water saturated wet chlorine gas caused by partial pressure and temperature difference in the lining. A close-up picture of an average sized blister with a diameter of 55 mm is shown in figure 20.

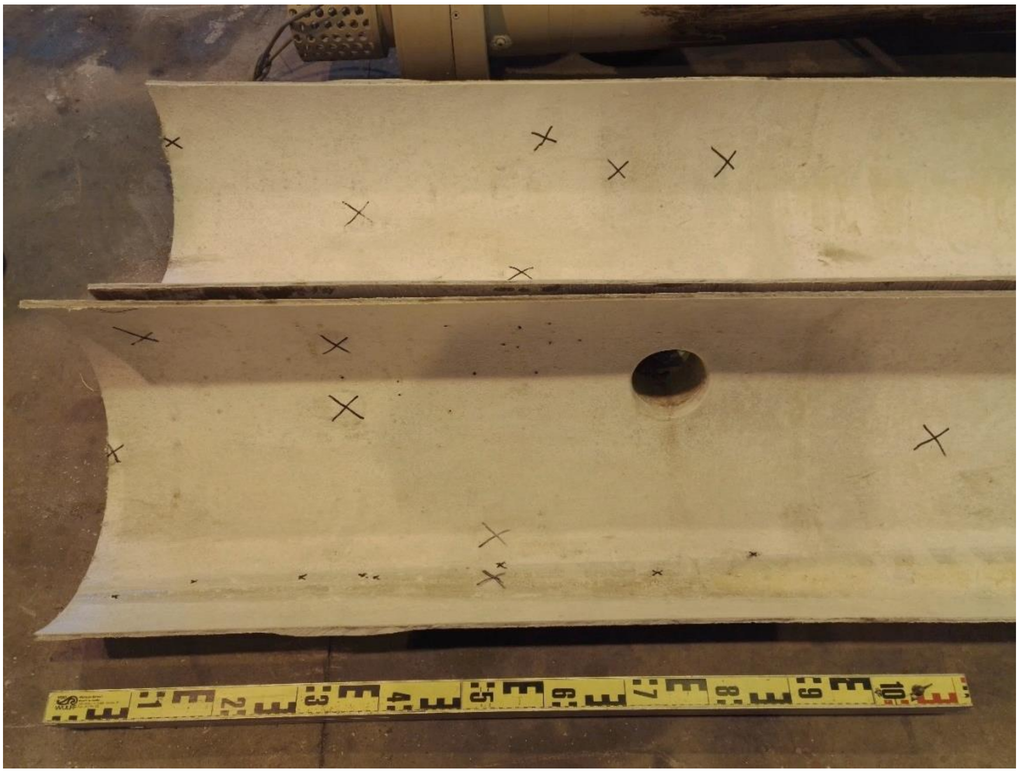


Figure 19. Blisters marked with an X in chlorine header pipe, with a reference gauge of 1100 mm.

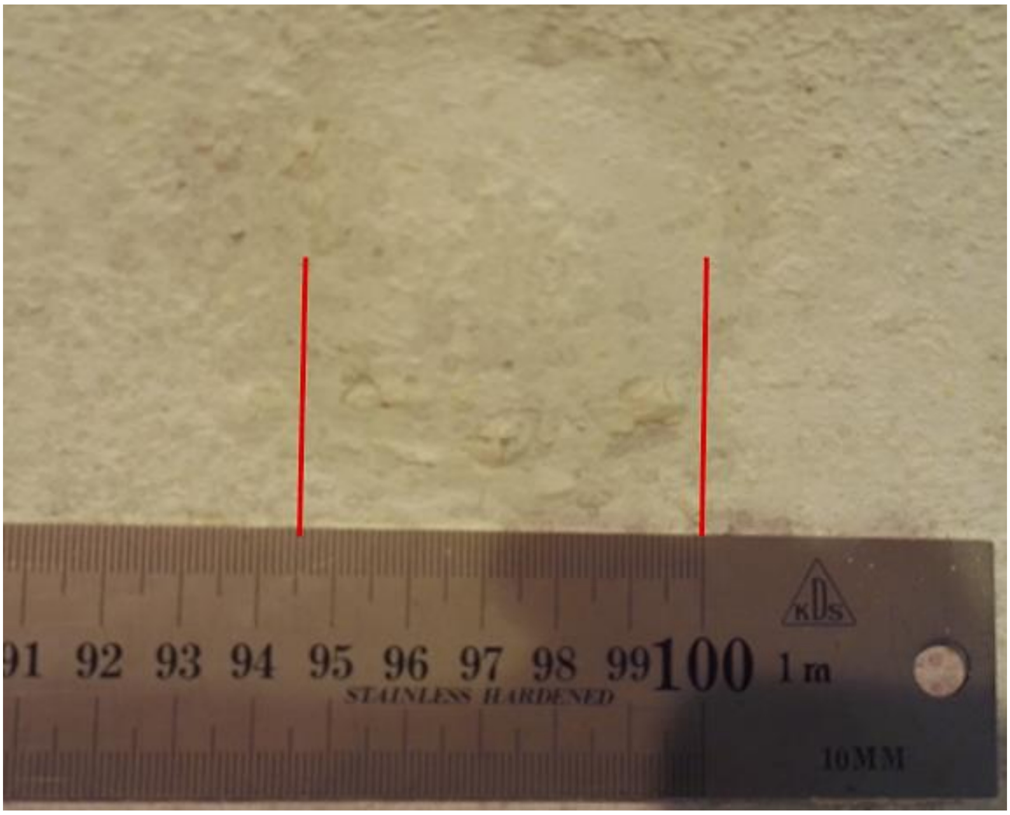


Figure 20. Close-up picture of an average sized blister in ECTFE/FRP chlorine header pipe.

Two of the blisters were dissected and the cutoff surface was polished with grinding paper. The cross-section of one of the samples is shown in figure 21. The different layers of the piping wall are clearly visible and it can be seen, that the permeation of chlorine has advanced through the ECTFE liner and embedded fabric backing used for ensuring adhesion to the resin. The VE-resin filled contact/secondary corrosion layer has been separated from the fluoropolymer lining. The VE-glass fiber structural layer seems unharmed. According to Salakka (2017) the separation of the lining is caused by the higher density of resin and fiberglass composite compared to the fluoropolymer layer. The chlorine solution contained in the blisters is dilute and thus the structural layer could withstand long periods of blistering without noticeable corrosion if the blisters do not rupture due to ductile fracture and let the saturated chlorine gas in contact with it.

Figure 21. The cross-section of a permeation caused blister in ECTFE/FRP chlorine header pipe, showing that the permeation has stopped at the higher density VE-resin layer causing the bulging of the ECTFE-layer.

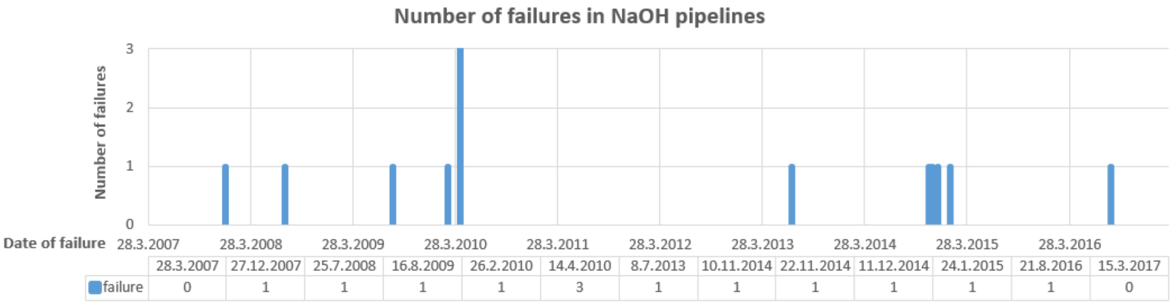
There is no FRP gelcoat used with fluoropolymer lined piping. The lining has bulged 6 mm outward from its original position but has not yet suffered from cracking. It can be assumed that the rate of permeation due to microvoids only increases within the polymer because of tensional stress pulling the polymers further apart. This stress caused by the expanding gas between the layers eventually leads to cracking. The $wRPN_{15}$ value for ECTFE-FRP composite piping used in wet chlorine service is 0,54.

4.2 Caustic soda pipeline failure rates and failure types

Caustic soda (NaOH) is a highly alkaline (100 % NaOH, pH=14) substance. It is composed of sodium and hydroxide ions. Sodium hydroxide solution is a colorless liquid. It is toxic if ingested. Contact with NaOH may severely irritate skin, eyes, and mucous membranes. It is also corrosive to metals and tissue. (PubChem, 2017.)

Caustic soda is used in variety of industries, mainly by the CPI (chemical process industry), petroleum refining, alumina production, pulp and paper, waste disposal and food production industries as a reagent or pH adjusting agent. (Rebak, 2006, pp. 3-5.)

The Joutseno chlor-alkali plant's cell room caustic soda pipelines are constituted of PP (polypropylene) with structural FRP layers for mechanical strength and leakage protection. There has been a total of 13 separate piping failures in caustic soda pipelines between the dates 28.3.2007 and 15.3.2017. All the failures recorded have been in polypropylene (PP) lined FRP piping. The number of failures and the dates of failure are depicted in visualization 22.



	28.3.2007	27.12.2007	25.7.2008	16.8.2009	26.2.2010	14.4.2010	8.7.2013	10.11.2014	22.11.2014	11.12.2014	24.1.2015	21.8.2016	15.3.2017
🟦 failure	0	1	1	1	1	3	1	1	1	1	1	1	0

Figure 22. The number of caustic soda pipeline failures at Joutseno chlor-alkali plant, of which all are different sections of piping. This implies that the timeframe of recurring failures is higher than 10 years.

All of the failed sections can be differentiated and thus the lifecycle of PP/FRP piping is >10 years. The failure mechanism is ageing of PP caused by NaOH solution which leads to the material turning brittle, causing cracks in weld seams and other joints. The continuous failure rate implies that a large section of piping in the cell room has reached the end of its lifecycle and needs replacement. The lifecycle of PP/FRP piping is estimated to be approximately 25-30 years based on the fact that there are large portions of first-installation pipes from the construction phase of the plant in 1983 still in service today.

Altogether 11 out of 13 failures have caused a direct leakage. All of the failures leading to direct leakage of NaOH solution have been minor so the solution has crystallized and formed a "cake" that prevents further leakage. None of the failures have led to an unplanned shutdown of the plant. Similar failures can be seen in brine, sodium chlorate and sodium hypochlorite pipelines. A leakage caused by crevice corrosion in sodium chlorate pipeline is depicted in figure 23.

Figure 23. A minor leakage caused by crevice corrosion, that has crystallized and formed a “cake” that prevents further leakage in sodium chlorate pipeline.

The ageing of PP in caustic solutions is first seen as leakage from joints or welded seams. Two of the failures were contained inside the FRP layer and can be seen as de-layering and color transformations. This type of a failure is depicted in figure 24, which shows a leaking piping socket.

Figure 24. Delayering and color transformation in failed PP/FRP pipeline containing caustic soda.

Due to the age of piping, most of the construction phase-installed pipelines suffer from UV-radiation induced resin degradation at the outer layer that leaves visible glass-fiber mats to the surface. This has not caused any recorded acute failures in the pipeline, but is a situation that must be dealt with to prevent further failures. This type of failure is depicted in figure 25.

Figure 25. A UV-radiation caused failure in the outer layer of a NaOH PP/FRP pipeline.

Because of the recorded failure timeframe of >10000 days, the failure not leading to unplanned shutdowns with an easily contained leakage and high detectability of failures with visual inspection of the substrate, the $wRPN_{15}$ evaluation of PP/FRP piping in the cell room returned a low value of 0,09.

4.3 Brine pipeline failure rates and failure types

Feed brine is a purified (removal of calcium, magnesium and strontium etc.) saturated solution of NaCl and water. The concentration of NaCl in the solution is between 260…280 g/l. The depleted brine leaves the cells containing chlorine, sodium hypochlorite and sodium chlorate and has a pH value of 4. HCl is added to depleted brine before the anolyte tanks to dissolve the chlorate and react with hypochlorite to release chlorine. HCl is also used to adjust the pH of the solution to 2…2,5 for chlorine removal. Most of the chlorine is released from brine in anolyte tanks. The solution is then fed to chlorine removal tank. In chlorine removal tank the chlorine gas is removed with a vacuum process. The brine contains <10 ppm of chlorine after chlorine removal. The pH of brine is raised to 6 for the total removal of chlorine chemically with activated carbon filtration. Because of the high temperature of solution (max. 90 °C), the hazardousness of the reagents from cells and the acidity of solution, brine is considered hazardous to humans and thus catastrophic leakages of piping must be avoided.

The feed line coming from brine heater to cells is made from PP/FRP laminate. The feed header and feed pipes are also made from PP/FRP. The end-section before the cell is made from Ti gr. 2. The depleted brine and chlorine T-branch separator pipe exiting the cells is made from titanium Gr. 2. The depleted brine dropdown pipes connected to the T-branch are made from PTFE lined carbon steel with an epoxy coating on the outer surface. The header pipes for depleted brine are also made from PTFE/carbon steel. The pipeline leading to anolyte tanks is made from Ti gr. 2. The line from anolyte tanks to pH adjustment is made from Ti gr. 2.

In brine pipelines, there have been a total of 13 failed sections when combining both depleted and saturated brine. The failures and according dates are depicted in figure 26.

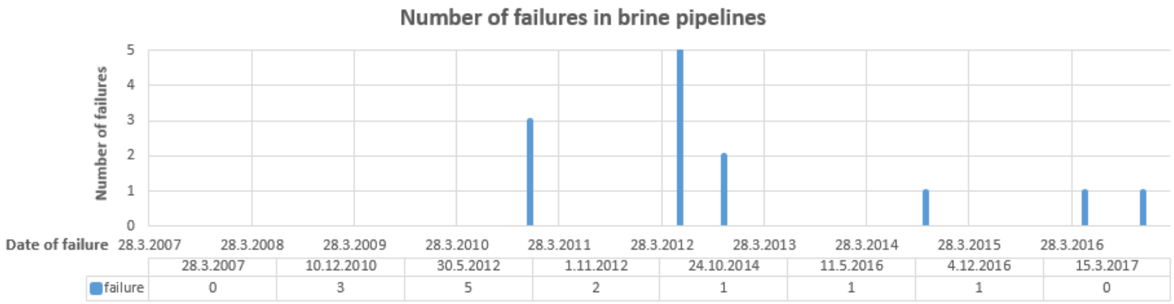


Figure 26. The number of brine pipeline failures at Joutseno chlor-alkali plant, of which all are different sections of piping. This implies that the timeframe of recurring failures is higher than 10 years.

The majority of failures (12/13) have been in the depleted brine dropdown and header pipelines. There has been one spot leakage occurring in a PP/FRP feed brine line just before the cells. The leakage of PP/FRP feed line has been caused by thermal expansion induced mechanical stresses causing the pipeline weld to fracture. None of the titanium lines have suffered from corrosion in the timeline of the gathered data.

The depleted brine dropdown pipes and headers are made out of PTFE lined steel. The main destruction mechanism is permeation of chloride solution and chlorine gas through the liner. The pipes have weep holes that let condensate and trapped gases between the liner and substrate to flow out. It can be observed from these weep holes that the carbon steel is corroded by the permeate leaking through the liner. A leaking weep hole in PTFE/steel pipe is depicted in figure 27.

Figure 27. Permeate from depleted brine PTFE/steel pipeline's weep hole at the bottom of a dropdown pipe from electrolysis cell has corroded the steel substrate.

The lifespan of brine feed pipes is >10 years because there has only been one mechanically damaged pipeline section. The depleted brine header pipes have suffered failures in 2012 and 2016. There have been failures detected in header and dropdown pipes in 2016. Thus, the failure rate of PTFE/steel pipeline is approximated to be four years.

Only the depleted brine dropdown and header pipes were taken into consideration in FMEA. The $wRPN_{15}$ value of PTFE/steel pipelines is 0,72. The value is relatively low even that there have been numerous failures in the pipelines. This is because the failures have been easily foreseeable, have caused no adverse effects to the process or human health and are easy to detect with visual inspection of the pipeline outer surface.

4.4 Hydrogen pipeline failure rates and failure types

Pure molecular hydrogen (H_2) is in ambient atmosphere (1 atm, 20 °C) in a gaseous form. It is lighter than air and forms a flammable mixture with air at a relatively wide range (4…75

%). Because hydrogen molecules are very small, low viscosity and high diffusivity the gas will easily escape containment the likes of piping with flanges, if not properly assembled. Hydrogen has a relatively high auto-ignition temperature of 560 °C, but its low ignition energy of 0,02 mJ makes it a very flammable substance. A pinhole type leak can cause the hydrogen gas to self-ignite when it comes to contact with air. Hydrogen is very hard to detect with human senses because it is an odorless and a colorless gas. Hydrogen is not rated as a toxic chemical for humans but it can cause asphyxiation if the air in the room has been displaced by hydrogen. (Pasman & Rogers, 2010, p. 698; Messaoudani, et al., 2016, p. 17514.)

Hydrogen can have adverse effects on the material properties of pipeline systems. Especially metallic materials are susceptible to hydrogen induced embrittlement that can cause a loss of strength and a catastrophic crack formation when coupled with stresses. Also, non-metallic materials can lose mechanical properties due to the same effect. These adverse effects occur in long term exposure and a material selection strategy is in order to combat them. (Pasman & Rogers, 2010, pp. 698-699; Messaoudani, et al., 2016, pp. 17514-17515.)

Hydrogen embrittlement is the only chemical failure mechanism associated with hydrogen gas at Joutseno plant’s maximum operating parameters of pressure 0,5 bar and temperature of 90 °C. The affinity for hydrogen embrittlement is highest at room temperature. (Øvland & Hansen, 2007, p. 2.) The possible mechanism of hydrogen damage in various temperatures and pressures are depicted in appendix II.

The main factors that are known to affect hydrogen embrittlement are the following (Messaoudani, et al., 2016, p. 17516):

- hydrogen concentration
- pressure and temperature of the environment
- exposure time
- stress state
- mechanical properties
- microstructure of the material
- surface conditions
- and the nature of the crack front of the material.

The most valuable quantitative measurements to determine the susceptibility of a hydrogen induced embrittlement of a metallic material are fracture toughness and fatigue strength (Messaoudani, et al., 2016, p. 17516). For steels in hydrogen service the maximum allowed hardness is 22 HCR (Hardness Rockwell C) and the equivalent tensile strength is 800 MPa. Because the welded sections of pipelines are often harder than the base material it may be necessary to limit the maximum strength of the steel to 500 MPa. (European Industrial Gases Association, 2004, p. 7.)

Hydrogen does not dissociate in polymers but is absorbed as a diatomic molecule. Hydrogen is inert in the presence of most polymers. Polymers are not known to be affected by hydrogen embrittlement in ambient pressure and temperatures. (Barth, et al., 2013, p. 11.)

The pipeline materials used with hydrogen gas at Joutseno chlor-alkali plant are:

- PP/FRP in hydrogen pipelines from cell and the header pipes
- AISI 316L in the line from headers to hydrogen cooler
- Polyvinyl Chloride (PVC)/FRP from H_2 cooler to the suction fan leading to the atmosphere. The suction fan is needed for the inertization of the pipelines with nitrogen for shutdowns of the factory
- S235 structural steel from cooler to the HCl burners.

The hydrogen gas coming from cells is saturated with water vapor. Because the hydrogen gas is bubbling through the liquid phase at the cathode some of the NaOH in the cell is transferred with the water vapor to the pipeline. The condensate formed in the pipelines is a dilute solution of NaOH in H_2O. Between the dates 28.3.2007 to 16.3.2017 there have been no recorded pipeline failures in hydrogen piping. This shows that water saturated gaseous hydrogen and the dilute NaOH condensate are not highly corrosive substances at pressures <10 bar and temperatures <100 °C when using “basic engineering” materials the likes of PP and AISI 316L. There are although failure mechanisms linked to both substances that can cause a catastrophic failure in materials if the effects of corrosion are not considered in material selection phase.

Because there have been no recorded failures the FMEA for hydrogen pipelines was left out of scope for the “Results of lifecycle and failure mechanisms analysis of process piping materials in chlor-alkali production”. A FMEA will be conducted for proposed pipeline materials in the material selection section of this thesis.

4.5 The utilization of results from lifecycle and FMEA in material selection strategy

The results of lifecycle and failure mechanism analysis will be used in determining the possible failure mechanisms of material groups for different media and the evaluation of pipeline wRPN values for different materials needed for the rating of materials against the demands and wishes. The lifecycles of materials will also have an effect in LCC calculations.

5 SELECTING OPTIMAL MATERIALS FOR PROCESS PIPING IN CHLOR-ALKALI MANUFACTURING

The basic demands of piping containing hazardous chemicals, are determined by the directives and legislation applied in the country in question. In Finland, the supervisory organization for the safety of operations of hazardous chemical producing plants is Tukes (Turvallisuus- ja kemikaalivirasto). According to Tukes (2017) guideline for the safety requirements for chemical piping “Kemikaaliputkistojen turvallisuusvaatimukset” all chemical piping containing hazardous substances follow the government decree for the safety requirements of industrial handling and storage of hazardous chemicals 856/2012 (Valtioneuvoston asetus vaarallisten kemikaalien teollisen käsittelyn ja varastoinnin turvallisuusvaatimuksista) and thus are under the effect of the pressure equipment decree 1548/2016 (Valtioneuvoston asetus painelaitteista).

All of the pipelines contained in the scope of the thesis are classified by the degree 856/2012 as hazardous substances. The pipelines at Joutseno chlor-alkali plant’s cell room divided to classes by the media contained in them as following:

- Class I
    - Chlorine
    - Hydrogen
- Class II
    - Caustic soda
    - Brine

Thus, a declaration of conformity must be requested from the producer of pipelines by the plant operating staff. All othe material prices were requested from suppliers to constructions that comply with the regulations. The pipeline vendors must take into account all of the material parameters so that they comply the requirements (e.g. required thickness of pipeline regarding to material parameters like yield strength to comply with required pressure rating).

There are differences in a specific material selection strategy for pipelines containing hazardous chemicals when compared to a universal material selection strategy. Universal strategies emphasize on matters the likes of feel and look of the material because most of the material selection literature focuses on the design of consumer products. With process pipelines this part of material selection can be left out of scope. The failure mechanisms analyzed in a universal strategy emphasize on mechanical properties whereas with highly corrosive substances the corrosion characteristics are of main importance. Still the mechanical properties must also be investigated in a pipeline selection strategy.

Because of the highly controlled subject of pipeline conformity in plants producing hazardous chemicals, there are numerous standards and guidelines for the manufacturing of pipelines of different material groups. To reduce the time taken by material selection strategy the pipeline material properties for mechanical demands and the proper design of the pipelines are left for the pipeline manufacturers to confirm. Whereas a universal strategy is focused on the safety of users, a pipeline selection strategy must also take into consideration the process usability because pipelines are always a key process equipment needed for the production of chemicals.

The first step in piping material selection is the determination of demands the piping material must withstand and the wishes the end user wants from the construction (e.g. suitability of standardized piping brackets, compatibility of pipeline with visual inspection). Some of the demands come directly from legislation and some come from the usage environment and end user. The demands from end user usually consists of an economic, process safety and usability standpoints and can include environmental and social demands. The second step of material selection for process piping is screening the compatible materials using material and chemical medium compatibility charts. Minimum of two charts will be used for assuring the quality of results. There is also the fact of acceptable engineering costs and availability taken into consideration.

Thirdly the material pool must be reduced by exterminating unsuitable materials from further study. Evident unsuitability takes into consideration the unacceptably high price of materials and the availability of materials in the local area. Materials are also exterminated from further study by measuring their properties to a set of requirements. Requirements of materials are divided into fixed and flexible classes. Fixed requirements are used for the elimination of totally incompatible materials. For example, if the chemical media contained by the piping is dry chlorine gas and it is a well-known fact that titanium reacts explosively with it, titanium is eliminated from further investigation on that basis.

Flexible requirements need a subtler approach like referencing CASE studies and scientific studies in approximating material compatibility with the process in question. The knowledge of the production process is also needed in this phase of extermination. E.g. the quality of end products need to be also taken into consideration. For example, if it is known that a metallic material has a high iso-corrosion rate of 0,1 mm/a in a specified media concentration at a specified temperature, the effects of corrosion products transferred to the end-product must be taken into consideration. If the quality of end-product is deteriorated, the material must be exterminated from further study. (Ali & Edwards, 2013, pp. 6-7.)

The fourth step is conducting a FMEA based on a literary review and expert interviews for the materials still being studied. Failure mechanism analysis can reveal unforeseen qualities of materials that could lead to a catastrophic failure of pipeline in a specific environment. It is also needed to ensure the process, human and environmental safety. Materials that show qualities of catastrophic failures are excluded from further study. It is not mandatory, but plausible to also conduct a research of previous pipeline failures in the same environment to detect possible failure mechanisms. The FMEA analysis reveals the material properties affecting the lifecycle of pipeline materials and is needed to carry out the comparison of material properties. The results of FMEA by executing equation 2 are depicted as weighted RPN values which can be used in determining the materials' compatibility with a specific environment.

The fifth step is to calculate the LCC costs of materials. LCC cost calculation will be conducted with equation 3 by utilizing the data of pipeline operating life from FMEA, the costs of "turnkey" pipeline materials from vendors and additional information like the current interest rate gathered from different sub organizations of the company in question. LCA analysis will be conducted by comparing the ecological indexes of materials. These EI values can be found from literature for different materials.

The sixth step is the weighted grading of material properties in comparison to the demands. Weighted grading will be conducted by allocating different weights (that all equal to 1), determined by the demands to the normalized properties. The material that receives the highest grade is the optimal material. The flow of the material selection process specifically formed for pipeline material selection is depicted in figure 28.

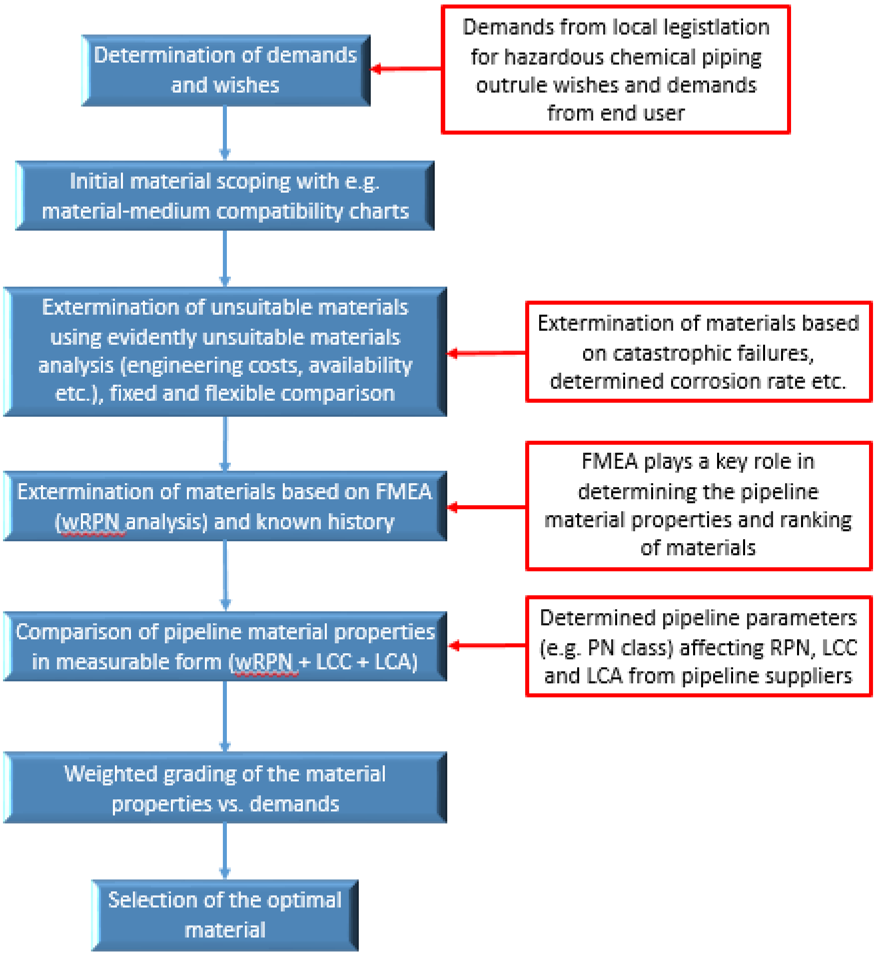


Figure 28. Developed material selection process diagram for piping material selection with text boxes highlighting the aspects of pipeline material selection strategy compared to a universal material selection strategy.

The optimal material selection for different media at Joutseno chlor-alkali plant’s cell room follows the principles determined previously. Firstly, there is a short section of the process parameters in the pipeline in question. Then, the material selection process is applied and finally the optimal material is chosen.

5.1 The optimal materials with wet chlorine

Chlorine gas pressure is kept at 1200 mmH_2O in the cell. This is also the pressure inside the piping in normal operating conditions. The maximum pressure of chlorine is 5000 mmH_2O

and is controlled by a bursting disc. Piping manufacturers test and give pressure ratings for their piping according to local laws and standards. A pressure class of minimum of PN10 is suitable for use in wet chlorine piping because the piping can also be subjected to vacuum in plant maintenance shutdowns when the pipelines are vented.

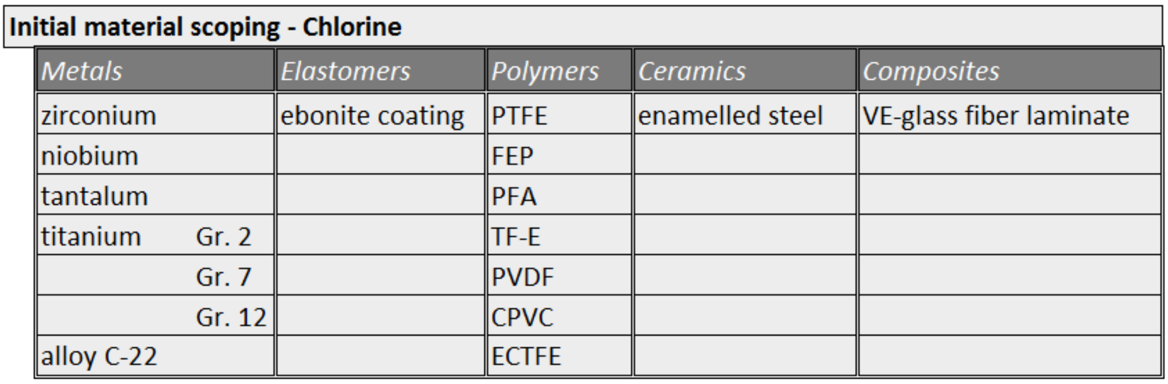
The temperature of wet chlorine gas from cell room to cooling tower is 85 ± 2 °C. After cooling the temperature is 25 °C. The maximum temperature after cooling is 35 °C and is controlled by a thermometer that controls the lockdown of cell room. Minimum temperature of chlorine is set to 15 °C because under operating pressure conditions chlorine gas will start to crystallize into chlorine hydrate and clog the cooler and pipes.

From this initial data, we can gather the demands affecting the material selection process that piping materials for wet chlorine piping must fulfill:

- minimum pressure class of PN10
- withstands temperature of maximum 90 °C
- material is compatible with wet chlorine at all process parameters
- acceptable engineering costs and availability.

Through the search of material selection literature, material-medium compatibility charts and CASE-examples of chlorine piping materials the materials shown in table 4 were chosen in the initial screening phase of the material selection process. By the demand of the end user all elastomers, polymers and ceramic piping materials are of a laminate nature and act only as a corrosion barrier layer in the piping with a structural reinforcement for leakage protection.

Table 4. Materials that fulfill the initial demands for wet chlorine gas piping.

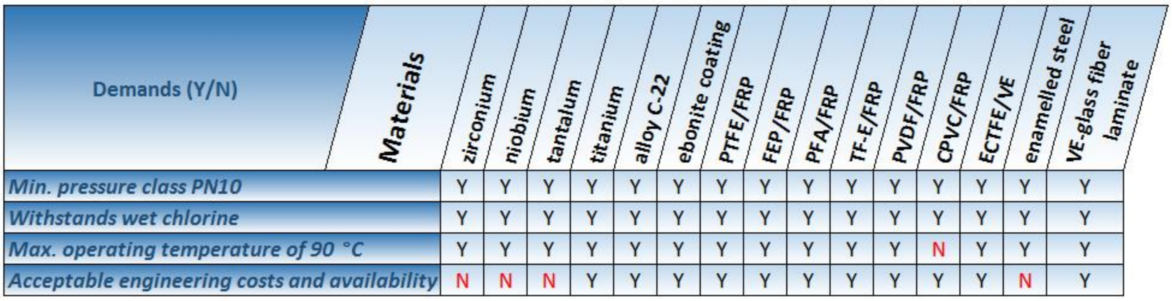


Initial material scoping - Chlorine

Metals	*Elastomers*	*Polymers*	*Ceramics*	*Composites*
zirconium	ebonite coating	PTFE	enamelled steel	VE-glass fiber laminate
niobium		FEP		
tantalum		PFA		
titanium Gr. 2		TF-E		
Gr. 7		PVDF		
Gr. 12		CPVC		
alloy C-22		ECTFE		

First a fixed material extermination was conducted based on the process parameters the process piping must withstand or fulfill, local engineering material cost approximation and availability of the material. The table 5 shows the results that were formulated.

Table 5. The results of fixed material extermination for chlorine piping.



Demands (Y/N) / Materials	zirconium	niobium	tantalum	titanium	alloy C-22	ebonite coating	PTFE/FRP	FEP/FRP	PFA/FRP	TF-E/FRP	PVDF/FRP	CPVC/FRP	ECTFE/VE	enamelled steel	VE-glass fiber laminate
Min. pressure class PN10	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Withstands wet chlorine	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Max. operating temperature of 90 °C	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	N	Y	Y	Y
Acceptable engineering costs and availability	N	N	N	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	N	Y

Based on the fixed extermination, the following materials were exterminated from further investigation:

- CPVC, chlorinated polyvinyl chloride, because of limited temperature resistance of 80 °C with wet chlorine gas without safety allowance (O'Brien, et al., 2005, p. 767).
- Tantalum, because of the controversies regarding the trading of tantalum; tantalum is not traded in pure form, only tantalum ores. This causes a high fluctuation in negotiation prices and in the price of end products. Also, the demand varies annually which causes high volatility in tantalum prices. The price of tantalite ore rose from 100.38 €/kg in 2009 to 312.30 €/kg in 2011. The price of tantalite ore is at current USD/EUR exchange rate in 18.4.2017 at 118.97 €/kg. It is also estimated that the known tantalite mines will be depleted in the following 50 years, which is bound to increase the price of tantalum in the future. (Metalary, 2017a)

- Zirconium, because of the high price of the metal at approximately 1 858.96 €/kg at the USD/EUR exchange rate in 20.4.2017 (CRC, 2013, p. 42). Zirconium tubes are usually used in heat exchanger applications and thus pipe sizes bigger than outside diameter 38.1 mm are hard to find on the market (Sandvik, 2017).
- Niobium, because of limited availability (two mines in the world in 2010) caused by high volatility of production and high cost variation based on international markets and demand (Business Insider, 2010). The price of niobium ore is at current USD/EUR exchange rate in 18.4.2017 at 38,86 €/kg (Metalary, 2017b).
- Enameled steel was not found available from suppliers. Thus, the cost factors and availability is unknown and the material is excluded from further study. Glass lined steel is also typically used in small diameter (max. 200 mm) application due to the fragility and the low mechanical strength. (Riskin, 2008, p. 56.)

All the metallic materials excluded from further study can also be used in alloying other metals, as thin surface layers and in composites, but none of them were found available in pipe form from suppliers at the time of the thesis.

The next step was the flexible extermination of materials based on their attributes and the environmental corrosion factors. Based on corrosion theory and FMEA sections of this thesis the failure mechanisms of different materials based on the atmospheric and parameter conditions in the pipeline in question can be determined. The following factors were considered for chlorine piping materials:

- the possibility of crevice corrosion, especially in passively protected metal flanges
- unacceptable uniform corrosion rate, especially in metallic alloys
- unacceptable permeation rate, especially in polymer linings
- softening of material leading to blisters and loss of mechanical properties, especially in elastomer linings.

The crevice corrosion vulnerability of commercially pure titanium gr. 2 in sodium chloride solution in Joutseno plants’ operating parameters is shown in figure 15. Crevice corrosion leads to an emission of chlorine gas and is impossible to detect without removing pipeline sections for a visual inspection of pipe collars. A chlorine emission cannot be tolerated and thus titanium gr. 2 is excluded from further study.

For alloy C-22 the uniform corrosion rate in 3000 ppm Cl solution adjusted to pH 1.5 (T = 95 °C) with chlorine and HCl gas (T = 90 °C) bubbled though the liquid is 0,0229 mm/y for the liquid phase and 0,1125 mm/y for the vapor phase. This would limit the maximum service life of a 2 mm thick walled pipeline to 3 years. There is also a high risk of crevice corrosion in pipeline flanges in tests done with 0.5 M NaCl solution at 90°C which cannot be allowed in chlorine header pipes. (Haynes International, 2017.) Thus, alloy C-22 is excluded from further study.

For permeation, the data is shown as a rate of 1/*t.* The calculations take into consideration the thickness of lining and pressure so permeation rate is shown as a relative figure and does not apply differently to changes in liner thickness. The permeation rate calculations are always made on a case-by-case basis and the values attained can differ so the comparison of different sources is difficult if comparable results in a set environment want to be obtained. Therefore, results of a single study can be used as a basis for permeation rate approximation of materials. The figure 29 shows comparable permeation rates of different fluoropolymer linings and is used as a basis for comparing the permeation rate of chlorine in materials to known permeation failure rate of ECTFE. All the approximations are based on a lining thickness of 2,3 mm, except tetrafluoroethylene (TF-E) with a lining thickness of 4,5 mm. The rise in temperature increases the permeation rate.

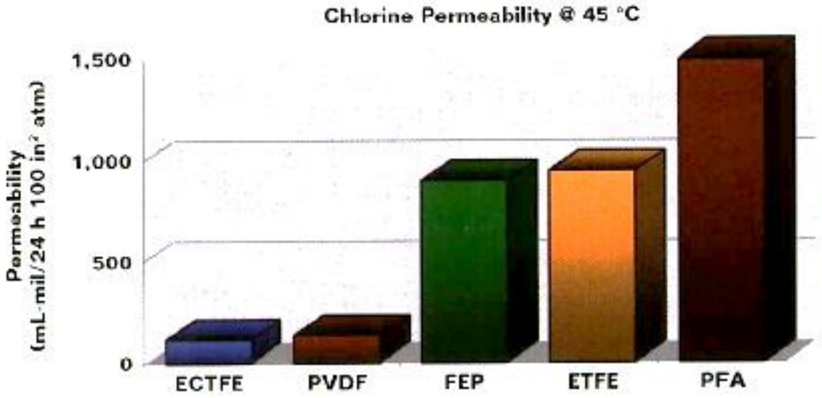


Figure 29. The permeation rates of chlorine with different fluoropolymer linings at 45 °C (Argasinski & Loosbergh, 2009, p. 48).

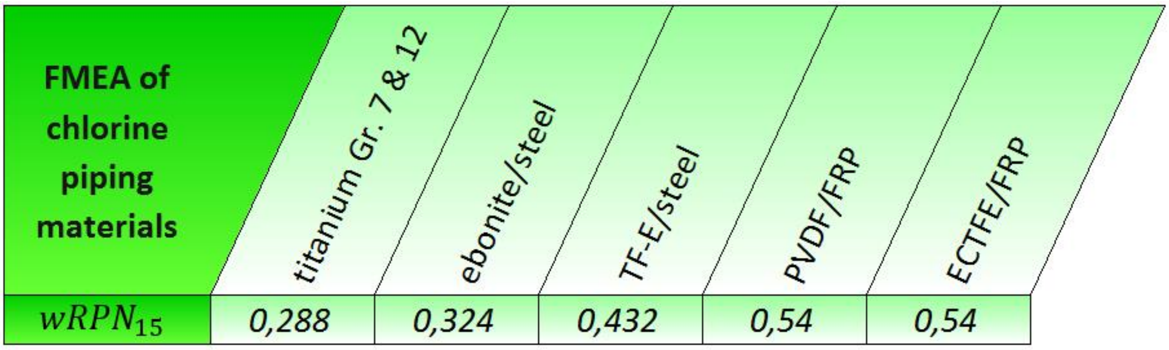
Ethylene-chlorotrifluoroethylene (ECTFE) has superior resistance to permeation by chlorine gas compared to PTFE and fluorinated ethylene propylene (FEP). It is approximately 10-

100 times better (Schweitzer, 2007a, p. 134). PTFE, FEP and perfluoroalkoxy alkane (PFA) with a thickness of 2,3 mm are approximated to reach failure by permeation of chlorine in under 2 years and are excluded from further study. Pure FRP with a gel coat 2,3 mm thick is also approximated to reach failure in 2 years because of permeation and is excluded from further study (Salakka, 2017).

The data for ebonite lined rubber's corrosion behavior with chlorine is incomplete, but the material has been used in chlorine pipelines at chlor-alkali factories with similar operating parameters before and the supplier estimates the lifetime of material to be >10 years. The lining will need NDT testing done with an interval of 3 years so the integrity can be confirmed. (Esko, 2017.) Wet chlorine and hydrochloric acid form a layer of chlorinated rubber film when in contact with ebonite. This film protects the bulk of the material from further reaction. (Chandrasekaran, 2010, p. 38.) Ebonite rubber lined steel pipes have been used in chlorine service at chlor-alkali plants for numerous years (Riskin, 2008, p. 142).

A FMEA analysis was conducted for all the pipeline materials still being examined. The most probable failure mechanisms and their effects for different materials were taken into consideration. The $wRPN_{15}$ values were calculated using the parameters from table 1 and applying the formula 2. The results are depicted in table 6.

Table 6. The results of FMEA on chlorine piping materials for a period of 15 years.



FMEA of chlorine piping materials	titanium Gr. 7 & 12	ebonite/steel	TF-E/steel	PVDF/FRP	ECTFE/FRP
$wRPN_{15}$	0,288	0,324	0,432	0,54	0,54

Titanium grades 7 and 12 get the lowest score because of their expected lifetime of over 15 years, and the low severity of possible failures that can be detected during routine manual inspections at maintenance shutdowns. Ebonite has the highest expected lifetime of 10 years for lined pipelines, but the severity of the failure is ranked higher compared to FRP-substrate lined pipes. When the likelihood of chlorine gas getting in contact with the steel substrate increases, the severity of the failure increases accordingly. The likelihood of this happening is lower in ebonite lined pipelines compared to TF-E, where permeation is the only cause of failure. Thus TF-E ranks lower than ebonite, but because of the high detectability of failures thanks to weep holes and an expected lifetime of 7 years it ranks higher than polyvinylidene fluoride (PVDF) and ECTFE lined pipelines. Failures of PVDF and ECTFE are identical at a cycle of 4 years, not severe, but not as easily detected as TF-E failures.

An analysis of LCCs in a usage period of 10 years were calculated with equation 3. with quotations of reference pipe sections (DN150, end flanges, L = 1 m) from vendors, the estimated lifecycles of materials from FMEA analysis and the estimated maintenance costs related to the inspection of the pipeline. The wall thickness of metallic pipes is 3,4 mm. The smaller the absolute value of the result the better the performance in LCC calculations. An LCC_{10} analysis of the materials produced the following lifecycle costs for a usage period of ten years, depicted in figure 28.

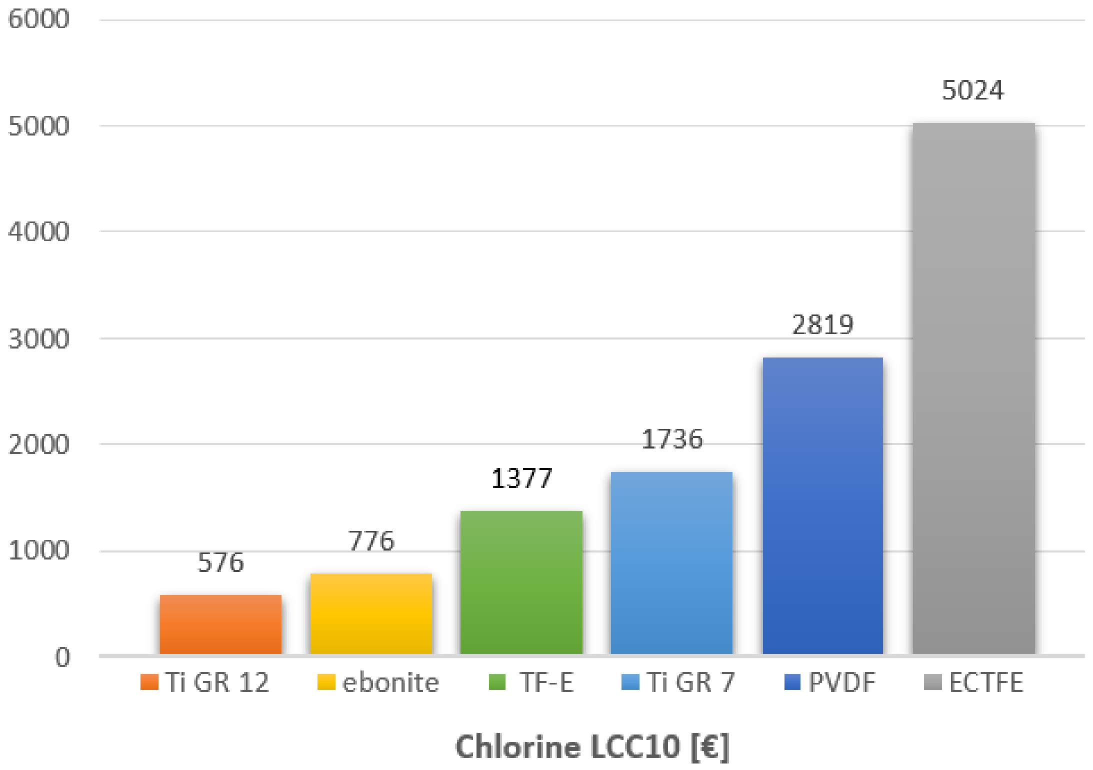
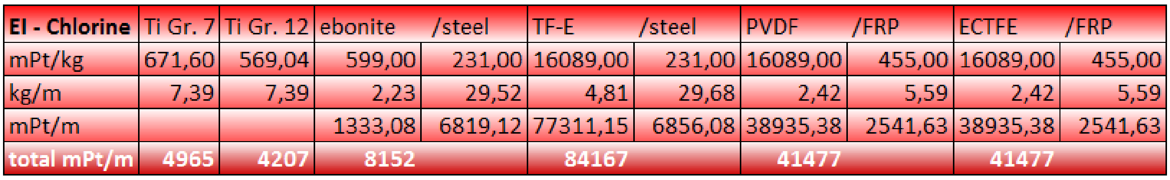


Figure 28. Lifecycle-costs of chlorine piping materials for a usage period of 10 years. The smallest value is the best.

LCA analysis was conducted with the ecological indicator method for all of the pipeline materials still in examination. All of the EI factors are depicted per kg of material. For metallic materials of which EI factors are unknown, approximations from substitute materials were made based on LCA analysis data of a study made by Nuss & Eckelman in 2014. This data shows the cumulative energy demands, terrestrial acidification, freshwater eutrophication and human toxicity factors for different metallic materials calculated with ReCiPe Midpoint method. For titanium, the EI factors of stainless steel were used as basis and the factors of alloying elements were added to the total impact of the material based on the composition of the grade. Ti Gr 7 is alloyed with Pd and the EI factor used for Pd was for secondary, recycled palladium. Impurities were not taken into consideration. (Nuss & Eckelman, 2014, pp. 4-6.)

The values of fluoropolymer linings were approximated from data of PTFE. For FRP the EI factor was calculated with values of epoxy resin filled glass fibers. The values for ebonite rubber was approximated from EI data of natural rubber. The weight of the reference pipeline section was calculated by comparing the density of each material to the different wall layers' volumes. The result is the total mPt value for 1000 mm of the pipeline in size DN150 and pressure class of PN10. The results of LCA for chlorine pipeline materials are shown in table 7.

Table 7. The results of LCA analysis for chlorine pipeline materials. The lower the total mPt/m the more ecologically friendly the material is.



EI - Chlorine	Ti Gr. 7	Ti Gr. 12	ebonite	/steel	TF-E	/steel	PVDF	/FRP	ECTFE	/FRP
mPt/kg	671,60	569,04	599,00	231,00	16089,00	231,00	16089,00	455,00	16089,00	455,00
kg/m	7,39	7,39	2,23	29,52	4,81	29,68	2,42	5,59	2,42	5,59
mPt/m			1333,08	6819,12	77311,15	6856,08	38935,38	2541,63	38935,38	2541,63
total mPt/m	4965	4207	8152		84167		41477		41477	

It can be seen from the results of LCA analysis that fluoropolymers suffer from high ecological impacts when compared to titanium and ebonite. The fluorine compounds used in the production of fluoropolymers are considered harmful to the environment and humans and this raises the mPt/kg value considerably.

The determination of the optimal pipeline material was conducted by comparing the direct weighted normalized values of LCC analysis, FMEA and LCA. Because of the high error rate of LCA caused by the approximation of material EI values, the weighing parameter of the results of LCA was set to 0,1. The weighing parameters are 0,45 for LCC and 0,45 for FMEA. The normalization was conducted by determining the mean value and the standard deviation of all the parameters and standardizing the actual values of different materials against them using equation 5. Zero represents a neutral material, the more positive the normalized value, the more optimal the material is for the application. The results of normalized material analysis are depicted in figure 29.

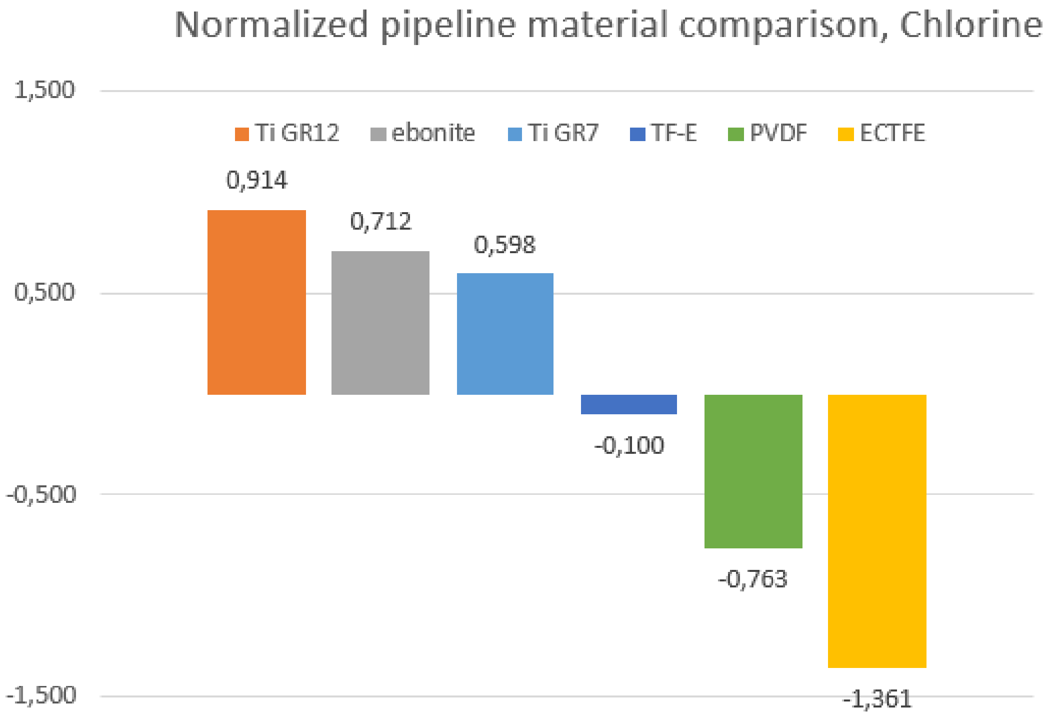


Figure 29. The results of direct weighed and normalized pipeline material parameter comparison (LCC, FMEA and LCA) that determines the optimal material for the application. The most positive value is the optimal material for the application.

The optimal material for wet chlorine pipelines according to the piping material selection process is titanium grade 12. Titanium materials rank high because of the low wRPN values and the considerably low cost when compared to fluorocarbon lined pipeline materials. Ebonite’s higher wRPN value compared to Ti materials effects the ranking considerably even that the LCCs is lower than both titanium’s. Ebonite ranks second highest because of the low LCCs and the low wRPN values. It is also the most optimal non-conductive material for chlorine pipelines. Fluoropolymers suffer from high lifecycle-costs and high EI-values, even though the failures are not severe and easily predictable.

5.2 The optimal materials with caustic soda

The temperature of outgoing NaOH from cell is kept at 87 ± 3 °C by cooling or in rare cases by heating the incoming NaOH. The concentration of incoming NaOH to membrane cell is 31,5 % and the concentration of outgoing NaOH from cell is 32,5 %. The NaOH solution is pure and can be used for intermediate and end-product manufacturing without chemical filtration. There are mechanical filters for ensuring the purity of NaOH products in later stages of the process. In pipelines a maximum nominal water pressure at 20 °C that the pipeline can support can be determined with the pressure nominal (PN) number. Because the pipelines can be subjected also to outer mechanical forces a PN class of 10 is demanded.

From this initial data, we can gather the demands that pipeline materials for caustic soda piping must fulfill:

- minimum PN class of 10
- withstands temperature of maximum 90 °C
- material is compatible with caustic soda at all process parameters
- acceptable engineering costs and availability.

Through the search of material selection literature, material-medium compatibility charts, manufacturer data and CASE-examples of caustic soda materials; the materials shown in table 6 were chosen in the initial screening phase of the material selection process. Materials that are not vulnerable to alkali induced cracking at Joutseno plant’s process parameters were chosen for initial material scoping. The figure 30 depicts some of the plausible materials’ usability window with NaOH solution concentration and temperature with the operating point of Joutseno plant marked. The material classes included are (O'Brien, et al., 2005, p. 949):

- I. Cast iron, steel, stainless steel, copper alloys, nickel, many plastics and elastomers
- II. Steel, Monel, Hastelloy B and C, Zirconium, nickel and its alloys, neoprene

- III. Monel, Hastelloy, Inconel, nickel
- IV. Cast iron, nickel, silver
- V. Steel, stainless steel, nickel and its alloys.

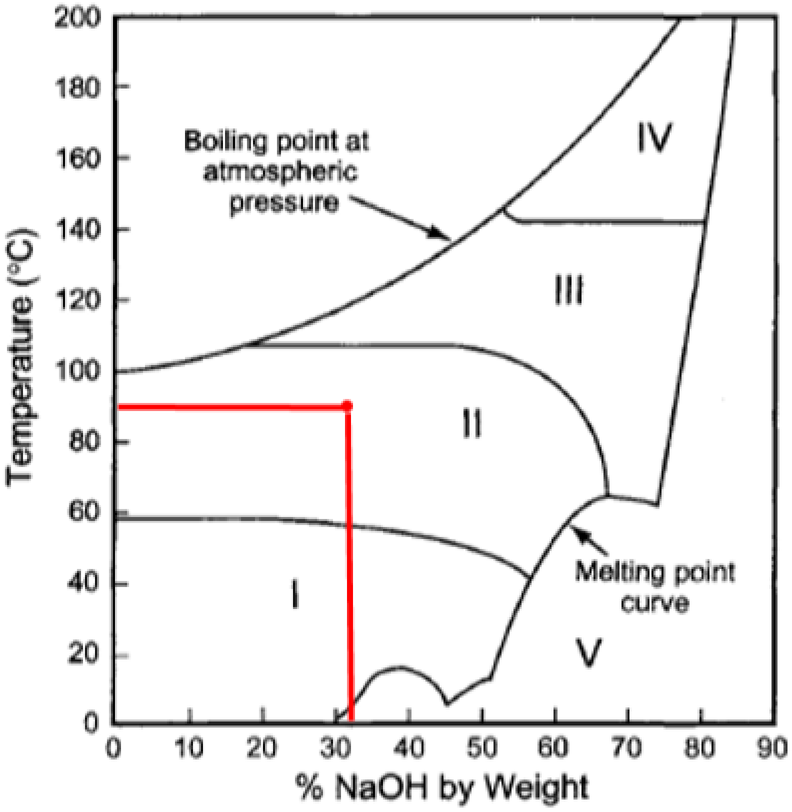


Figure 30. The usability window for materials divided into classes according to NaOH concentrations' and temperatures' effect on cracking vulnerability (O'Brien, et al., 2005, p. 949).

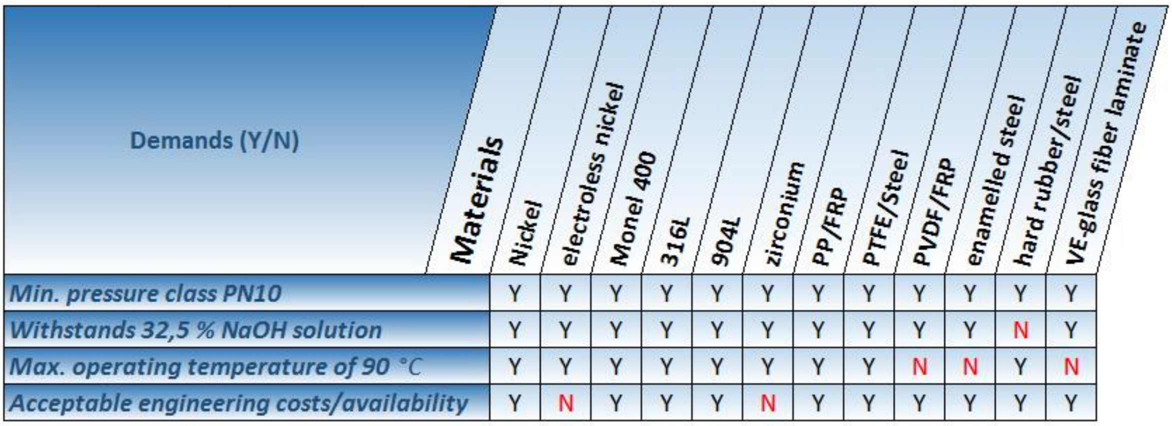
By the demand of the end user all the elastomers, polymers and ceramic piping materials are of a laminate nature and act only as a corrosion barrier layer in the piping with a structural reinforcement for added leakage protection. Electroless nickel (EN) is used as a thin (typically 50 µm) coating on steel pipes. All of the other metallic materials are used as a 3,4 mm thick walled pipelines. Glass enamel is used as an inner coating for steel pipelines. Hard rubber and PTFE are used as liners with a steel substrate. PP and PVDF are used as liners with a FRP substrate. The results of initial material scoping for NaOH service are depicted in table 8.

Table 8. Materials that fulfill the initial demands for NaOH piping.

Initial material scoping - Sodium hydroxide				
Metals	*Polymers*	*Elastomers*	*Ceramics*	*Composites*
nickel N200	PP	hard rubber	enamelled steel	VE-glass fiber laminate
electroless nickel	PTFE			
Monel 400	PVDF			
zirconium				
316L				
904L				

A fixed material extermination was executed to rule out materials that are not compatible with the demands, are not easily available or have unacceptable engineering costs. Results are shown in table 9.

Table 9. The results of fixed material extermination for NaOH piping.



Demands (Y/N) / ***Materials***	*Nickel*	*electroless nickel*	*Monel 400*	*316L*	*904L*	*zirconium*	*PP/FRP*	*PTFE/Steel*	*PVDF/FRP*	*enamelled steel*	*hard rubber/steel*	*VE-glass fiber laminate*
Min. pressure class PN10	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Withstands 32,5 % NaOH solution	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	N	Y
Max. operating temperature of 90 °C	Y	Y	Y	Y	Y	Y	Y	Y	N	N	Y	N
Acceptable engineering costs/availability	Y	N	Y	Y	Y	N	Y	Y	Y	Y	Y	Y

Based on the results of fixed extermination, the following pipeline materials were omitted from further investigation:

- Zirconium, because of the high price of the metal at approximately 1 858.96 €/kg at the USD/EUR exchange rate in 20.4.2017 (CRC, 2013, p. 42). Zirconium tubes are usually used in heat exchanger applications and thus pipe sizes bigger than outside diameter 38.1 mm are hard to find on the market (Sandvik, 2017).
- Enameled steel, because of the unacceptably high uniform corrosion rate of >0,2 mm/y in 32,5 % NaOH solution at a temperature of 90 °C (De Dietrich Process Systems, 2017).

- PVDF because of concentration of NaOH as low as 0,15 % causing stress cracking of the material at a temperature of 25 °C (Dyneon, 2004, p. 6).
- Hard rubber, because no corrosion data was found to prove that the material withstands concentrated alkali media without corrosion.
- VE-FRP because of limited chemical resistance to 32,5 % NaOH solution at operating temperatures (Reichhold, 2009, p. 12).
- Electroless nickel (EN) coated steel pipes were not found available from pipeline vendors. Thus, no cost data was found and the availability of material in large quantities is not known.

Even though EN coating was discarded from further study the low-phosphorus type (1-2 % P) show excellent service life in caustic soda applications. In a 35 % NaOH solution at a temperature of 93 °C the corrosion rate of EN coating is 5,3 µm/year while in comparison the nickel grade N200 shows a corrosion rate of 5.1 µm/year. The corrosion rate for stainless steel 316L in the same environment is 52 µm/year. (O'Brien, et al., 2005, p. 952.)

The next step was the flexible extermination of materials based on their attributes and the environmental corrosion factors. Based on corrosion theory and FMEA sections of this thesis the failure mechanisms of different materials based on the atmospheric and parametric conditions in the pipeline in question can be determined. The following factors were taken into account for NaOH piping materials:

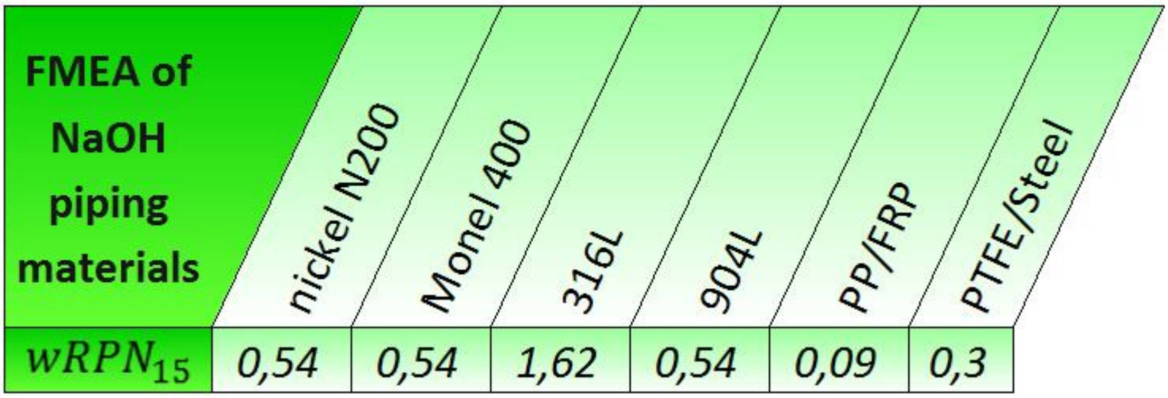
- unacceptable uniform corrosion rate, especially in metallic alloys
- ageing causing the increase of brittleness in polymeric materials, especially PP.

The uniform corrosion rates of metallic materials were determined by using tables of iso-corrosion rates, CASE studies at electrolysis process plants and manufacturer conducted studies. The appendix V shows that all of the metallic materials being examined can handle 35…40 % caustic soda solution with 6…7 % NaCl as an impurity (diagram cell process) at an average temperature of 116 °C (range of 102…127 °C) with a maximum corrosion rate of 0.0508 mm/y for AISI 316L. The NaCl in NaOH solution increases the corrosion rate of metallic alloys, so the results of corrosion rates at Joutseno plant’s cell room can be considered to be calculated with an increased safety allowance. All of the metallic materials in question are capable of handling NaOH from cells with a plausible pipeline lifetime expectancy and thus none were exterminated in this phase of the process. (Nickel Development Institute, 1983, pp. 7-13.)

The ageing characteristics of PP have been proven to give the material an expected lifetime of >25 years in NaOH service at Joutseno chlor-alkali plant. Thus, there is no need to exclude PP from further study. PTFE shows no ageing characteristics in NaOH solutions.

A FMEA was conducted for all of the pipeline materials still being examined. The most probable failure mechanisms and their effects for different materials were taken into consideration. The corrosion allowance for metallic pipelines was set to 0,4 mm with a wall thickness of 3,4 mm. The results of FMEA are depicted in table 10.

Table 10. The $wRPN_{15}$ *values for proposed NaOH pipeline materials.*



FMEA of NaOH piping materials	nickel N200	Monel 400	316L	904L	PP/FRP	PTFE/Steel
$wRPN_{15}$	0,54	0,54	1,62	0,54	0,09	0,3

Because of the highly predictable corrosion rate of metallic materials, the materials that show >15 years of service get lower $wRPN_{15}$ values than AISI 316L. PP/FRP has the lowest $wRPN_{15}$ rating because it has a service life of >15 years and the failures are easily detectable and have no impacts on process or human safety. PTFE/steel also has a high service life compared to the other materials, and the failures are easy to detect before causing any harm to the process.

An analysis of LCC in a usage period of 10 years were calculated with equation 3 from quotations of reference pipe sections (DN150, end flanges, L = 1 m) from vendors, which were compared to the estimated lifecycles of materials from FMEA analysis. The wall thickness of metallic pipes is 3,4 mm. The smaller the absolute value of the result the better performance in LCC calculations. An LCC_{10} analysis of the materials produced the following lifecycle costs for a usage period of ten years, depicted in figure 31.

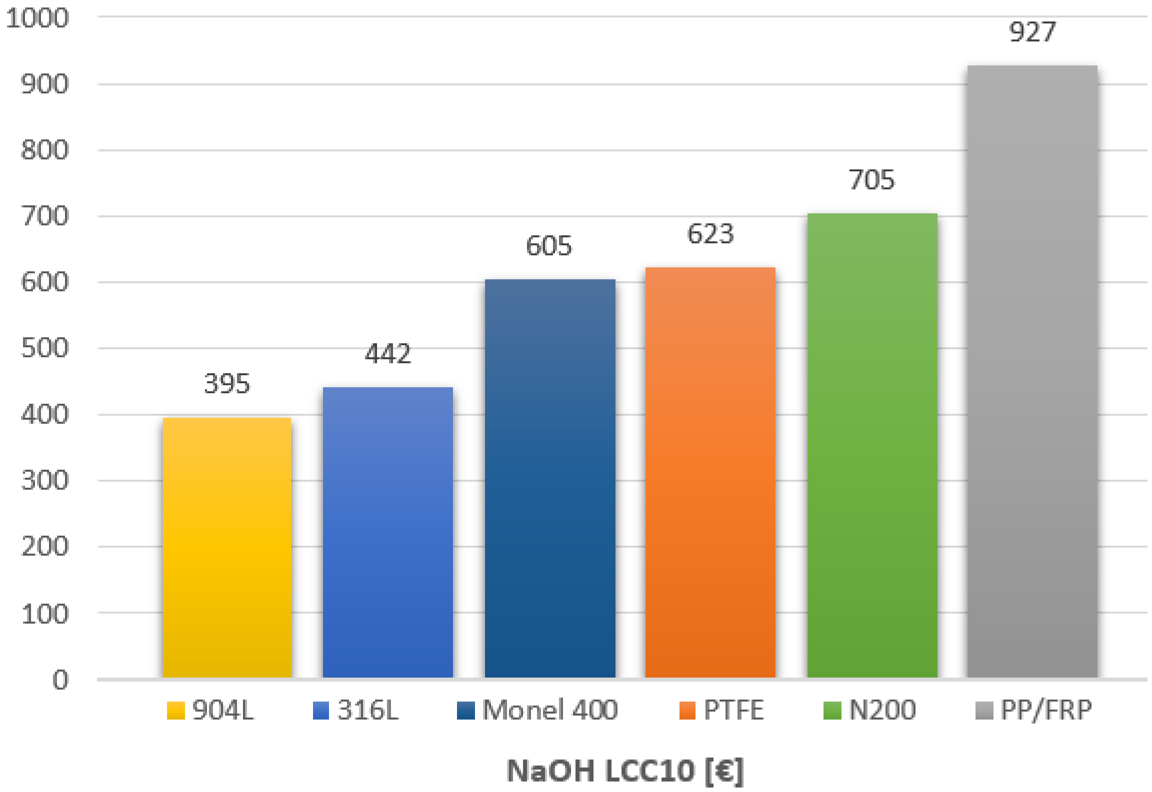
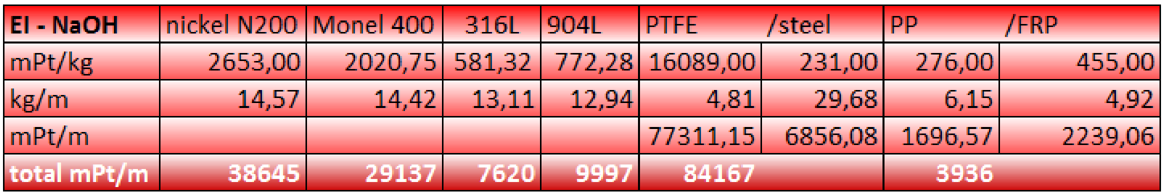


Figure 31. LCC costs of NaOH piping materials for a usage period of 10 years. The smallest absolute is the best.

The iron based alloy's procurement costs are lower than nickel based alloy's which is clearly shown in the results of the LCC analysis. The superaustenitic 904L has the lowest lifecycle-costs because of procurement price of 300 € and high service life of >16 years in cell room caustic soda solutions. Nickel N200 has the highest service life of 39 years, but the initial procurement cost of 610 € cannot be compensated in the timeframe of the analysis. AISI 316L pipelines must be renewed after 8 years of service, but the low procurement price of 160 € compensates the renewal rate in the timeframe of the analysis resulting in second best performance. PTFE and PP lined pipelines suffer from high procurement costs even though their service life exceeds those of 904L, 316L and Monel 400.

LCA analysis was conducted with the ecological indicator method for all the pipeline materials still in examination. All of the EI factors are depicted per kg of material. The EI values were approximated for metallic alloys from chemical composition data and the density of each component. The FRP's EI factor was calculated with values of epoxy resin filled glass fibers. The weight of the reference pipeline section was calculated by comparing the density of each material to the different wall layers' volumes. The end-result is the total mPt value for 1000 mm of the pipeline in size DN150 and pressure class of PN10. The results of LCA for NaOH pipeline materials are shown in table 11.

Table 11. The results of LCA analysis for NaOH pipeline materials. The lower the total mPt/m the more ecologically friendly the material is.



EI - NaOH	nickel N200	Monel 400	316L	904L	PTFE	/steel	PP	/FRP
mPt/kg	2653,00	2020,75	581,32	772,28	16089,00	231,00	276,00	455,00
kg/m	14,57	14,42	13,11	12,94	4,81	29,68	6,15	4,92
mPt/m					77311,15	6856,08	1696,57	2239,06
total mPt/m	**38645**	**29137**	**7620**	**9997**	**84167**		**3936**	

It is clearly visible from reference data that PTFE suffers from high environmental load in the manufacturing process because fluorine and its compounds are highly toxic substances for humans and the environment. Nickel based alloys have higher EI values than iron based alloys, because the production of nickel is less environmentally friendly than the production of iron. PP is more environmentally friendly and lower in density than FRP and thus the EI value for similar PN class pipeline is lower than pure FRP material.

The determination of the optimal pipeline material was conducted by using direct weighted normalization of the values of LCC, FMEA and LCA analysis. The according weighing parameters are 0,4 for LCC, 0,4 for FMEA and 0,2 for LCA. The normalization was conducted by determining the mean value and the standard deviation of all the parameters and standardizing the actual values of different materials against them using equation 5. Zero represents a neutral material, the more positive the normalized value, the more optimal the material is for the application. The results of normalized material analysis are depicted in figure 32.

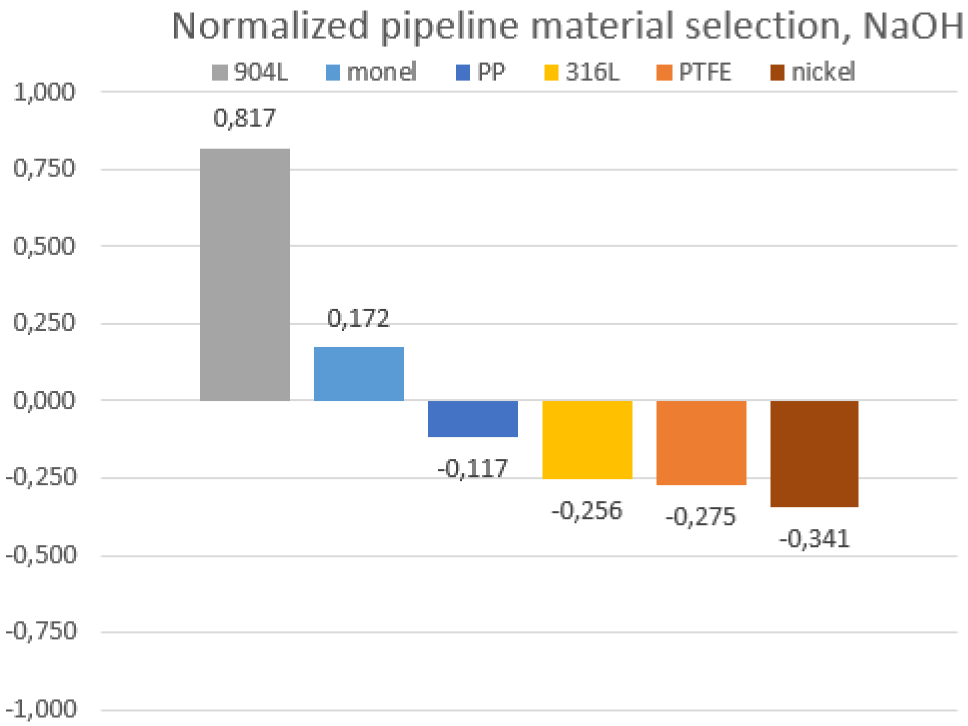


Figure 32. The results of direct weighed and normalized material parameters (LCC, FMEA and LCA) that determine the optimal material for the application. The most positive value is the optimal material for the application.

The optimal material for caustic soda pipelines according to the piping material selection process is AISI 904L. The most optimal electrically non-conductive material is PP/FRP.

5.3 The optimal materials with brine

The material selection of brine focuses on depleted brine because the corrosion characteristics of pure brine are less demanding than depleted brine because of the absence of free chlorine. (O'Brien, et al., 2005, p. 784.) As a side notion, the purity of feed brine must be kept at levels suitable for the membrane cells. For the brine feed lines after the mechanical and ion-exchange filtration systems, the materials of construction should be limited to fully brine-caused corrosion resistant materials the likes of titanium and PTFE, because the purity requirements for optimal membrane function are in the range of low ppb for metallic corrosion products like Ni and Fe hydroxides and ions. (O'Brien, et al., 2005, p. 655.) The purification of these chemical compounds is achieved by raising the pH to 9…9,5 after activated carbon filtration allowing the ionic species to form metallic hydroxides so the mechanical filtration can remove these impurities.

Caution should be taken when choosing the piping materials to the downstream lines of the brine purification ion-exchange system. The widely used polymeric piping materials like PVC and PP contain compounding ingredients the likes of calcium carbonate and calcium stearate which could cause adverse effects to the cell membranes. There have been cases in which these compounds have contaminated purified brine. (O'Brien, et al., 2005, p. 624.) These kinds of impurities are filtrated from brine circulation in the ion-exchange system before the cells.

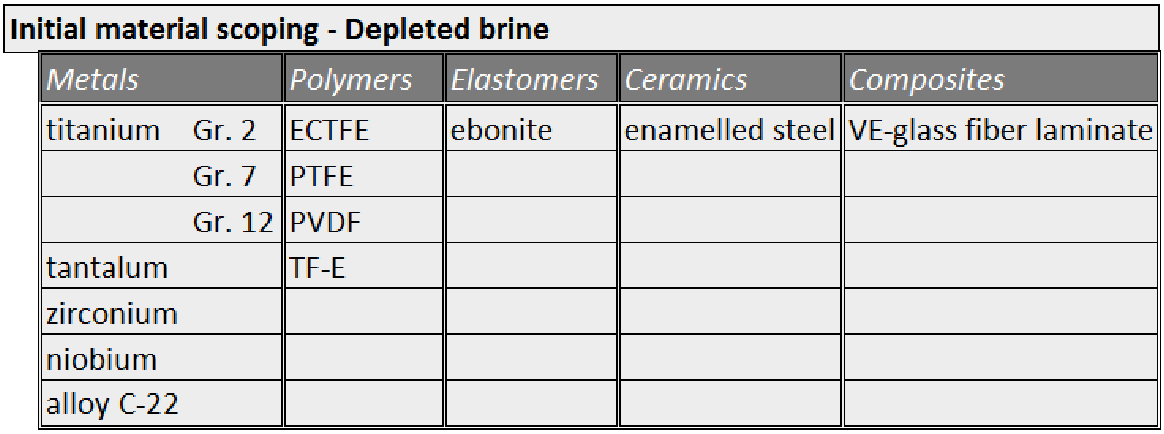
With depleted brine from cells, HCl addition before anolyte tanks lowers the pH to as low as 2,0. The maximal pH value of brine is 6 before activated carbon filtration. Depleted brine is saturated with chlorine and is thus very corrosive (O'Brien, et al., 2005, p. 748). Because the pipelines can be subjected also to outer mechanical forces a PN class of 10 is demanded.

From this initial data, we can gather the demands that piping materials for depleted brine piping must fulfill:

- minimum PN class of 10
- withstands temperature of maximum 90 °C
- material is compatible with depleted brine at all process parameters
- acceptable engineering costs and availability.

Through the search of material selection literature, material-medium compatibility charts and manufacturer data the materials that are proven compatible with brine solution, no EAC induced cracking or crevice corrosion is allowed at Joutseno plant’s parameters. The materials shown in table 12 were chosen in the initial screening phase of the material selection process. By the demand of the end user, all of the elastomeric and polymeric materials are of a laminate nature and act only as a corrosion barrier layer in the piping with a structural reinforcement for leakage protection, except FRP where the corrosion barrier is achieved with a gel-coat layer as the inner layer of the pipeline.

Table 12. Materials that fulfill the initial demands for depleted brine piping.

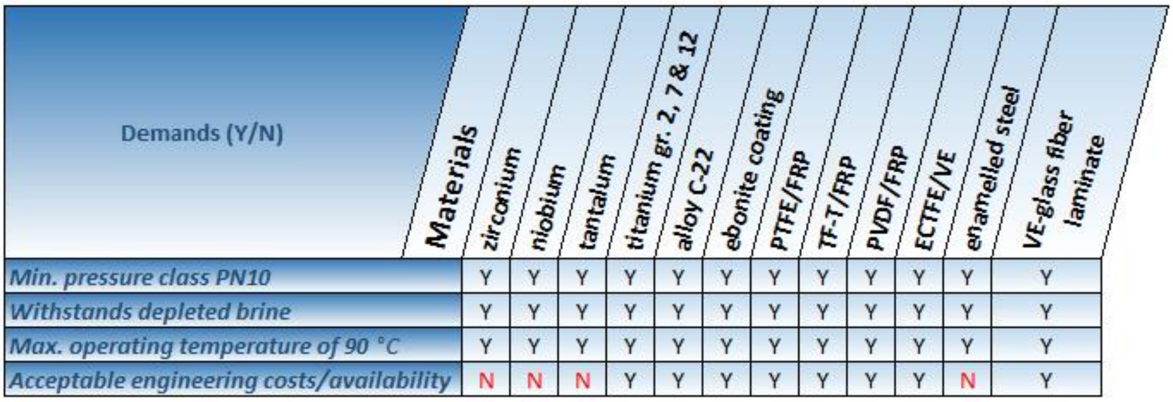


Initial material scoping - Depleted brine

Metals	*Polymers*	*Elastomers*	*Ceramics*	*Composites*
titanium Gr. 2	ECTFE	ebonite	enamelled steel	VE-glass fiber laminate
Gr. 7	PTFE			
Gr. 12	PVDF			
tantalum	TF-E			
zirconium				
niobium				
alloy C-22				

A fixed material extermination was executed to rule out materials that are not compatible with the demands, are not easily available or have unacceptable engineering costs. Results are shown in table 13.

Table 13. The results of fixed material extermination for depleted brine piping.



Demands (Y/N) / **Materials**	zirconium	niobium	tantalum	titanium gr. 2, 7 & 12	alloy C-22	ebonite coating	PTFE/FRP	TF-T/FRP	PVDF/FRP	ECTFE/VE	enamelled steel	VE-glass fiber laminate
Min. pressure class PN10	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Withstands depleted brine	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Max. operating temperature of 90 °C	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Acceptable engineering costs/availability	N	N	N	Y	Y	Y	Y	Y	Y	Y	N	Y

Based on the fixed extermination of the demands the following materials were exterminated from further investigation:

- Tantalum, because of the controversies regarding the trading of tantalum; tantalum is not traded in pure form, only tantalum ores. This causes a high fluctuation in negotiation prices and in the price of end products. Also, the demand varies annually which causes high volatility in tantalum prices. The price of tantalite ore rose from 100.38 €/kg in 2009 to 312.30 €/kg in 2011. The price of tantalite ore is at current USD/EUR exchange rate in 18.4.2017 at 118.97 €/kg. It is also estimated that the known tantalite mines will be depleted in the following 50 years, which is bound to increase the price of tantalum in the future. (Metalary, 2017a)

- Zirconium, because of the high price of the metal at approximately 1 858.96 €/kg at the USD/EUR exchange rate in 20.4.2017 (CRC, 2013, p. 42). Zirconium tubes are usually used in heat exchanger applications and thus pipe sizes bigger than OD 38.1 mm are hard to find on the market (Sandvik, 2017).
- Niobium, because of limited availability (two mines in the world in 2010), high volatility of production and high cost variation based on international markets and demand (Business Insider, 2010). The price of niobium ore is at current USD/EUR exchange rate in 18.4.2017 at 38,86 €/kg (Metalary, 2017b).
- Enameled steel was not found available from suppliers. Thus, the cost factors and availability is unknown and the material is excluded from further study.

The next step was the flexible extermination of materials based on their attributes and the environmental corrosion factors. Based on corrosion theory and FMEA sections of this thesis the failure mechanisms of different materials based on the atmospheric and parametric conditions in the pipeline in question can be determined. The following factors were taken into account for depleted brine piping materials:

- the possibility of crevice corrosion, especially in passively protected metal flanges
- unacceptably high uniform corrosion rate
- impurities transferred to brine
- unacceptable permeation rate of media, especially in fluoropolymer linings
- softening of material leading to blisters and loss of mechanical properties, especially in elastomer linings.

The effects of erosion corrosion were left out of scope because it is assumed that all of the compounds of depleted brine are dissolved in the solution at the operating temperature and that the flow velocities are kept at Joutseno plant's design velocity of maximum 3 m/s.

Titanium grade 2 was excluded from further study because of the vulnerability to crevice corrosion in depleted brine at 90 °C depicted in figure 15. Titanium grades 7 and 12 are not susceptible to crevice corrosion in the atmospheric conditions of Joutseno chlor-alkali plant's cell room's depleted brine pipelines. Titanium grades 7 and 12 withstand oxidizing acidic circumstances of pH as low as 1,5 without observable uniform corrosion. (Riskin, 2008, p. 81.)

For C-22 the uniform corrosion rate in 3000 ppm Cl solution adjusted to pH 1.5 (T = 95 °C) with chlorine and HCl gas (T = 90 °C) bubbled though the liquid is 0,0229 mm/y for the liquid phase and 0,1125 mm/y for the vapor phase (Haynes International, 2017). This would limit the maximum service life of a 3,4 mm thick walled pipeline to 4 years if the corrosion allowance is 0,4 mm. Crevice corrosion initiation has been observed in alloy C-22 at highly chlorinated sodium chloride solutions at room temperature, which cannot be allowed in depleted brine pipelines (Aezeden, 2013, p. 20). Thus, alloy C-22 is excluded from further study.

Pure FRP with a gel coat 2,3 mm thick is approximated to reach failure in 2 years because of chlorine permeation and is excluded from further study (Salakka, 2017). The research data for ebonite lined rubber’s behavior with chlorine and chlorides is incomplete, but it has been used in chlorine pipeline service at chlor-alkali factories with similar operating parameters before and the supplier estimates the lifetime of material to be >10 years. (Esko, 2017.) Wet chlorine and hydrochloric acid form a layer of chlorinated rubber film when in contact with ebonite. This film protects the bulk of the material from further reaction. (Chandrasekaran, 2010, p. 38.)

None of the remaining materials show qualities of corrosion characteristics that could lead to impurities being transferred to brine.

A FMEA was conducted for all of the pipeline materials still being examined. The most probable failure mechanisms and their effects for different materials were taken into consideration. The failure rates for PTFE lined steel pipes were gathered from Joutseno’s SAP PM database. The failure rate of TF-E (the other nomination is TFM) was approximated from the ratio of permeation from data gathered in a permeation study of PTFE and TF-E sheets with a thickness of 1 mm with chlorine gas at a temperature of 54 °C. The ratio of permeation is 0,6 for TF-E compared to PTFE. The in-situ permeation rate at the cell room pipelines differs because of the maximum operating temperature of 90 °C and the wall thickness of 4,5 mm of PTFE and TF-E lining, but the results are implemented to FMEA because of the scarcity of available data. The permeation rates of PTFE and TF-E are shown in figure 33.

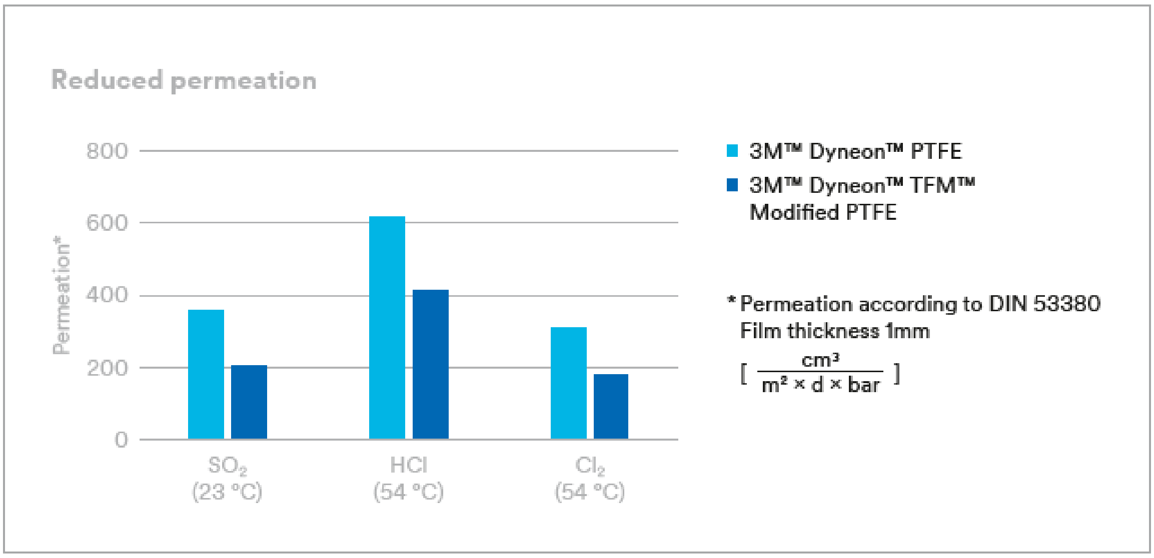
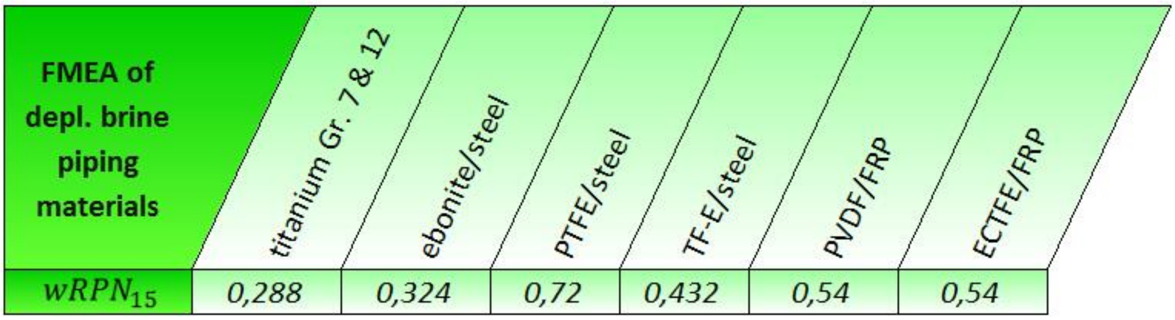


Figure 33. The permeation rates of 1 mm thick PTFE and TF-E (TFM) sheets with different gases at constant temperatures. Permeation is calculated with the equation from DIN 53380 standard, where cm^3 is the gas volume, m^2 is the surface area of the polymer, d is one day, and bar is the pressure of the permeant. (Dyneon GmbH, 2017, p. 6.)

The next step is the FMEA for the pipeline materials still being considered. The $wRPN_{15}$ values were calculated using the parameters from table 1 and applying the formula 2. The results of FMEA for depleted brine pipeline materials are depicted in table 14 as $wRPN_{15}$ values.

Table 14. The $wRPN_{15}$ *values for depleted brine pipeline materials studied.*



FMEA of depl. brine piping materials	titanium Gr. 7 & 12	ebonite/steel	PTFE/steel	TF-E/steel	PVDF/FRP	ECTFE/FRP
$wRPN_{15}$	0,288	0,324	0,72	0,432	0,54	0,54

Titanium grades 7 and 12 get the lowest score because of their expected lifetime of over 15 years, and the low severity of possible failures that can be detected during routine manual inspections at maintenance shutdowns. Ebonite has the highest expected lifetime of 10 years for lined pipelines, but the severity of the failure is ranked higher compared to FRP-substrate lined pipes. When the likelihood of chlorine gas getting in contact with the steel substrate increases, the severity of the failure increases accordingly. The likelihood of this happening is lower in ebonite lined pipelines compared to PTFE and TF-E, where permeation is the only cause of failure. Thus, PTFE and TF-E rank lower than ebonite. But because of the high detectability of failures thanks to weep holes and an expected lifetime of 7 years TF-E ranks higher than PVDF and ECTFE lined pipelines. Failures of PVDF and ECTFE are identical at a cycle of 4 years, not severe, but not as easily detected as TF-E failures. PTFE pipelines suffer failures at a rate of four years, but the failures are more severe than FRP substrate pipelines. Thus, PTFE gets the highest overall wRPN number.

An analysis of LCCs in a usage period of 10 years were calculated from quotations of reference pipe sections (DN150, end flanges, L = 1 m) from vendors taking into account the estimated lifecycles of materials from FMEA analysis. The only maintenance costs in the period are the NDT test done for the materials. For titanium pipelines a mechanical removal of the pipeline section is needed for a visual inspection of the flange collar at an interval of five years. Similar procedure is used for ebonite rubber inspection at an interval of three years. For all the other materials, an inner visual inspection with a sewer camera is sufficient for determining the integrity of the material. For fluoropolymer linings, an interval of two years is sufficient. The more positive the value of the result, the better the performance in LCC analysis. An LCC_{10} analysis of the materials produced the following lifecycle costs for a usage period of ten years, depicted in figure 34.

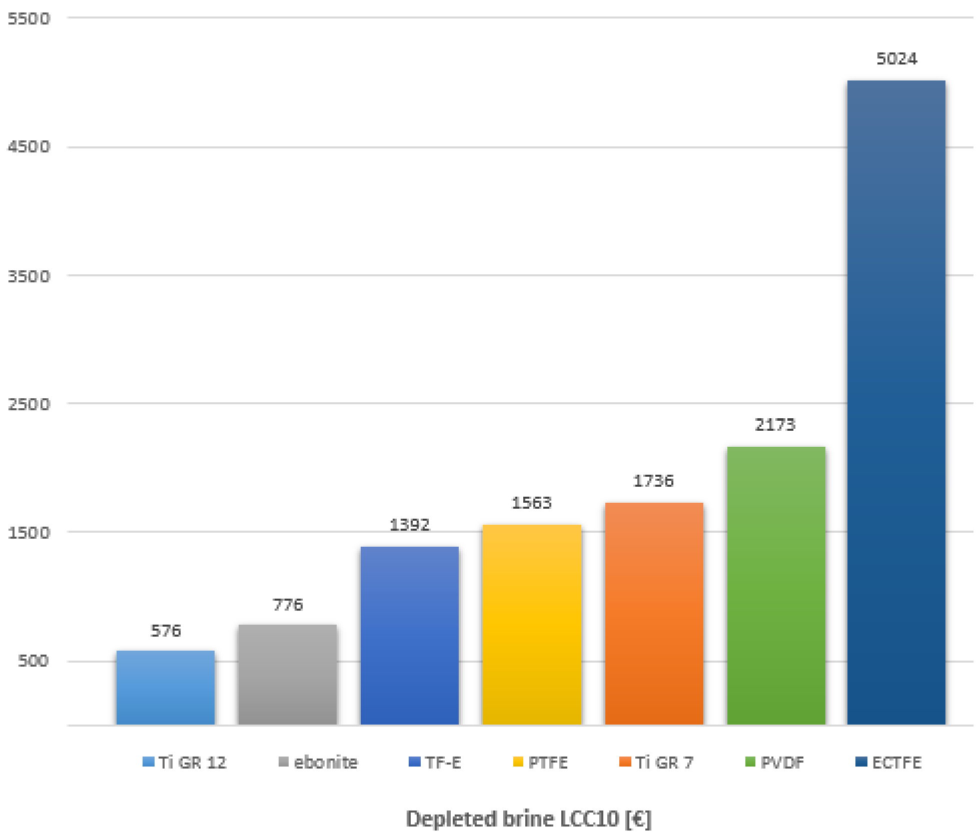


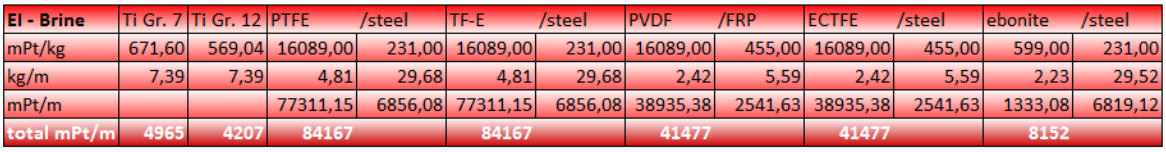
Figure 34. LCC costs of depleted brine piping materials for a usage period of 10 years. The lowest value is the best performing material.

It can be seen from the results of LCC analysis that titanium gr. 12 has the lowest lifecycle costs followed by ebonite. The steel substrate fluoropolymers have lower procurement costs than FRP substrate materials even though the liner thickness is higher. The steel substrate pipelines will have to be renewed one year earlier than FRP pipelines because steel is not as corrosion resistant as FRP. This has little overall effect on the LCCs. ECTFE’s high procurement price results in high overall lifecycle costs.

LCA analysis was conducted with the ecological indicator method for all of the pipeline materials still in examination. All of the EI factors are depicted per kg of material. For metallic materials, of which the EI factor is unknown, approximations from substitute materials were made based on LCA analysis data of a study made by Nuss & Eckelman in 2014. This data shows the cumulative energy demands, terrestrial acidification, freshwater eutrophication and human toxicity factors for different metallic materials calculated with ReCiPe Midpoint method. For titanium, the EI factors of stainless steel were used as basis and the factors of alloying elements were added to the total impact of the material based on the composition of the grade. Ti Gr 7 is alloyed with Pd and the EI factor used was for secondary, recycled palladium. Impurities were not taken into consideration. The EI factor for Mo was not found, but copper's EI factor was used as a basis for approximation. (Nuss & Eckelman, 2014, pp. 4-6.)

The values of fluoropolymer linings were approximated from data of PTFE from Ecolizer 2.0 data. The FRP EI factors were calculated with values of epoxy resin filled glass fibers. The values for ebonite rubber was approximated from EI data of natural rubber. The weight of the reference pipeline section was calculated by comparing the density of each material to the different wall layers' volumes. The end result is the total mPt value for 1000 mm of the pipeline in size DN150 and pressure class of PN10. The results of LCA for depleted brine pipeline materials are shown in table 15.

Table 15. The results of LCA for depleted brine pipeline materials. The lower the total mPt/m the more ecologically friendly the material is.



EI - Brine	Ti Gr. 7	Ti Gr. 12	PTFE	/steel	TF-E	/steel	PVDF	/FRP	ECTFE	/steel	ebonite	/steel
mPt/kg	671,60	569,04	16089,00	231,00	16089,00	231,00	16089,00	455,00	16089,00	455,00	599,00	231,00
kg/m	7,39	7,39	4,81	29,68	4,81	29,68	2,42	5,59	2,42	5,59	2,23	29,52
mPt/m			77311,15	6856,08	77311,15	6856,08	38935,38	2541,63	38935,38	2541,63	1333,08	6819,12
total mPt/m	**4965**	**4207**	**84167**		**84167**		**41477**		**41477**		**8152**	

The EI values for titanium grades 7 and 12 do not differ significantly because of the low concentration of alloying elements which are 0,3 % Pd in Gr. 7 and 0,8 % Ni with 0,3% Mo in Gr. 12. Ebonite's low EI values can be explained by the low initial mPt/kg values of both natural rubber and steel. PVDF and ECTFE have the lowest results of fluoropolymers, because of the lining thickness of 2,3 mm compared to PTFE's and TF-E's 4,5 mm.

The determination of the optimal pipeline material was conducted by using direct weighted normalization of the values of LCC, FMEA and LCA analysis. The according weighing parameters are 0,45 for LCC, 0,45 for FMEA and 0,1 for LCA. The weighting of LCA was set to 0,1 because of the high rate of error caused by the approximation of EI values for different materials including titanium, PVDF, TF-E and ebonite rubber. The normalization was conducted by determining the mean value and the standard deviation of all the parameters and standardizing the actual values of different materials against them using equation 5. Zero represents a neutral material, the more positive the normalized value, the more optimal the material is for the application. The results of normalized material analysis are depicted in figure 35.

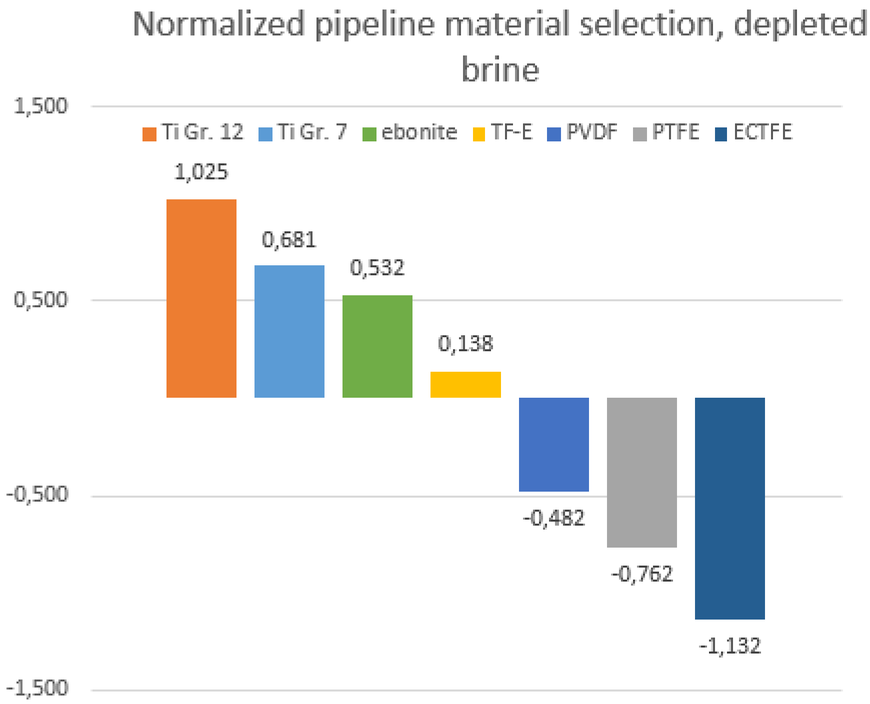


Figure 35. The comparison of direct weighed and normalized material parameters (LCC, FMEA and LCA) that determine the optimal material for the application. The most positive value is the optimal material for the application.

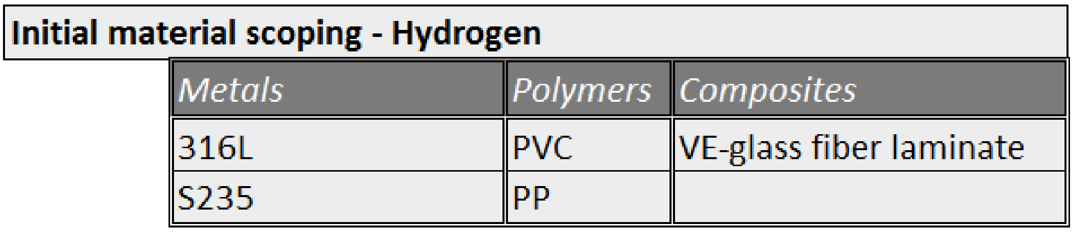
The optimal material for depleted brine pipelines according to the piping material selection process is titanium grade 12. When comparing titanium gr. 7 to gr. 12 it is clearly visible that the cost difference of the materials favor gr. 12. The low grading of fluoropolymer lined materials is affected by both the high costs and the high environmental impacts of the materials. The best performing non-conductive material is ebonite rubber lined steel.

5.4 The optimal materials with hydrogen

The pressure inside hydrogen pipes is maintained at a slight overpressure compared to chlorine. The amount of overpressure in the cell is 60 mmH_2O and the total pressure is thus 1260 mmH_2O. Maximum pressure of hydrogen inside the piping is 5000 mmH_2O and is controlled by a bursting disc. The hydrogen gas coming from cells is saturated with water and the condensate produced is dilute with NaOH. The temperature of hydrogen gas coming from the cells is 85±2 °C. After the hydrogen cooler, the temperature of hydrogen is 30 °C. Because the pipelines can be subjected to vacuum and external mechanical loads a PN class of minimum PN10 is required.

Through the search of material selection literature, material-medium compatibility charts and manufacturer data the materials that are proven compatible with hydrogen. No EAC induced cracking at Joutseno plant's parameters is approved. The materials shown in table 16 were chosen in the initial screening phase of the material selection process. By the demand of the end user all of the polymeric piping materials are of a laminate nature and act only as a corrosion barrier layer in the piping with a structural reinforcement for leakage protection, except FRP where the corrosion barrier is achieved with a gel-coat layer as the inner layer of pipeline. AISI 304L is substituted by AISI 316L because of the wish from end user to unify the material pallet already in use at the factory.

Table 16. Materials that fulfill the initial demands for hydrogen piping.



Initial material scoping - Hydrogen

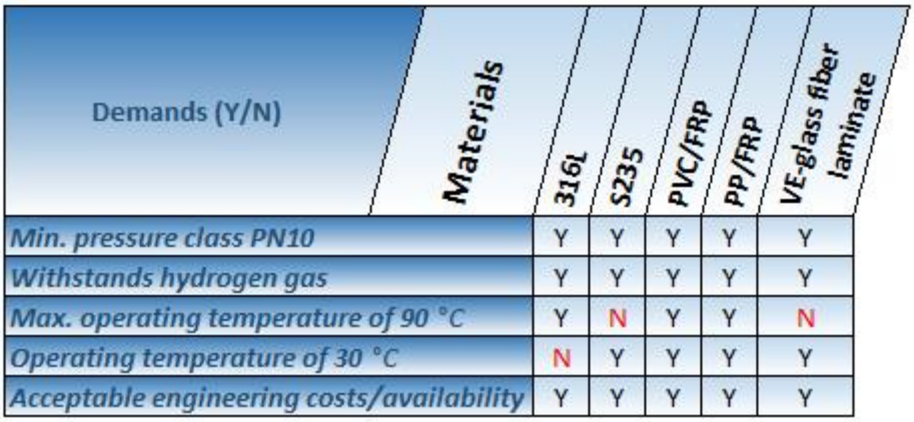
Metals	*Polymers*	*Composites*
316L	PVC	VE-glass fiber laminate
S235	PP	

The next step was the fixed extermination of materials based on their attributes and the environmental corrosion factors. Based on corrosion theory the failure mechanisms of different materials based on the atmospheric and parameter conditions in the pipeline in question can be determined. The following factors were considered for hydrogen piping materials:

- minimum PN class of 10
- withstands temperature of maximum 90 °C before cooling
- withstands operating temperature of 30 °C after cooling
- material is compatible with hydrogen at all process parameters
- acceptable engineering costs and availability.

A fixed material extermination was executed to rule out materials that are not compatible with the demands, are not easily available or have unacceptable engineering costs. Results are shown in table 17.

Table 17. The results of fixed material extermination for hydrogen piping.



Demands (Y/N) / Materials	316L	S235	PVC/FRP	PP/FRP	VE-glass fiber laminate
Min. pressure class PN10	Y	Y	Y	Y	Y
Withstands hydrogen gas	Y	Y	Y	Y	Y
Max. operating temperature of 90 °C	Y	N	Y	Y	N
Operating temperature of 30 °C	N	Y	Y	Y	Y
Acceptable engineering costs/availability	Y	Y	Y	Y	Y

Based on the fixed extermination of the demands the following materials were exterminated from further investigation:

- Carbon steel is excluded for the 90 °C hydrogen gas because of the caustic soda contained in the condensate. The risk of caustic cracking of steel S235 can be confirmed from figure 30 and the material is excluded from further study on that basis.
- The stainless steel 316L is excluded from 30 °C hydrogen gas after cooling because of surpassing the 22 HCR hardness limit defined for steels in hydrogen use. The highest affinity for hydrogen embrittlement is near room temperature. The AISI 316L material has been proven to withstand hydrogen embrittlement at higher operating temperatures at Joutseno chlor-alkali plant. The hardness value of AISI 316L is within 25…39 HRC (VGTL Asia, 2017).
- Because of the sodium hydroxide content of the hydrogen condensate, VE-glass fiber laminate was excluded from further study for the 90 °C hydrogen gas. FRP cannot withstand the corrosive environment caused by dilute 90 °C NaOH. (Ashland, 2017, p. 65.)

Because of the nature of temperature affecting the usability of materials before and after cooling the next steps of material selection were divided into two distinct phases; before cooling and after cooling. The material selection parameters are hereafter abbreviated with according nominations BC, before cooling and AC, after cooling.

The next step was the flexible extermination of materials based on their attributes and the environmental corrosion factors. Based on corrosion theory and FMEA sections of this thesis the failure mechanisms of different materials based on the atmospheric and parameter conditions in the pipeline in question can be determined. The following factors were taken into account for hydrogen piping materials:

- the possibility of hydrogen embrittlement, especially in metallic materials
- the possibility of caustic cracking, especially in metallic materials
- unacceptable uniform corrosion rate, especially in metallic materials
- the possibility of chemical degradation, especially in polymeric materials.

All the materials still being examined show no behavior that should lead to their extermination from further study based on the factors given in flexible extermination phase and according to the designated use of the material before or after cooling.

A FMEA was conducted for all of the pipeline materials still being examined. The most probable failure mechanisms and their effects for different materials were taken into consideration. The failure rates were not found from Joutseno plant's SAP PM data base because there were no failures in the timeline of the search. Because of the non-reactive nature of hydrogen and hydrogen embrittlement being the only possible hydrogen associated failure mechanism in cell room parameters, dilute sodium hydroxide was considered to be the main corrosive agent affecting the materials' lifetime. With Joutseno plant's data of NaOH induced pipeline failures and corrosion data from literature the lifetime of all pipeline materials was estimated to be in excess of 15 years. The failure rate $wRNP_{15}$ values before cooling are depicted in table 18 and the $wRNP_{15}$ values after cooling are depicted in table 19.

Table 18. The wRPN$_{15}$ values for hydrogen pipeline materials before cooling.

FMEA of hydrogen piping materials BC	AISI 316	PP/FRP	PVC/FRP
weighted RPN	*0,448*	*0,128*	*0,128*

*Table 19. The wRPN$_{15}$ val*ues for hydrogen pipeline materials after cooling.

FMEA of hydrogen piping materials AC	S235	PP/FRP	PVC/FRP	VE-FRP
weighted RPN	*0,448*	*0,128*	*0,128*	*0,384*

The main factors affecting the wRNP$_{15}$ values of hydrogen pipelines are the detectability of failures and the effect of the failure to process stability and safety because the lifetime expectancy of all materials is in excess of 15 years. Thus, lined pipelines rank the lowest scores because the failure of the lining can be easily detected with visual inspection of the outer surface of the pipelines and because the failure is contained inside the structural layer and does not affect process stability and safety.

An analysis of LCCs in a usage period of 10 years were calculated from quotations of reference pipe sections (DN150, end flanges, L = 1 m) from vendors and an estimated cost for S235 steel from appendix III compared to the estimated lifecycles of materials from FMEA analysis. The wall thickness of metallic pipes is 3,4 mm for AISI 316L and 7,112 mm for S235. The smaller the absolute value of the result the better the material performance in LCC evaluation. An LCC$_{10}$ analysis of the materials produced the following lifecycle costs for a usage period of ten years, depicted in figure 36 for hydrogen pipelines before cooling. The results for hydrogen pipelines after cooling are depicted in figure 37.

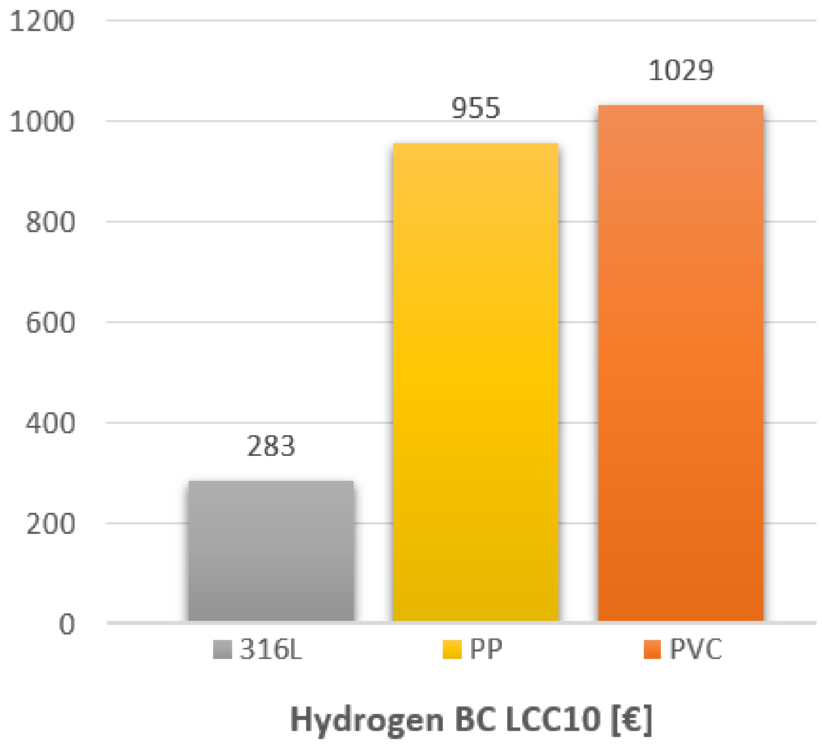


Figure 36. LCC costs of hydrogen piping materials before cooling for a usage period of 10 years. The most cost-effective material is the one with the lowest value.

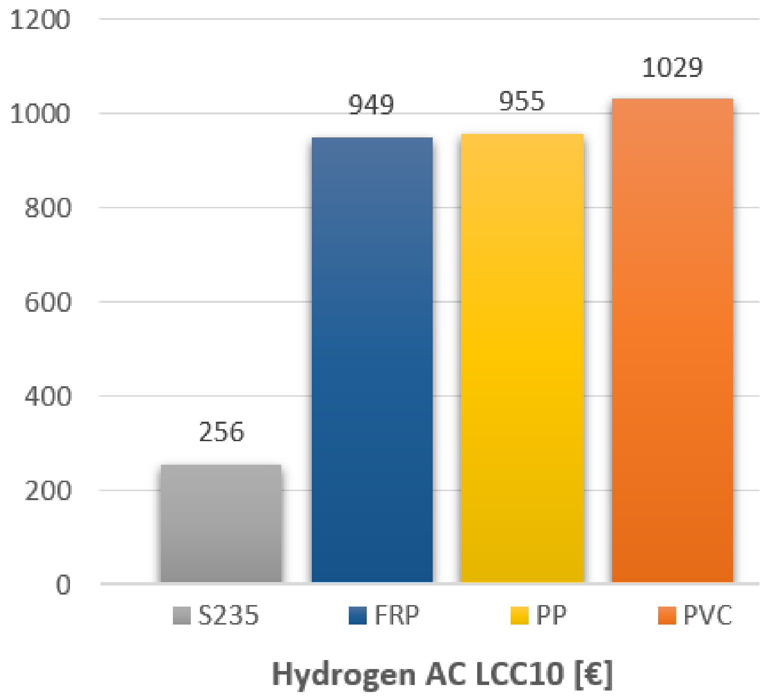
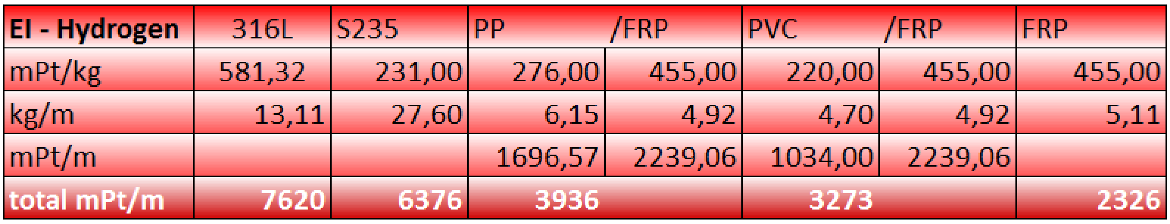


Figure 37. LCC costs of hydrogen piping materials after cooling for a usage period of 10 years. The most cost-effective material is the one with the lowest value.

Steel grade S235's and SS 316L's lifecycle costs are lower than the polymeric materials' because of the lower initial procurement costs of the pipelines. The higher costs of manual inspection do not affect the total LCCs significantly because of the less frequent inspection rate and the discounting of future costs.

LCA analysis was conducted with the ecological indicator method for all the pipeline materials still in examination. All the EI factors are depicted per kg of material. The weight of the reference pipeline section was calculated by comparing the density of each material to the different wall layers' volumes. The result is the total mPt value for 1000 mm of the pipeline in size DN150 and pressure class of PN10. The LCA analysis was conducted for all the materials from BC and AC categories as a whole, Because the mPt values does not take into account the usage caused environmental effects. The results of LCA analysis are shown in table 20.

Table 20. The results of LCA for hydrogen pipeline materials. The lower the total mPt/m the more ecologically friendly the material is.



EI - Hydrogen	316L	S235	PP	/FRP	PVC	/FRP	FRP
mPt/kg	581,32	231,00	276,00	455,00	220,00	455,00	455,00
kg/m	13,11	27,60	6,15	4,92	4,70	4,92	5,11
mPt/m			1696,57	2239,06	1034,00	2239,06	
total mPt/m	**7620**	**6376**	**3936**		**3273**		**2326**

It can be seen from the data of the LCA that polymeric materials show lower total mPt/m values than metallic materials. Even though the EI values of polymeric material per kg is higher compared to metallic materials, the density of polymers is less than metals and thus the weight of the pipeline is lower. This affects the total mPt/m because EI factors are based on the weight of the material.

The determination of the optimal pipeline material was conducted by using direct weighted normalization of the values of LCC, FMEA and LCA analysis. The according weighing parameters are 0,4 for LCC, 0,4 for FMEA and 0,2 for LCA. The normalization was conducted by determining the mean value and the standard deviation of all the parameters and standardizing the actual values of different materials against them using equation 5. Zero represents a neutral material, the more positive the normalized value, the more optimal the material is for the application. The results of normalized material analysis are depicted in figure 38 for hydrogen before cooling and in figure 39 for hydrogen after cooling.

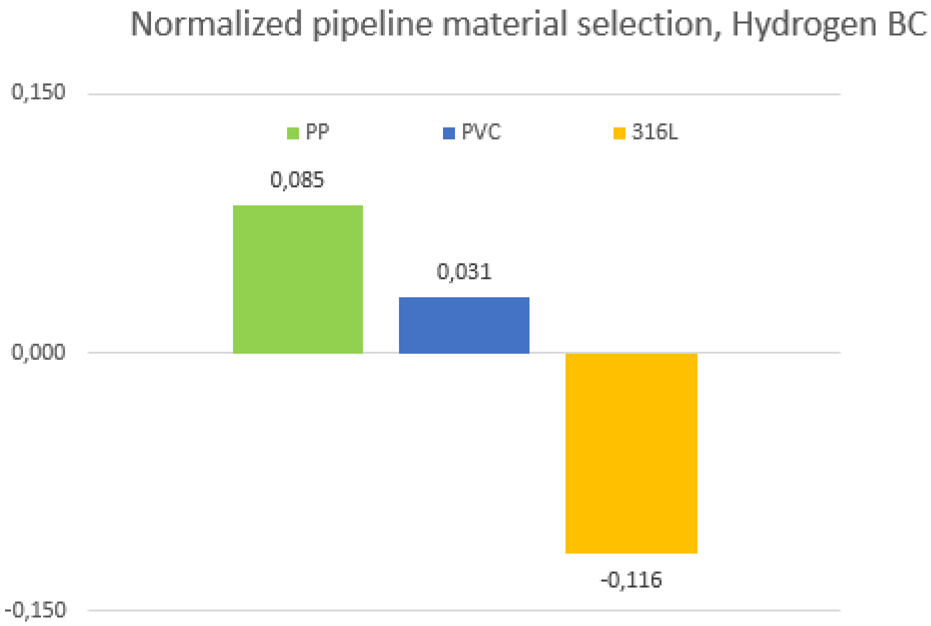


Figure 38. The results of direct weighed and normalized pipeline material factors (LCC, FMEA and LCA) for hydrogen pipelines after cooling, that determine the optimal material for the application. The most positive value is the optimal material for the application.

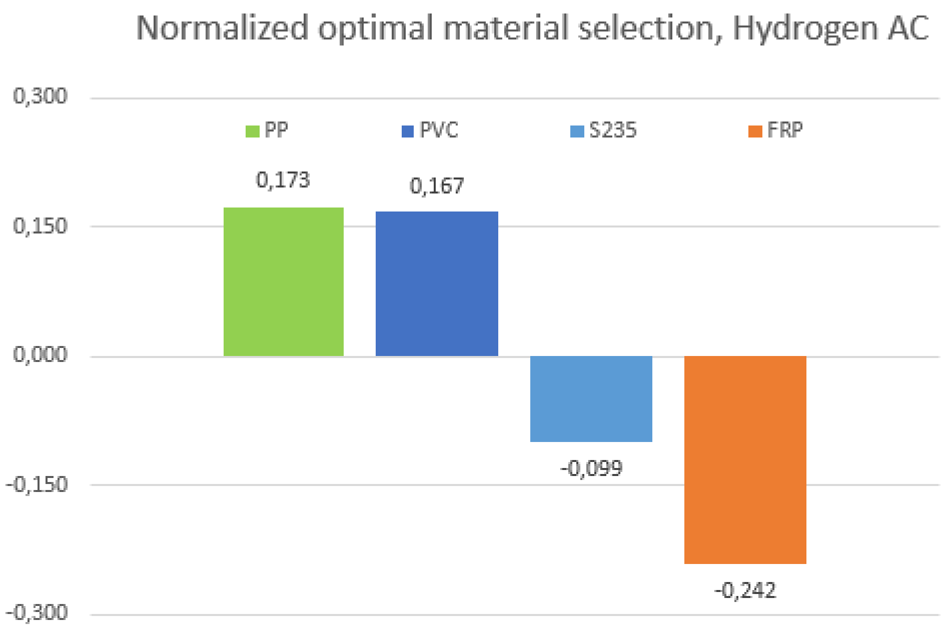


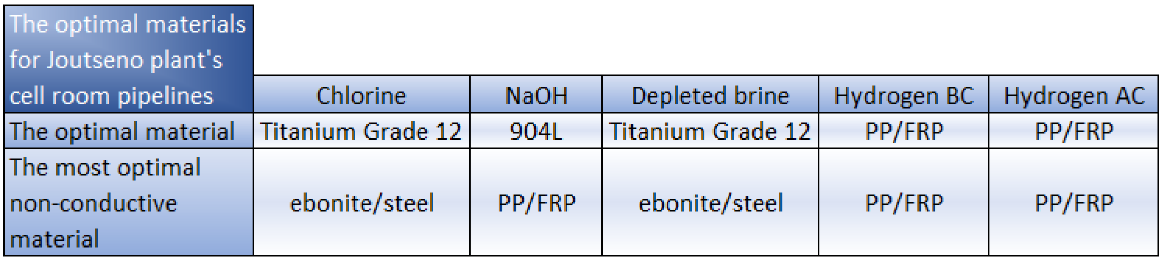
Figure 39. The results of direct weighed and normalized pipeline material factors (LCC, FMEA and LCA) for hydrogen pipelines after cooling, that determine the optimal material for the application. The most positive value is the optimal material for the application.

The optimal material for pipelines of hydrogen BC and hydrogen AC is PP/FRP. It can be seen from the results that normalized material comparison for hydrogen pipelines favors the polymer lined FRP materials, because of their improved safety, resulting in lower $wRNP_{15}$ values compared to single walled materials and the low environmental impacts when compared to metallic materials.

5.5 The optimal materials for chlor-alkali cell room pipelines at Joutseno plant

To summarize the results of the material selection strategy for chemical pipelines, table 21 depicts the optimal pipeline materials for different media of the cell room. These results are based on the literature research, calculations, expert interviews and experimental data, which were collected during this research. It must be noted that the effects of stray currents were not taken into consideration in the determination of optimal materials. If there are external currents acting on the pipeline, calculations and field testing must be made to ensure the compatibility of materials. Electrically non-conductive materials should be used to prevent any corrosion damage caused by external currents. Thus, the most optimal non-conductive material for different media is also given in table 21.

Table 21. The optimal materials for cell room pipelines highlighting also the most optimal non-conductive materials.



The optimal materials for Joutseno plant's cell room pipelines	Chlorine	NaOH	Depleted brine	Hydrogen BC	Hydrogen AC
The optimal material	Titanium Grade 12	904L	Titanium Grade 12	PP/FRP	PP/FRP
The most optimal non-conductive material	ebonite/steel	PP/FRP	ebonite/steel	PP/FRP	PP/FRP

6 DISCUSSION

All the research questions were answered in the results sections. The failure types were found to be caused by chlorine permeation in ECTFE/FRP and PTFE/steel pipeline, the corrosion in titanium headers were found out to be chlorine induced crevice corrosion in the flanges and the failures of PP/FRP piping is caused by the ageing caused by NaOH.

Previously unused pipeline materials were found and some were found out to be acceptable for Joutseno plant’s cell room pipelines. Titanium grade 12 is a well-established material to be used with chlorine and brine duties. Ebonite rubber was proven to be compatible for chlorine and brine pipelines, although a long term in-situ test must be conducted before large scale commissioning. Electroless nickel proved to be a good candidate material for NaOH service, but it was not available from pipeline manufacturers at the time of the thesis. Also, exotic metallic materials, the likes of tantalum, niobium and zirconium can be used for different sections of the cell room piping, but due to cost factors and availability had to be excluded from further study at an early phase. These materials can also be used for coating and alloying purposes, but none of the materials were found available from suppliers at the time of the thesis.

The main differences of a pipeline specific material selection strategy and a universal material selection strategy were discussed. The main difference is the quality of demands to a material selection strategy for pipelines transporting hazardous chemicals that come from legislation and the demands for a universal material selection strategy that usually focuses on the needs of the end-users. Pipeline manufacturing is standardized and thus the mechanical demands of pipeline materials are already taken into consideration by the manufacturers. Process safety and usability is another aspect unique to pipeline material selection. The selection of materials for aggressive media focuses on the corrosion behavior of the material rather than only the mechanical properties of materials.

The optimal materials cannot be universally applied to all chlor-alkali processes because the process parameters and process atmospheres have such a crucial impact on the material selection process. Material selection must always be conducted on a case-by-case basis, even though there are universally applicable guidelines of compatible materials to most well-known processes and media. A HAZOP (hazard and operability study) is always mandatory when choosing a different type of material to existing pipelines containing hazardous chemicals or selecting materials for new pipelines. When choosing new previously unused materials for a specific application, it must be noted that the long-term properties of the environment and materials cannot always be foreseen with the data available at the time of selection. Therefore, engineers may choose well known, established materials even if there are previously unused materials that are more cost-effective, possess enhanced lifetime and are more sustainable to the environment. (Ali & Edwards, 2013, pp. 9-10.)

6.1 Strength and weaknesses of proposed material selection strategy for chlor-alkali cell room’s pipeline materials

The piping material selection strategy is easy to follow and does not take insurmountable amount of time for a single pipeline or a piping system. The selection strategy ensures that the LCC costs are kept at minimum, that process safety is addressed and possibly improved and that the sustainability of materials is taken into consideration. The material selection strategy can also be applied for different CPI branches like sodium chlorate production and oil refining.

A negative aspect of the proposed material selection strategy is that some methods like FMEA in it demand the use of expert knowledge to determine the possible failure methods and their impacts on the process. The LCC analysis was conducted in this thesis with a reference pipeline section. Thus, the results can vary from real life applications. The validity of LCC analysis in real life conditions is strengthened by the fact that for an investment or maintenance project, the advantage of asking quotations directly from vendors to a pipeline with known diameters and configurations is able to give accurate information on pipeline material prices.

The proposed method for LCA analysis is difficult to conduct, because there is insufficient data for a wide comparison of materials and approximations of data inside material groups must be used. This lowers the sensitivity of the results. EI data can still be used as a referential method for comparing the environmental impacts of materials.

6.2 Objectivity of results

The author of this thesis has approximately three years of experience in the maintenance of the chlor-alkali factory in question. Some of the initially suggested pipeline materials and material exterminations may have been influenced by past experience unintentionally. There were no intentional or externally influenced decisions made, that affect the results of this thesis.

6.3 Reliability of results

The study was conducted by using IMRAD-structure for the reproducibility of the results. The method section describes the methods used in detail for the previous reason. Some of the values used for calculations have not been depicted because of the limited space allocations of the thesis. This data is available from the author.

Only full text articles were used as reference materials for this thesis. The newest possible research data was gathered but some older materials had to be used because of the scarcity of information. The number of references by decades are:

- 1980s - 1
- 1990s - 3
- 2000s - 24
- 2010s – 36.

This data clearly shows that the novelty value of references is high, resulting in the best available knowledge on the subjects researched. Reviewed articles were placed highest if the references considering a specific subject had controversial remarks.

The subject of leakage currents acting on passively protected metal structures was researched, but only few sources regarding this matter were found. The most comprehensive source was the book written by Joseph Riskin (2008) “Electrocorrosion and protection of metals: general approach with particular consideration to electrochemical plants”. It shed insight on many of the corrosion mechanism linked to leakage currents at electrolysis plants. But this data could not be verified from other literature. An interview with an expert on the matter was to be arranged but it was cancelled due to time allocation problems.

6.4 Validity of results

Triangulation method was applied as much as possible, but it was not possible for all of the reference data. The results of LCA analysis are questionable. All LCA methods to date are based on approximations of used raw ingredients, environmental and health impacts and manufacturing methods. The weighing and rating of data is always subjective and usually relies on a panel of experts and non-experts. There is not sufficient data available for the validation of the EI values for every material in question so approximations have to be used in LCA calculations.

The approximation of error rates for LCC, FMEA and LCA analysis was found to be an impossible task. The fluctuations of error rates would have been high because there are numerous factors influencing the different parameters. Thus, the results are depicted without error rates and are considered to be referential to real-life values. The results can be used as a guideline for pipeline renewal.

The costs of the pipeline materials used in LCC analysis come from various suppliers of pipeline materials. Only few of the pipeline material costs were verified from two or more sources. All the suppliers were asked to provide cost data based on the same requirements of the reference pipe section. Some of the cost data was approximated from material cost data tables thus increasing the error in LCC calculations.

6.5 Important regards to be taken into consideration when choosing previously unconfirmed materials for a specific pipeline application

When choosing materials that are previously unapproved for an application, it is mandatory to conduct long term field-testing in-situ in pipeline sections that can be easily isolated (e.g. process measurement pipelines isolated by valves) in the case of an acute failure before large term usage of the material in main process lines. This way the process safety and usability can be confirmed. For example, there might be laboratory tests conducted but real-life process conditions may vary from these tests. Another aspect that verifies the need for in-situ testing is the use of different types of gasket materials in pipelines. They have an influence on the crevice corrosion formation in pipeline flanges.

Real life corrosion behavior experience must also be taken into consideration when selecting a material to a specific application. For example, if a material selection chart says a material is resistant but in real life conditions (e.g. lower pH, contaminants, high flow velocities, turbulent flow) fails at a more accelerated rate, the real-life behavior will ultimately determine the suitability of the material. One example of such a behavior of materials is the accelerated corrosion rate of AISI 316Ti plate heat exchanger plates in 32,5 % sodium hydroxide solution observed at Joutseno chlor-alkali plant. The iso-corrosion chart by Nickel develpment Institute (Appendix IV) gives all AISI 316 materials a corrosion rate of under 0,0254 mm/y at a temperature of 80 °C, giving the material with a thickness of 0,6 mm a lifetime expectation of >7 years. It has been witnessed at Joutseno plant that the plates with a thickness of 0,6 mm have uniformly corroded through at a rate of 24 months. The temperature of the solution has been constantly ~80 ± 2 °C at the inlet side. This deems the material unusable in that atmosphere and it must be excluded from further stages of material selection. The material composition was confirmed to be within the limits determined by the according standards with a spectroscopic analysis.

6.6 Discussion on the use of the proposed optimal materials in cell room pipelines

The leakage currents inside the cell room piping must be taken into consideration when selecting passively protected metallic materials to the cell room pipelines in the direct vicinity of the cells. The determination of leakage current intensities always needs experimental measurements of different pipeline sections and is dependent on the number of cells in the set and the operating current. All the metallic materials can be protected by e.g. applying an external current or using dimensionally stable anodes with the pipeline base material to keep the passive layer from dissolving.

Leakage current data was insufficient to be taken into consideration in this thesis. Therefore, caution should be taken when replacing the pipeline materials with the proposed optimal materials. All direct pipelines from cells are subjected to notable leakage currents. As a caution if a leakage current study is not conducted only non-conductive materials should be used for construction in the pipelines before grounding. The most optimal non-conductive materials for cell room pipelines are:

- chlorine: ebonite/steel
- NaOH: PP/ FRP

- depleted brine: ebonite/steel
- hydrogen: PP/FRP.

The production methods of pipeline materials were not taken into consideration in the LCC calculations. Thus, some of the materials cannot be formed to specific pipeline sections in real life. For example, PTFE lining is impossible to weld so many of the structures that include complex branches cannot be manufactured or must be manufactured with separate parts. This raises the LCC costs of the pipeline in real life. It also raises the LCA values of pipeline materials due to an increase in the material usage.

There are various types of resins that can be used in manufacturing FRP piping. The vinyl ester resins provide the most comprehensive corrosion resistance to the chemicals in a chlor-alkali plant’s cell room. The type of resin must always be chosen accordingly to the specific media contained in the pipeline. For example, there are different types of resins intended for chloride and alkali service. The glass fiber type must always be a corrosion resistant type like C or ECR glass in cell room pipelines.

Permeation in polymer and elastomer materials can be reduced by increasing the liner thickness. This of course raises the price of the pipeline and must be considered in the LCC analysis. For PVDF liner in chlorine use there are numerous tables that approve its use with wet chlorine at temperatures as high as 100 °C, but Dyneon (2004, p. 3) warns about stress cracking susceptibility of PVDF with molecular chlorine. Thus, it is necessary to conduct tests before large scale use of the material with chlorine or depleted brine.

The purity of brine must be ensured for optimal membrane function. The major impurities of brine are calcium, magnesium, and sulfate. Metallic ions also tend to deteriorate the membrane functions and thus it must be ensured that their concentrations are in the ranges specified by membrane suppliers. The harmful ions include the likes of Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Hg^{2+}. (O'Brien, et al., 2005, p. 649.) The corrosion products of metallic alloys can contain a variety of these harmful ions. The filtration system of the plant must be ensured to be able to reduce the harmful concentrations to acceptable levels before the use of metallic alloys as pipeline materials for brine and chlorine service.

6.7 Possible high-risk scenarios caused by material selection

Material selection can have consequences that are not easily foreseeable. Therefore, thorough FMEA, HAZOP, research of possible failure scenarios and in-situ testing of materials play a key role in the final commissioning of optimal materials.

For example, the use of commercially available CPVC lining created especially for chlorine service could have disastrous effects. CPVC is treated with a high amount of compounding and other property enhancing materials (e.g. calcium carbonate) to improve its mechanical properties, manufacturing and UV-resistance. If it is not taken into consideration that high temperature (~90 °C) chlorine gas can dissolve these filler materials from the bulk CPVC material, they could be transferred to feed brine via condense returned to the anolyte tanks. (O'Brien, et al., 2005, p. 623.) If the filtration system is not designed to cleanse these types of impurities they can be circulated to the cells by the feed brine circulation. Then the feed brine containing impurities could start to foam inside the cell and lead to a premature membrane destruction.

The destroyed membranes let hydrogen gas through to the anodic chamber to mix with chlorine. The mixture of chlorine and hydrogen is explosive. Because of this explosive nature the percentage of hydrogen in chlorine is monitored online and the rise of hydrogen percentage in chlorine could lead to the emergency shutdown of production and start accumulating production losses. There is also a possibility of explosion inside the pipeline, cooling tower or chlorine filtration system. The damaged cells need membrane replacement, leading to excess labor and parts costs that could be upwards of >1 M€.

Also, the fact of leakage currents must be specifically investigated when determining the optimal material for electrolysis plants cell room. For instance, if titanium is selected for the dropdown and header pipeline material for depleted brine lines, the always inherent leakage currents must be taken into consideration because they affect the stability of the oxide layer protecting the material from chlorides. If an external anodic current in combination with the oxidation of chlorine exceeds the safe polarization values of titanium an anodic dissolution is propagated and the material will fail leading to a possibly catastrophic leakage of solution and unplanned downtime of the factory. The process of corrosion can be rapid depending on the nature and intensity of the current. This type of a failure could lead to a chlorine emission and depending on the pipeline position and scale, to an unplanned shutdown of production that starts to accumulate costs. The pipeline replacement needs extra labor and parts, which adds to the total costs of the failure.

6.8 Possible cost savings in the future

By following the optimal material selection strategy Joutseno chlor-alkali plant can have formidable cost savings in the future. There are also other cost saving methods that can be used to reduce pipeline and process equipment related costs. One of them is the use of alloyed titanium only as a flange material to reduce the cost of the pipeline and improve the crevice corrosion resistance of the pipeline. For example, the pipeline can be made from CP titanium and the collars from crevice corrosion resistant titanium materials like gr. 7 or gr. 12. (ASM International, 2003, p. 917.)

6.8.1 An additional viewpoint on the possible magnitude of LCC reduction in chlorine header pipelines by implementing a specific material selection strategy for pipelines

A specific LCC study was conducted for the chlorine header pipelines of the cell room. The operation period was set to 15 years and the present state of piping renewal was used as a reference. The costs were approximated from data found from SAP and calculated to include all pipeline sections of the headers. A section of DN300 (median pipe size of headers) ECTFE/VE pipeline costs 13848,533 € to replace based on data from SAP PM data base. There are in total 8 sections (A-header: 4, B-header: 4) that need to be replaced periodically five years apart. The pipeline is determined to have a visual NDT inspection every two years. The approximated cost of inspection, including manual dismantling of the pipeline end sections, scaffolding and the cost of inspection is 2000 € per inspection. The cost of recycling the material was approximated to be 250 € per dismantled section. The interest rate used for LCC calculations was 8 %. The total LCC cost of pipeline in the investigation period is 214 259,12 €.

By using the proposed material selection strategy, it was found that the best non-conductive material for wet chlorine gas is ebonite rubber lined steel. Ebonite rubber lined steel pipe with an approximated cost of 40 % of the procurement price of ECTFE/FRP piping has an expected lifetime of 10 years and an NDT inspection period of three years. The total LCC_{15} cost of ebonite is 50 328,81 € if the whole pipeline is replaced today. The possible discounted cost saving in the period of 15 years is thus 163 930,32 € when compared to the costs of ECTFE/VE pipelines. This proves the fact that by applying the optimal piping selection strategy the cost savings can be formidable compared to the current state of piping renewal.

A similar study with a usage period of 10 years returned a possible saving of 132 920,78 €. With a five-year usage-period, the saving is 73 392,46 €. If the replacement of the pipeline is done at a similar pace than ECTFE/FRP pipelines in present; two or three sections at a time with a renewal period of five years, the cost savings will further increase because the present value method discounts the future values. The discounting mechanism takes into consideration the possibility of investing the capital saved today and earning revenue with it in the future.

6.8.2 Online corrosion monitoring

For FRP laminate (e.g. FRP + fluoropolymer lining) materials, low cost NDT could be used to monitor the state of piping periodically. Currently the methods used for pipeline inspection of different material classes besides monthly outer visual inspection include the likes of visual inspection with sewer camera equipment, ultrasound inspection and radiographic inspection of which all need expensive equipment and expert knowledge to ensure the inspection quality. A form of low cost monitoring for layered pipeline could be accomplished by adding radio frequency identification (RFID) slides inside the FRP layers. The RFID slides are corroded by the permeants and when there is no signal available from them, the operating staff can assume that the solution has permeated through the fluoropolymer lining and the pipeline needs replacement.

Electrical on-line monitoring systems are also available for NDT. Electrical resistance probes or linear polarization measurements can provide data about corrosion rates by checking the efficacy of corrosion inhibition or by detecting changes in process corrosivity.

6.8.3 Lowering the usage period costs by insulating or painting the pipelines

The usage period lifecycle costs (heat dissipation, degradation because of UV-radiation etc.) could in some cases be reduced by insulating or painting the chemical piping, but in many cases, it is better for a visual inspector to identify the inner failures at an early stage when the pipe is not insulated.

6.9 Areas that need further investigation

There are areas involved in pipeline corrosion that were noted to have an impact on corrosion rates, detectability of failures, material properties or costs of pipeline NDT but due to the limited timeframe, were not investigated. Also, different sections of Joutseno chlor-alkali plant's pipelines not involved in the scope of this thesis that contain corrosive solutions are listed in this section. Some emerging pipeline construction materials are also highlighted.

6.9.1 Different sections of piping at Joutseno chlor-alkali plant

At Joutseno plant there are numerous other highly corrosive atmospheres that are not in the scope of this study. The following are of most significance considering the environments and possible cost savings:

- NaOH evaporation, because of the higher concentration of NaOH and higher temperatures than cell room NaOH circulation
- Sodium hypochlorite production, because of the highly corrosive nature of NaClO and the production method where there are alkaline, chloride and chlorine solutions involved so there are different types of corrosion mechanisms affecting the piping systems
- HCl piping, because of the highly corrosive nature of HCl
- Loading spots, because of corrosive environment and mechanical impacts on loading pipes which call for specific types of ductile materials or surface finishes.

6.9.2 Gasket and process equipment materials

There is always a need for gasketing in process pipelines because of joints and process equipment. These discontinuities in pipes need to be sealed so the fluids or gases can be kept in containment. The most probable leakage points in piping are these gasketed joints according to failure data found at Joutseno plant's SAP PM data base. The porosity of the type of gasket used also affects the crevice corrosion behavior in pipeline flanged joints.

Process equipment like containers, valves, pumps, heat exchangers and scrubbers can also be made out of various different types of materials. The material selection strategy can also be used to lower the procurement and lifetime costs of these equipment.

6.9.3 Other corrosion controlling measures

All electrochemical corrosion processes can be controlled by applying an external current. Since all corrosion processes start when the characteristic polarization current limit is exceeded the corrosion characteristics can be altered to reduce or stop corrosion processes by inducing an external current to the structure.

The process is well understood, but hard to calculate and monitor due to the different process factors (including change of pH, change of redox, change of polarization due to corrosion products etc.). There is therefore always need for calculations, design and laboratory/field testing of the equipment and corrosion rate in real process parameters when applying external currents for corrosion control. In these types of corrosion controlling processes there is also always a need for electricity. When calculating the LCCs for applications this fact must be considered.

Corrosion inhibitors can also be used to reduce corrosion in pipelines. They can be used to reduce the redox potential, adjust pH or to form a protective film on the pipeline walls. The setbacks with using corrosion inhibitors are, to name a few:

- additional costs of dosing the chemicals
- purity of products; the need for removing the inhibitors from end-product
- dosing and removal equipment costs
- possible health hazards of used inhibiting chemicals.

The quality and amount of used chemicals must always be studied on a case-by-case basis to ensure the wanted end results.

6.9.4 Nanomaterials and nano surface modifications of materials for improved corrosion characteristics

New types of base material and surface modifications for well-established engineering materials are being conducted to improve their corrosion characteristics. Most modifications rely on changing the grain size of metals or alloying the surface of metals with other corrosion inhibiting elements that normally cost too much to use as construction materials. By utilizing these types of materials for constructions it could be possible to reduce LCC costs and improve process safety. Nanofillers and nanofibers are also being studied for composite constructions to improve their mechanical and corrosion characteristics (Biron, 2014, p. 312).

6.9.5 Ceramic coatings and cermets for corrosive media

The study for finding corrosion resistant ceramic coatings with adequate mechanical properties is ongoing. Ceramics like silicon carbide and aluminum oxide have been tested to withstand wet chlorine, but the data is scarce. At 2016 these ceramic coatings have suffered from temperature shock caused cracking, but with improved production methods and compositions they could be improved to be formidable materials for corrosion and erosion resistant chemical pipelines.

Cermets can be used as metal-ceramic composites or cermet coatings. Cermets are usually used in environments demanding wear and high temperature resistance. The performance of cermets in corrosive environments is ongoing and the likes of titanium carbide (TiC) and tungsten carbide-cobalt (WC-Co) are studied. So far, the data is discouraging for acidic and chloride containing media, but plausible corrosion rates for alkaline media have been seen. As with ceramic coatings the continuous improvement of cermets may improve the corrosion characteristics to usable levels in corrosive media in the near future.

6.9.6 Fluoropolymers with increased permeation resistance

New improvements on increasing the permeation resistance of fluoropolymers include the likes of adding a reactive additive to reduce diffusion to a specific element or compound. At least PVDF and ECTFE have been proven to resist permeation more than the base material by adding reactive groups that react with the permeant. The additive can be hindered phenol, hindered amine, vitamin E, lignin, or phenols; depending on the permeating element. The use of filler materials and protective multilayer fluoropolymer coatings are also being studied.

6.10 Literature helping the piping material selection for chlor-alkali plant pipelines

There are also non-mandatory recommendations from roof organizations of chlor-alkali manufacturers; The World Chlorine Council, EuroChlor and ChlorineInstitute that can be used for insuring the operational safety for chemical piping used in chlor-alkali plants. These publications were used for finding reference materials for material selection.

There are multiple available handbooks and publications incorporating corrosion control in their scope. The most comprehensive books on the subject of corrosion found in the literary review of this thesis were “*ASM Handbook Volume 13A, Corrosion: Fundamentals, Testing, and Protection*” published in 2003 by ASM International, “*Handbook of Chlor-Alkali Technology*” written by Thomas F. O'Brien, Tilak V. Bommaraju and Fumioin Hine in 2005 and published by Springer Science+Business Media, Inc and “*Electrocorrosion and Protection of Metals*” by Joseph Riskin in 2008 published by Elsevier B.V.

7 SUMMARY

This thesis was made for Kemira Chemicals Oy's Joutseno chlor-alkali plant. All the chemical media contained in the electrolysis cell room piping are classified as hazardous substances. They also cause a corrosion atmosphere to the pipelines which are a key process equipment for ensuring the usability of the process. There were multiple failure types in different pipeline sections, where research of the corrosion processes was needed to determine the failure types. There was a need for pipeline material selection strategy to ensure that corrosion is kept at sustainable levels, process and human safety is considered, costs are kept at a minimum and for ensuring that the pipeline materials are produced in a sustainable way.

The thesis follows IMRAD structure for ensuring that the results are reproducible and fulfill the demands for a scientific study. The study was conducted mainly by a literary review based on reference materials from scientific Internet sources, books, data from pipeline material producers and the maintenance database of Joutseno plant. Experts on the regarding subjects were also interviewed. Also, a small-scale destructive test for finding out the failure mechanism of ECTFE/FRP pipeline section was conducted.

The results of determination of possible corrosion mechanisms, failure timeframes, possible pipeline materials and the formation of a systematic material selection strategy and the methods used in it were gathered from scientific literature. The methods used in the strategy include FMEA, LCC, LCA analysis and normalized weighted scoring of materials. FMEA data was gathered from SAP PM data base, experimental observations and literature. Some expert interviews were also used to strengthen the validity of results. LCC analysis calculations were based on data gathered from pipeline suppliers, real life experience of NDT testing, expert interviews and failure timeframe data and were calculated with a software application. LCA data was gathered purely from literature and calculated with a software application. The ranking of materials was based on expert interviews, results from FMEA, LCC and LCA calculations and were formulated with a software application. The validity and strength of the results were reviewed in the discussion section and found out to be applicable in real life process conditions.

7.1 The main results of the thesis

New previously unused materials at Joutseno plant that were found to be suitable for different chemical media in the chlor-alkali cell room were found. For chlorine pipelines titanium grade 12 was discovered to be able to substitute previously used titanium grade 7. Ebonite rubber lined steel pipelines can also be used in chlorine and brine pipelines. For depleted brine a more permeation resistant grade of PTFE lined steel pipeline was found and is TF-E lined steel. For caustic soda, a previously unused material that shows promising corrosion resistance characteristics is electroless nickel plated stainless steel, which was found to be unavailable from pipeline suppliers at the time of the thesis and thus excluded from further research.

The corrosion failures were discovered to be caused by chlorine permeation in ECTFE/FRP and PTFE/steel pipeline, the corrosion in titanium chlorine headers was found out to be chlorine induced crevice corrosion in the flanges and the failures of PP/FRP pipelines transporting NaOH are caused by ageing of the material leading to fractures. The lifecycles of currently used pipeline materials were also investigated and can be used in planning the pipeline renewal periods.

A systematic approach to pipeline material selection for chlor-alkali process was introduced and found out to be usable for the determination of optimal pipeline materials for different pipeline sections. The main differences of a pipeline specific material selection strategy and a universal material selection strategy are the quality of demands to a material selection strategy for pipelines transporting hazardous chemicals that come from legislation and the demands for a universal material selection strategy that usually focuses on the needs of the end-users. Pipeline manufacturing is standardized and thus the mechanical demands of pipeline materials are already taken into consideration by the manufacturers. Process safety and usability is another aspect unique to pipeline material selection. The selection of materials for aggressive media focuses on the corrosion behavior of the material rather than only the mechanical properties of materials. The pipeline material selection strategy ensures that all of these considerations are taken into account and ensures a safe, cost effective and environmentally sustainable way to determine the optimal materials for chemical pipelines.

Because of the lack of measurement data for leakage current induced corrosion, non-conductive pipeline materials should be used before grounding in the vicinity of the electrolysis cells. The optimal materials for different pipeline sections were found, also highlighting the most optimal electrically non-conductive materials. For chlorine pipelines the optimal material is titanium grade 12 and the most optimal non-conductive material is ebonite lined steel. Similarly, for the depleted brine lines the optimal material is titanium grade 12 and the most optimal non-conductive material is ebonite lined steel. The feed brine lines were left out of scope because there are no observable corrosion failures in the current pipeline materials. For caustic soda, the optimal material is AISI 904L stainless steel and the most optimal non-conductive material is PP/FRP. For hydrogen pipelines before and after cooling, the optimal material which is also non-conductive is PP/FRP.

7.2 The usability and discussion of the results

The proposed material selection strategy was found to be useful in determining the optimal pipeline materials for all of the chemical media of the cell room. The material selection strategy can also be used for different branches of the CPI. Formidable cost savings can be achieved by using the strategy in comparison to the current state of piping renewal. Process safety is kept at current level or increased by implementing the pipeline material selection strategy. The sustainability of materials can be compared by using the material selection strategy. Multiple areas that need further study were also found.

REFERENCES

Aezeden, M., 2013. Crevice Corrosion of Inconel and Hastelloy in a 60^{o}C 3.5% Sodium Chloride Solution. IOSR Journal of Engineering, 3(5), pp. 17-20.

Ali, J. & Edwards, K. L., 2013. Multi-criteria Decision Analysis for Supporting the Selection of Engineering Materials in Product Design. s.l.:Elsevier Inc.

Argasinski, J. K. & Loosbergh, M. E., 2009. Fluoropolymer Lining for a Chlorine Scrubber. Materials Performance, pp. 47-49.

Aromaa, J., 2005. Korroosionestotekniikan perusteet. Espoo: Teknillisen korkeakoulun materiaalitekniikan julkaisuja.

Ashland, 2017. Chemical Resistance Guide. [Online] Available at: www.ashland.com/ industries/corrosion-resistant [Accessed 29 4 2017].

ASM International, 2003. ASM Handbook . In: S. D. Cramer & B. S. Jr. Covino, eds. Volume 13A, Corrosion: Fundamentals, Testing, and Protection. Materials Park: ASM International, p. 1050.

ASTM B265-15, 2015. Standard Specification for Titanium and Titanium Alloy Strip, Sheet, and Plate. West Conshohocken: ASTM International.

Barth, R. R., Simmons, K. L. & San Marchi, C., 2013. Polymers for Hydrogen Infrastructure and Vehicle Fuel Systems: Applications, Properties, and Gap Analysis, Springfield: U.S. Department of Commerce.

Biron, M., 2014. Thermosets and Composites, The Selection, Applications, Manufacturing and Cost Analysis. In: S. Ebnesajjad, ed. PDL HANDBOOK SERIES. 2nd ed. Chadds Fond: Elsevier, pp. 300-417.

Business Insider, 2010. Niobium: The Critical Strategic Metal That's Only Mined Two Places On Earth. [Online] Available at: http://www.businessinsider.com/niobium-the-critical-strategic-metal-thats-only-mined-two-places-on-earth-201012?r=US&IR=T&IR=T [Accessed 18 4 2017].

Chandrasekaran, V., 2010. Rubber as a Construction Material for Corrosion Protection: A Comprehensive Guide for Process Equipment Designers. s.l.:Wiley.

CRC, 2013. The Elements. In: W. M. Haynes, ed. CRC Handbook of Chemistry and Physics, 94th Edition. Boca Raton: Taylor & Francis Group, LLC, pp. 1-42.

D´Errico, F., 2015. Material Selections by a Hybrid Multi-Criteria Approach. Milan: Springer International Publishing.

De Dietrich Process Systems, 2017. Introductory gyide to glass-lined steel equipment. [Online] Available at: http://blog.ddpsinc.com/hs-fs/hub/47823/file-24022062-pdf/docs/ddps_introduction_to_glass-lining_.pdf [Accessed 5 5 2017].

DuPont, 2017. Permeation — Its Effects on Teflon® Fluoropolymer Coatings. [Online] Available at: http://www.magnatexpumps.com/pdf/permeation_effects.pdf [Accessed 7 5 2017].

Dyneon GmbH, 2017. Brochures. [Online] Available at: http://multimedia.3m.com/mws/media/802318O/3m-dyneon-tfm-modified-ptfe-brochure.pdf?fn=TFM_Product_Information_EN.pdf [Accessed 18 5 2017].

Dyneon, 2004. Dyneon™ PVDF (Polyvinylidene Fluoride). [Online] Available at: http://multimedia.3m.com/mws/media/242249O/dyneontm-pvdf-chemical-resistance-tables.pdf [Accessed 9 3 2017].

Ernzer, M. & Wimmer, W., 2002. From environmental assessment results to Design for Environment product changes: An evaluation of quantitative and qualitative methods. Journal of Engineering Design, 13(3), pp. 233-242.

Eskelinen, H. & Karsikas, S., 2013. Vihreän teknologian näkökulmat konstruktiomateriaalien valinnassa. Lappeenranta: LUT Scientific and Expertise Publications.

Esko, M., 2017. Materiaalikysely; eboniittivuorattu teräsputki märällä kloorikaasulle [Interview] (17 3 2017).

Euro Chlor, 2015. The membrane cell process. [Online] Available at: http://www.eurochlor.org/the-chlorine-universe/how-is-chlorine-produced/the-membrane-cell-process.aspx [Accessed 15 February 2017].

European Industrial Gases Association, 2004. Hydrogen Transportation Pipelines. Brussels: European Industrial Gases Association.

European Union, 2007. European Union Risk Assessment Report Chlorine (Environment) CAS No: 7782-50-5, Luxembourg: Office for Official Publications of the European Communities.

Haynes International, 2017. HASTELLOY® C-22® & C-276 alloys in Saturated Wet Chlorine. [Online] Available at: http://www.haynesintl.com/tech-briefs/corrosion-resistant-alloys/corrosion-resistant-alloy-applications/hastelloy-c-22-c-276-alloys-in-saturated-wet-chlorine-(H-2032) [Accessed 5 6 2017].

Horvath, D., 1992. Chlorine, Chlorine compunds and their environmental impact. Luxembourg, European Parliament, Scientific and Technological Options Assessment.

International Organization for Standardization, 2017. ISO 14040:2006. [Online] Available at: https://www.iso.org/standard/37456.html [Accessed 10 5 2017].

Kaesche, H., 2003. Corrosion of metals; Physiochemical Principles and Current Problems. Erlangen: Springer-Verlag Berlin Heidelberg.

Kemira Chemicals Oy, J. t., 2013. Joutsenon yleisesittely, Tervetuloa Joutsenoon!. [Online] [Accessed 2017].

Kemira Oyj, 2017. Ethics and compliance at Kemira. [Online] Available at: http://www.kemira.com/en/corporate-responsibility/business-practices/ethics-and-compliance/pages/default.aspx [Accessed 30 4 2017].

Landolt, D., 2007. Corrosion and surface chemistry of metals. Lausanne: EPFL Press.

Liedtke, C. et al., 2014. Resource Use in the Production and Consumption System — The MIPS Approach. Resources, Issue 3, pp. 544-574.

Lindgren, C., 2017. Failures of cell room pipelines [Interview] (12 10 2017).

Lokka, M. & Hänninen, H., 1994. Elinjaksokustannus- ja elinkaarianalyysi ja niiden soveltaminen materiaalinvalinnassa. Espoo: Teknillinen korkeakoulu, Konetekniikan osasto, Materiaalitekniikan laboratorio.

Marcus, P., 2003. Introduction to Fundamentals of Corrosion Thermodynamics, Corrosion: Fundamentals, Testing and Protection, Vol 13A, ASM Handbook. Paris: ASM International.

Messaoudani, Z. I., Rigas, F., Hamid, M. D. B. & Che Hassan, C. R., 2016. Hazards, safety and knowledge gaps on hydrogen transmission via natural gas grid: A critical review. International Journal of Hydrogen Energy, Issue 41, pp. 17511-17525.

Metalary, 2017a. Tantalum Price. [Online] Available at: https://www.metalary.com/tantalum-price/ [Accessed 20 4 2017].

Metalary, 2017b. Niobium Price. [Online] Available at: https://www.metalary.com/niobium-price/ [Accessed 18 4 2017].

Ministry of Housing, Spatial planning and the Environment, 2013. Eco-indicator 99 Manuals. [Online] Available at: https://www.pre-sustainability.com/download/EI99_ Manual.pdf [Accessed 10 5 2017].

Murakami, K. & Takemoto, M., 2005. Precursor of hydroigen induced glass lining chipping by AE monitoring. Journal of Acoustic Emission , Volume Volume 23, pp. 215-223.

Nickel Development Institute, 1983. Corrosion Resistance of Nickel and Nickel-containing Alloys in Caustic Soda and Other Alkalies, s.l.: Nickel Development Institute.

Nuss, P. & Eckelman, M. J., 2014. Life Cycle Assessment of Metals: A Scientific Synthesis. PLoS One, 9(7), pp. 1-12.

O'Brien, T. F., Bommaraju, T. V. & Hine, F., 2005. Handbook of Chlor-Alkali Technology. New York: Springer Science+Business Media, Inc.

OVAM, 2009. Ecolizer 2.0, Mechelen: Danny Wille, OVAM. Paidar, M., Fateev, V. & K., B., 2016. Membrane electrolysis—History, current status and perspective. Electrochimica Acta, Issue 209, pp. 737-756.

Pasman, H. J. & Rogers, W. J., 2010. Safety challenges in view of the upcoming hydrogen economy: An overview. Journal of Loss Prevention in the Process Industries, Issue 23, pp. 697-704.

Pillay, A. & Wang, J., 2003. Modified failure mode and effects analysis using approximate reasoning. Reliability Engineering & System Safety, 79(1), pp. 69-85.

Protopopoff, E. & Marcus, P., 2003. Electrode Potentials, Corrosion: Fundamentals, Testing, and Protection, Vol 13A, ASM Handbook. Paris: ASM International.

PubChem, 2017. Sodium hydroxide. [Online] Available at: https://pubchem.ncbi.nlm.nih. gov/compound/sodium_hydroxide#section=Top [Accessed 3 5 2017].

Rebak, R. B., 2006. Industrial Experience on the Caustic Cracking of Stainless Steels and Nickel Alloys - A Review. San Diego, Corrosion/2006 Conference and Exposition.

Reichhold, 2009. FRP Material Selection Guide, Druham: Reichhold, Inc.

Riskin, J., 2008. Electrocorrosion and protection of metals : general approach with particular consideration to electrochemical plants. Oxford: Elsevier B.V.

Salakka, R., 2017. Area manager, Sulmu Oy [Interview] (28 February 2017).

Sandvik, 2017. Zirconium tubes. [Online] Available at: http://smt.sandvik.com/en/products/tube-pipe-fittings-and-flanges/tubular-products/zirconium-tubes/ [Accessed 20 4 2017].

Schweitzer, P. A., 2007a. Corrosion of linings and coatings. 2nd ed. New York: Taylo and Francis Group, LLC.

Schweitzer, P. A., 2007b. Corrosion of polymers and elastomers. 2nd ed. New York: Taylor and Francis Group, LLC.

Schweitzer, P. A., 2007c. Fundamentals of metallic corrosion : atmospheric and media corrosion of metals. 3rd ed. Florida: Taylor and Francis Group, LLC.

Singh, R. K., Murty, H., Gupta, S. & Dikshit, A., 2012. An overview of sustainability assessment methodologies. Ecological Indicators, Issue 15, pp. 281-299.

The Engineering ToolBox, 2017. Piping Materials and Cost Ratios. [Online] Available at: www.engineeringtoolbox.com/piping-materials-cost-ratios-d_864.html [Accessed 17 2 2017].

Tukes, 2017. Kemikaaliputkistojen turvallisuusvaatimukset. [Online] Available at: www.tukes.fi/Tiedostot/kemikaali_kaasu/Kemikaaliputkistojen_turvallisuusvaatimukset.pdf [Accessed 22 March 2017].

Työterveyslaitos, 2016. OVA-ohje: KLOORI. [Online] Available at: http://www.ttl.fi/ova/kloori.html [Accessed 1 3 2017].

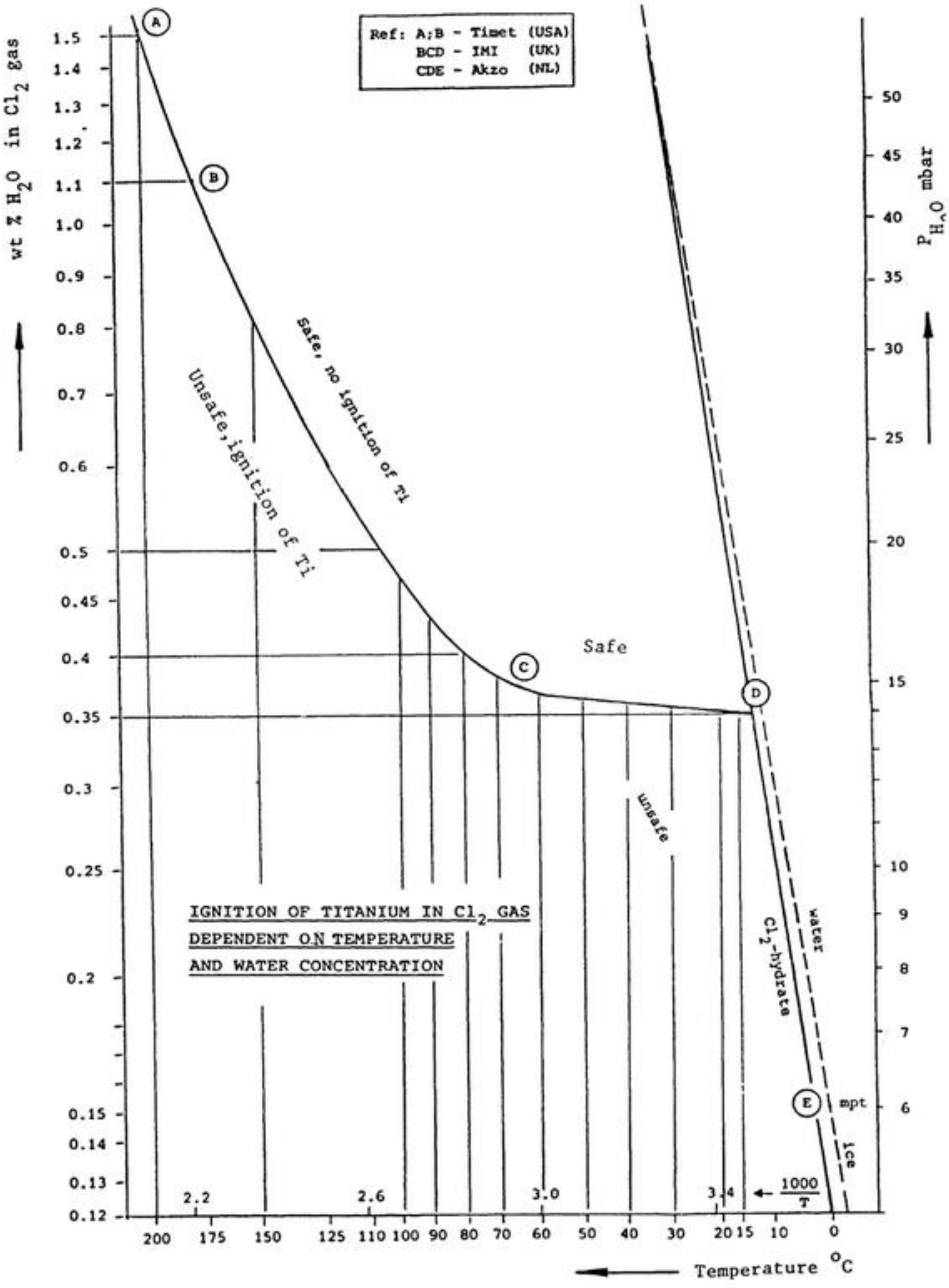
Wang, P., 2012. The General Properties and Applications of Ceramic Materials. Applied Mechanics and Materials, Volume 174-177, pp. 215-218.

Wellington, T., 1992. Modern Chlor-Alkali Technology. 5th ed. London and New York: Elsevier Applied Science.

VGTL Asia, 2017. Stanless Steel AISI 316 (Austenitic). [Online] Available at: http://www.vtlg-asia.com/products/precision-balls/stainless-steel-balls/stainless-steel-aisi-316-austenitic/ [Accessed 18 5 2017].

Øvland, S. & Hansen, R., 2007. Materials Considerations in Hydrogen Production, Porsgrunn: Hydro.

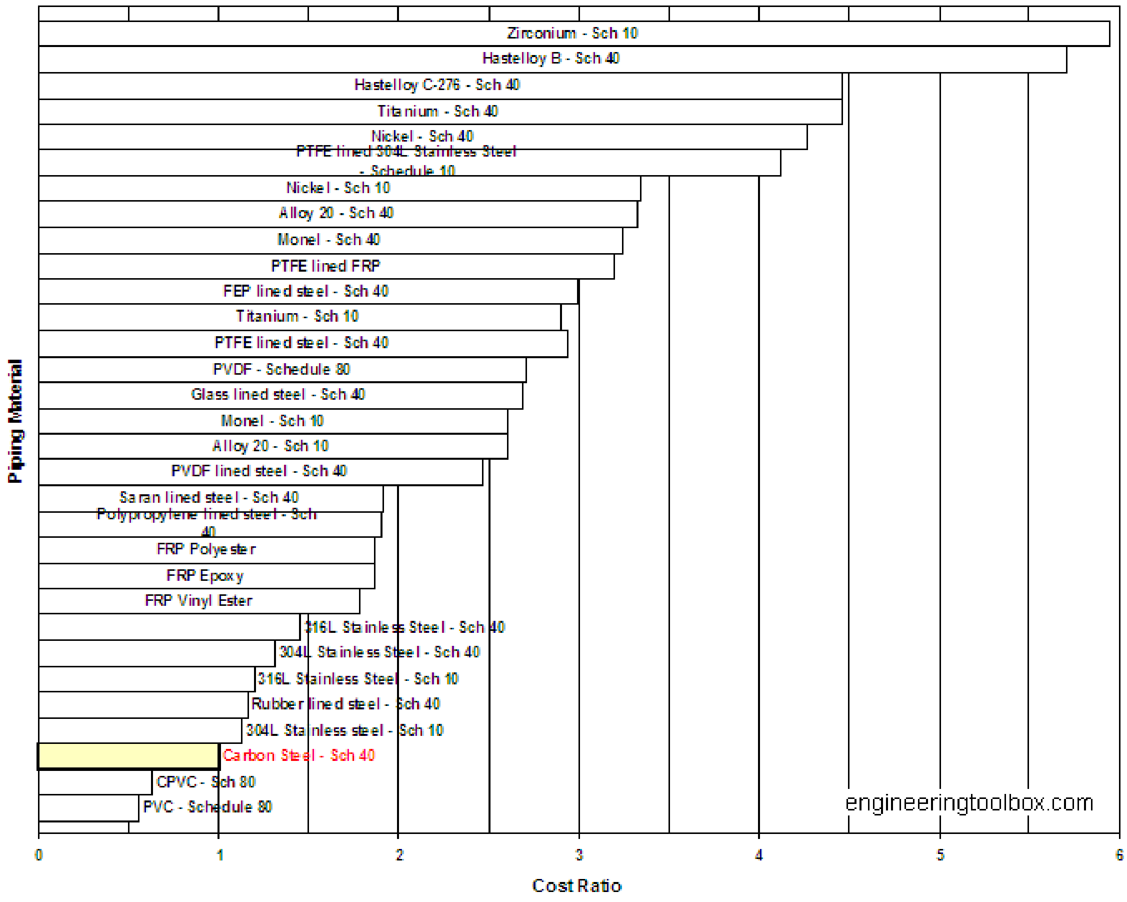
APPENDIX I



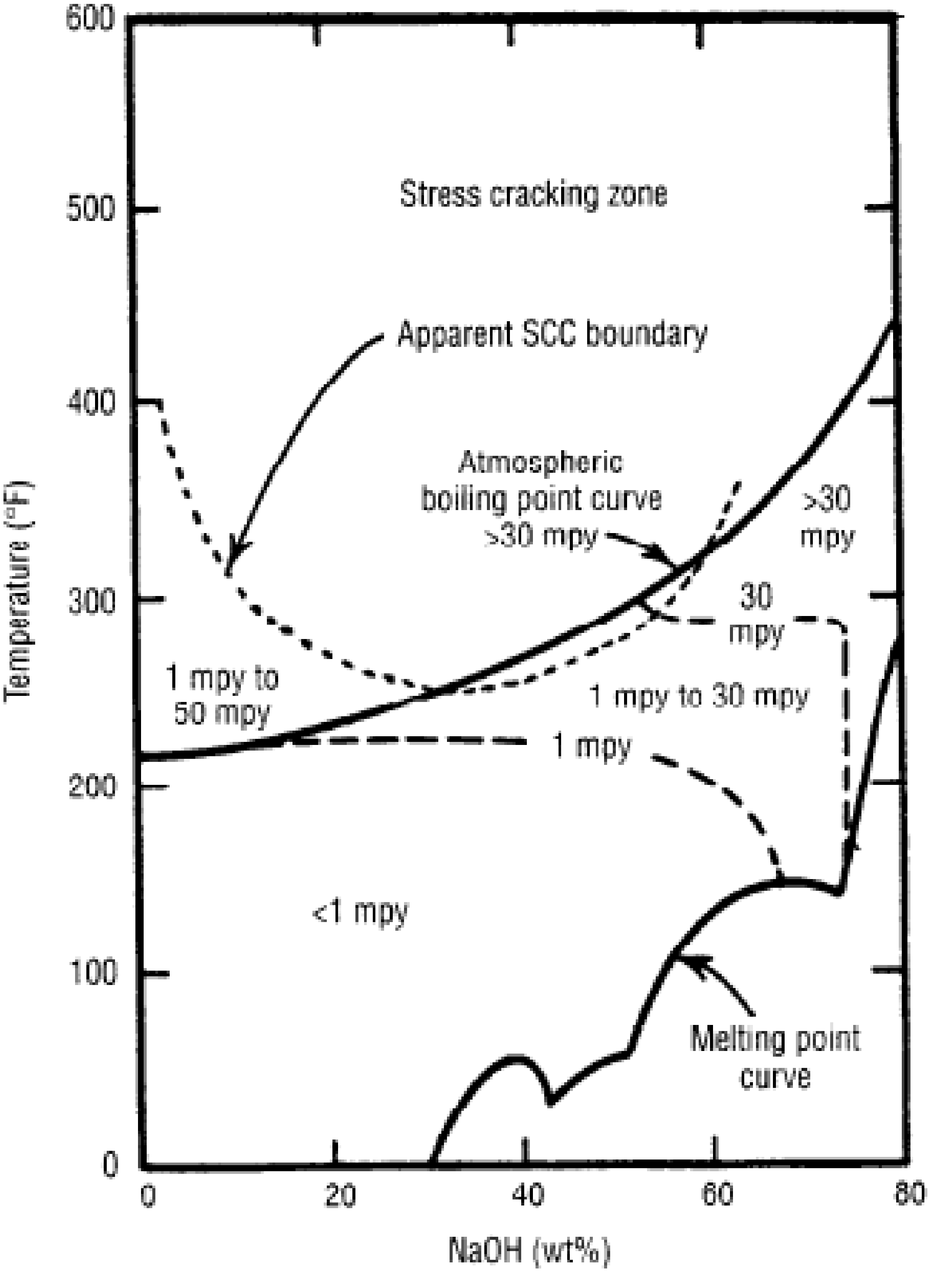
Ignition of titanium in Cl_2 gas dependent on temperature and water concentration (Wellington, 1992, p. 238).

Classifications of processes of hydrogen degradation of metals (ASM International, 2003, pp. 368-369).

	Hydrogen embrittlement			Hydrogen attack	Blistering	Shatter cracks, flakes, fisheyes	Micro-perforation	Degradation in flow properties	Metal hydride formation
	Hydrogen environment embrittlement	**Hydrogen stress cracking**	**Loss in tensile ductility**						
Typical materials	Steels, nickel-base alloys, metastable stainless steel, titanium alloys	Carbon and low-alloy steels	Steels, nickel-base alloys, Be-Cu bronze, aluminum alloys	Carbon and low-alloy steels	Steels, copper, aluminum	Steels (forgings and castings)	Steels (compressors)	Iron, steels, nickel-base alloys	V, Nb, Ta, Ti, Zr, U
Usual source of hydrogen (not exclusive)	Gaseous H_2	Thermal processing, electrolysis, corrosion	Gaseous hydrogen, internal hydrogen from electrochemical charging	Gaseous	Hydrogen sulfide corrosion, electrolytic charging, gaseous	Water vapor reacting with molten steel	Gaseous hydrogen	Gaseous or internal hydrogen	Internal hydrogen from melt; corrosion, electrolytic charging, welding
Typical conditions	10^{-12} to 10^2 MPa (10^{-10} to 10^4 psi) gas pressure	0.1 to 10 ppm total hydrogen content	0.1 to 10 ppm total hydrogen content range of gas pressure exposure	Up to 10^2 MPa (15 ksi) at 200–595 °C (400–1100 °F)	Hydrogen activity equivalent to 0.2 to 1 × 10^2 MPa (3–15 ksi) at 0–150 °C (30–300 °F)	Precipitation of dissolved ingot cooling	2 to 8 × 10^6 MPa (30–125 ksi) at 20–100 °C (70–210 °F)	1–10 ppm hydrogen content (iron at 20 °C, or 70 °F) up to 10^2 MPa (15 ksi) gaseous hydrogen (various metals, $T > 0.5$ melting point)	0.1 to 10^2 MPa (15–15,000 psi) gas pressure hydrogen activity must exceed solubility limit near 20 °C (70 °F)
	Observed at -100 to 700 °C (-150 to 1290 °F); most severe near 20 °C (70 °F)	Observed at -100 to 100 °C (-150 to 210 °F); most severe near 20 °C (70 °F)	Observed at -100 to 700 °C (-150 to 1290 °F)	…	…	…	…	…	…
	Strain rate important; embrittlement more severe at low strain rate; generally more severe in notched or precracked specimens	Strain rate important; embrittlement more severe at low strain rate; always more severe in notched or precracked specimens	Occurs in absence of effect on yield stress; strain rate important	…	…	…	…	…	…
Failure initiation	Surface or internal initiation; incubation period not observed	Internal crack initiation	Surface and/or internal effect	Surface (decarburization); internal carbide interfaces (methane bubble formation)	Internal defect	Internal defect	Unknown	…	Internal defect
Mechanisms	Surface or subsurface processes	Internal diffusion to stress concentration	Surface or subsurface processes	Carbon diffusion (decarburization); hydrogen diffusion; nucleation and growth (bubble formation)	Hydrogen diffusion; nucleation and growth of bubble; steam formation	Hydrogen diffusion to voids	Unknown	Adsorption to dislocations; solid-solution effects	Hydride precipitation



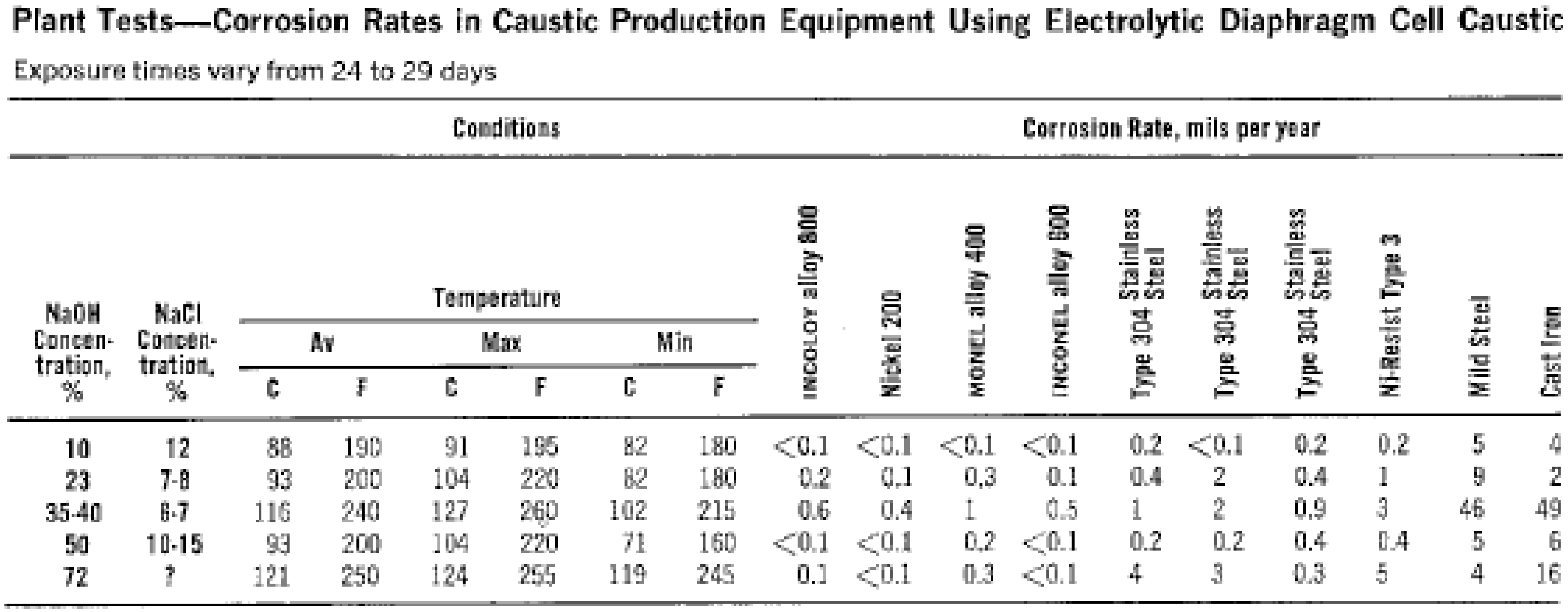
Piping materials and cost ratios (The Engineering ToolBox, 2017).



Isocorrosion chart for austenitic chromium nickel stainless steels in sodium hydroxide (Nickel Development Institute, 1983, p. 14).

APPENDIX V

Plant Tests - Corrosion Rates in Caustic Production Equipment Using Electrolytic Diaphragm Cell Caustic (Nickel Development Institute, 1983, p. 13).



Plant Tests—Corrosion Rates in Caustic Production Equipment Using Electrolytic Diaphragm Cell Caustic

Exposure times vary from 24 to 29 days

Conditions								Corrosion Rate, mils per year									
NaOH Concentration, %	NaCl Concentration, %	Temperature						INCOLOY alloy 800	Nickel 200	MONEL alloy 400	INCONEL alloy 600	Type 304 Stainless Steel	Type 304 Stainless Steel	Type 304 Stainless Steel	Ni-Resist Type 3	Mild Steel	Cast Iron
		Av		Max		Min											
		C	F	C	F	C	F										
10	12	88	190	91	195	82	180	<0.1	<0.1	<0.1	<0.1	0.2	<0.1	0.2	0.2	5	4
23	7-8	93	200	104	220	82	180	0.2	0.1	0.3	0.1	0.4	2	0.4	1	9	2
35-40	6-7	116	240	127	260	102	215	0.6	0.4	1	0.5	1	2	0.9	3	46	49
50	10-15	93	200	104	220	71	160	<0.1	<0.1	0.2	<0.1	0.2	0.2	0.4	0.4	5	6
72	?	121	250	124	255	119	245	0.1	<0.1	0.3	<0.1	4	3	0.3	5	4	16

APPENDIX VI

Chlorine pipeline failures at Joutseno chlor-alkali plant's cell room between at 28.3.2007 to 16.3.2017. Data gathered from SAP PM.

18.04.2008 Kloorirunkolinjan uusiminen A22-A26

18.04.2008 Kloorirunkolinjan uusiminen B21-B26

27.02.2009 Putken uusiminen A11-A16 Putki ECTFE GK-90 2,3 mm / LMVE

27.02.2009 Putken uusiminen A17-A21

27.02.2009 Putken uusiminen B10-B16

27.02.2009 Putken uusiminen B17-B20

15.04.2010 Ti-putken DN600 valmistus ja asennus. Putken vaakaosa ja käyrä uusittu seisakissa 4/10, YIT. 4174751

01.06.2013 Kloorin runkolinjan uusinta kennopaikoille B05-B09

01.06.2013 Kloorin runkolinjan uusinta kennopaikoille B10-B16

30.06.2014 Runkolinjan uusinta. A05-A10 4992729

30.06.2014 Runkolinjan uusinta. A11-A16 4992730

30.06.2014 Runkolinjan uusinta. A22-A26 4992731 yht. 24290,1

12.06.2014 Karppua ja vuotaa useammasta kohdasta 5101049

19.7.2015 Kloorin runkolinjan titaanisen Y-haaran vaihto 5158284 15187e

18.02.2016 Kloorin runkolinjojen uusinta. Uusitaan runkolinjat B17-20, B21-26 ja A17-21. 5320614

NaOH pipeline failures at Joutseno chlor-alkali plant's cell room between at 28.3.2007 to 16.3.2017. Data gathered from SAP PM.

25.07.2008 Lipeän kierrätysputkessa lipeäkarppu. 4076191

27.12.2007 Kennolipeäputkivuoto, vuoto vuorauksen välissä 4087354

16.08.2009 Lipeän näytekontin tyhjennyslinjassa vuoto ennen tuotelipeälinjaa.

14.04.2010 Lipeän syöttöputkien 3 kpl uusiminen 4340510

08.07.2013 Lipeäputkessa vuoto. Välivarastosäiliön hullunkiertolinjassa pieni vuoto pumpun paine-puolella 4893373

10.11.2014 lipeävuoto pumpun paineputkessa 5115095

22.11.2014 Kennolipeän runkolinjan ja kennolta tulevan lipeän t-haarassa
lipeäkarppu. Kennopaikalla A24. 5120557

11.12.2014 Kiertolipeäputki puhki. 5127885

24.01.2015 Lipeän ulostuloputkessa vuoto 5145970

21.08.2016 Tyhjennys linja vuotaa 5403247

Brine pipeline failures at Joutseno chlor-alkali plant's cell room between at 28.3.2007 to 16.3.2017. Data gathered from SAP PM.

10.12.2010 Karppuja laihaliuoksen runkoputkissa 4457163

30.05.2012 Laihaliuos runkoputkien ja laskuputkien vaihto seisokissa 4701799

01.11.2012 Laihaliuoksen Fe/PTFE putkien vaihtoa 4777425

04.10.2014 Laihaliuoksen näytteenottokaapin jälkeen oleva muovimuhvi vuotaa. 5098191

24.10.2014 Vuoto suolaliuoslinjassa, laihaliuos A 17 kenno käyrässä vuoto 5108255

11.05.2016 Laihaliuoslinjojen uusinta (runko + kennoilta tulevat linjat)
lipeätehtaan kennosalin alakerrassa syksyn 2016 seisakissa.