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WASTE WATER TREATMENT COSTS CAUSED BY BOILER PRE-OPERATIONAL CHEMICAL CLEANING

Master of Science Thesis

Examiner: prof. Jukka Rintala
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ABSTRACT

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The aim of this thesis was to clarify the factors affecting the treatment costs of boiler pre-operational chemical acid cleaning. Up to 1000 m^3 of waste water may be produced during the chemical cleaning procedure prior to boiler startup. Is it possible to sewer most of that water, but there are also waters, which are challenging even for hazardous waste treatment processes. So far it has been slightly unclear, which are the waste water features that causes the highest treatment costs. Sometimes sewage treatment plant can treat all the waste water produced in the cleaning process, but occasionally, the whole amount must be transported to hazardous waste treatment plant.

In order to deal with the waste water treatment costs, the work was to find out which chemical properties the waste water has, and how compositions of different types of cleanings differ from each other. Composition data was collected from analysis of previous cleaning cases, and two analyses were carried out during the thesis. After that, specialists of both municipal waste water treatment plants and hazardous waste treatment plants were interviewed. Discussions revealed, how each chemical property affect the used treatment method and which are those features that disable water sewage.

There were significant differences in treatment prices between hazardous waste treatment services in Finland. There is not any noticeable variation in the prices for hydrofluoric acid and hydrochloric acid sludge treatment, but for citric acid, the prices between the service providers may vary from 300 €/m^3 to 800 €/m^3. Still, transportation costs may balance the situation. Chemical features that most affect on sewage capacity are the amount of nickel and chromium and the value of biological oxygen demand (BOD). In addition to these, for non-dischargeable waste the most challenging and treatment price increasing features are nitrogen and oil content. Besides the treatment price, also scheduling and placing of storage containers have remarkable influence on total costs.

Limits for sewage water are constantly tightening in many countries, and thus, it is important to stay involved in the development of treatment technology. Increasing knowledge of both citric acid precipitation and on-site treatment processor engineering can lead to changes in current practices also in Finland.

TIIVISTELMÄ

SONJA KYRÖLÄ: Uuden voimalaitoskattilan peittauksesta aiheutuvien jätevesien käsittelykustannukset
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Tämän työn tarkoituksena oli selvittää tekijät, jotka vaikuttavat uuden voimalaitoskattilan peittauksessa syntyvien jätevesien käsittelykustannuksiin. Ennen kattilan käyttöönottoa suoritetussa peittauksessa jätevesien määrä saattaa olla yli 1000 m^3 .Suurin osa syntyneistä jätevesistä on mahdollista viemäröidä, mutta osan puhdistaminen on haastavaa jopa vaarallisen jätteen puhdistukseen keskittyneille laitoksille. Tähän saakka on ollut epäselvää, mitkä tekijät vaikuttavat käsittelykustannuksiin eniten. On mahdollista, että koko peittauksessa syntynyt vesimäärä voidaan viemäröidä, mutta joissakin tapauksissa koko määrä on käsiteltävä vaarallisen jätteen käsittelylaitoksella.

Aluksi määritettiin peittausjäteveden kemialliset ominaisuudet ja eri tyyppisten peittauksien jätevesien eroavaisuudet. Koostumustieto kerättiin aiemmista peittauksista sekä työn aikana tehdyistä mittauksista. Tämän jälkeen haastateltiin sekä kunnallisten jätevesipuhdistamojen että vaarallisen jätteen käsittelylaitosten asiantuntijoita. Haastatteluissa selvisi, kuinka mikäkin kemiallinen ominaisuus vaikuttaa jätteen käsittelymenetelmän valintaan ja mitä ovat ne tekijät, jotka estävät viemäröinnin.

Mielenkiintoisena yksityiskohtana esiin nousivat vaarallisen jätteen käsittelyhintojen eroavaisuudet. Fluori- ja suolahappopitoisten jätevesien käsittelyhinnat eivät eronneet kovinkaan paljoa, mutta sitruunahappoa sisältäville jätevesille käsittelyhinnat vaihtelivat välillä 300 €/m^3 – 800 €/m^3. Hintoja tasoittivat kuitenkin kuljetuskustannukset. Peittausveden viemäröitävyyteen eniten vaikuttavatominaisuudet ovat nikkeli- ja kromipitoisuudet sekä biologinen hapenkulutus (BOD). Viemäriin kelpaamattoman jätteen käsittelyssä monimutkaisimpia ja eniten käsittelyhintaan vaikuttavia tekijöitä ovat typpi- ja öljypitoisuus. Jätteen käsittelyn kokonaishintaan vaikuttaa käsittelykustannusten lisäksi myös jätteenhävitysprosessin aikataulutus sekä varastosäiliöiden sijoittelu ja hankintakustannukset.

Viemäröintirajat ovat monissa maissa jatkuvasti kiristymässä, minkä vuoksi on tärkeää pysyä mukana jäteveden käsittelymenetelmien kehityksessä. Tutkimustiedon lisääntyminen sitruunahapon saostamismenetelmistä sekä on-site- käsittelymenetelmistä saattaa aiheuttaa muutoksia nykyisiin toimintatapoihin Suomessa.

PREFACE

This Master's thesis was made for Valmet Technologies during 2017-2018. I am grateful for getting the opportunity of doing this work, in which my field-specific knowledge and other working life related skills developed much.

At first, I want to thank my supervisor Arja Lehikoinen, who gave me an excellent guidance and shared knowledge. Most of my work is based on discussions and interviews, and it was great to see how helpful the specialists from different areas were. Another special thanks I want to give fellow workers at Valmet, who maintained an excellent working atmosphere. From TUT side, I am pleased with Jukka Rintala, who took the thesis to examine and showed interest in the subject. Even though I will continue working on slightly different area of expertise, I hope that my job and created contacts will be useful in the future.

Still, the most important thing has been my family, who have encouraged me as much as possible since the beginning of my learning path.

Tampere, September 2018

Sonja Kyrölä

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LIST OF SYMBOLS AND ABBREVIATIONS

ABF	Ammonium bifluoride
ACN	Acid neutralizing capacity
BOD	Biological oxygen demand
CA	Citric acid
COD	Chemical oxygen demand
CYMIC	Advanced circulating fluidized bed boiler developed by Valmet
EDTA	Ethylenediaminetetra-acetic acid
EPA	United States Environmental protection Agency
EPRI	Electric Power Research Institute
EPSE	Global Ecoprocess Services
FGD	Flue gas desulfurization
HAF	Hydroxyacetic-formic acid
HCl	Hydrochloric acid
HF	Hydrofluoric acid
HSY	Helsinki region environmental services
L&T	Lassila & Tikanoja
TDS	Total dissolved solids
TOC	Total organic carbon
U.S.	United States of America

K_s	solubility product constant [M]
Q	ion equation [M]
T	temperature [°C, F]

1. INTRODUCTION

Prior to commissioning a new plant, inner surfaces of the boiler tubes must be cleaned from construction residues, corrosion and thick scale developed during erection or storage. Oxide layer begins to occur as soon as the inner surfaces of the boiler tubes become exposed to moisture. Acid treatment is the most effective method for clean tube inner surfaces, but in some cases, if relatively clean surfaces can be demonstrated to be clean enough, weak alkaline boil out treatment may be sufficient. In addition to before boiler commissioning, deposits will accumulate during the operation. Depending on the quality of boiler water chemistry, boiler must be chemically cleaned evenly at regular intervals. Boiler delivery usually includes pre-operational cleaning, while further maintenance and cleanings during operation are the responsibility of buyer's.

During circulation of acidic solution, deposits as well as fractions of tube inner surfaces will dissolve to the cleaning solution. Depending on the method used, there is waste water amount of 2 – 6 boiler volumes produced during the cleaning procedure. As an example, hydrofluoric acid cleaning of fluidized bed boiler of 150 m^3, approximately 400 m^3 of waste water and 200 m^3 of acidic waste water is generated. Waste water contains elevated concentrations of both heavy metals and organic constituents and therefore shall be handled as a hazardous waste. Treatment methods for acid cleaning waters vary depending on location and composition of waste, thus having significant differences also prices. In the most complex cases, treatment of waste water can cost almost as much as the cleaning procedure itself. [2, 3]

In most cases, pre-operational cleaning is included in the boiler delivery. Sometimes, responsibility of waste water treatment, also, lies with the builder. In order to price the boiler correctly, evaluation of treatment costs should be known early in the boiler commissioning. Although the responsibility of waste water treatment would lie with the customer, by owing the knowledge and capability for assist customer with waste treatment issues and answer questions related to treatment costs, may facilitate the progress of the cleaning project.

The main objective of this thesis is to clarify the costs share induced by waste water treatment. Another purpose is to create an overall picture of both the current stage and future trends in waste water treatment techniques. Subject of the study is to recognize the factors, which are affecting the treatment method chosen and which type of features are those having the biggest impact on total treatment cost of waste water. After understanding the determinant factors, proposals for chemical cleaning process improvement or alternative methods for waste water treatment can be presented.

This study consists of three main sections, which are step by step progressing to a more detailed. First, boiler chemical cleaning techniques and waste water composition and chemistry are introduced in general. After that, waste water treatment techniques are investigated based on waste water composition and opinions of waste water professionals. The last part is largely intended for Valmet's practicies, as all the composition analyzes gathered during the thesis work and already existing data have been collected together to form an understanding of the waste water generated during the cleaning process. Waste waters from different sources are compiled together and proposals for developing the cleaning process are done. Finally, cost evaluation for waste water treatment has been done on the basis of waste composition data.

Basically, there are two methods for cost characterization. Contacting as well as private water treatment experts and specialists of waste water treatment facilities, gives the most rewarding and unique knowledge of acid cleaning waste water treatment. These discussions are supported by site visits, in which the function of water treatment processes is explained and site operators interviewed. Co-operation with experts in various fields surrounding chemical cleaning waste treatment is the important part of this thesis, and it enables possibility of sharing information and understanding the overall picture of cleaning process, which have not been previously done. Although sources mostly consist of discussions and project databases of Valmet, the background theory is general and results are constantly equated with general research data.

The second way to approach the issue is analyzing waste waters from chemical cleanings performed by Valmet. As there were no Valmet's boiler pre-operational cleaning projects during the thesis period, samples were taken from small-scale partial cleanings done at the factory site as a service projects. With these samples, co-operation with treatment service contractors is done by delivering small experimental batches for testing to find out what the cost of processing should be, and also, to explore how new treatment techniques can be utilized.

2. BOILER ACID CLEANING

Steam boiler plant tubes can exposure rapid corrosion and creep, if humid air, dirt or dust are met. After manufacturing, there are some construction residues, such as mill scale, blasting media and welding consumables. There can also be non-protective oxides from corrosion and residues accumulated on unprotected metal surfaces during transport. Those deposits can be interlayered thick scales which greatly reduces heat transfer from tube internal surfaces. If deposited layer is thick enough, it can lead to blocking of drains and lowered boiler efficiency. It is possible to protect tubes and headers during transport, storage and construction but still it is appropriate to perform either mechanical or chemical cleaning. [1, 2]

Chemical acid cleaning means that the inner surface of boiler tubes is chemically cleaned by dissolving metals and other layered scales with cleaning liquor. There are couple of alternatives to choose the cleanser acid and additives, both organic and inorganic. After the treatment, inner surfaces are ready for boiler start-up. If boiler water chemistry is at high level, forming of deposits is extremely slow and there may be no need for re-cleaning for entire boiler life-time. [2, 3]

Pre-operational cleaning means washing of a new plant during commissioning, prior to initial start-up, while operational cleaning is performed to remove deposits accumulated during operation. Although operational cleaning is important and cost-effective procedure, this study focuses mainly on waste water treatment methods and treatment costs during pre-operational cleaning. That is chosen because of business perspective point of view; operational chemical cleaning usually tends to be customers responsibility, but depending on the scope of the boiler delivery, seller may have to take responsibility for pre-operational cleaning and waste water treatment. Usually the most challenging but least known part of the cleaning is waste water disposal: In most cases, disposal possibilities of waste water produced during the cleaning are not even known. Even if the customer is the responsible party, questions concerning acid cleaning and treatment of both waste water and hazardous sludge treatment may arise. In that case, it can be very advantageous to the supplier if they can give assistance and cost estimation for the water treatment methods chosen. [1, 2]

Acid cleaning procedure consists of the stages which are listed below:

1. Construction of circulation piping
2. Flushing of the boiler
3. Filling the circulation piping with water
4. Dosing and circulation of degreasing chemicals
5. Draining and filling circulation piping with water (optional)

6. Dosing and circulation of cleaning chemicals
7. Draining, water filling, flushing and filling (two times)
8. Dosing and circulating of neutralizing and passivating chemicals
9. Draining, filling with water, flushing and draining
10. Cooling of the boiler
11. Inspection
12. Removal of circulation piping, restoration
13. Pressure test of the boiler
14. Formation of magnetite layer

2.1 Weak alkaline boilout

Earlier, it was a common practice to perform alkaline boilout instead of pre-operational acid cleaning. According to the name alkaline boilout, the main function of the treatment is to boil alkaline mixture in a boiler and thus remove scale. Due to rapid pressure changes or excessive dissolution, and also, due to the influence of the chemicals added, iron oxide coatings, dust, oil and grease will be dissolved. Although the price of alkaline boilout is considerably lower and temporary pipework is simpler, nowadays weak boilout procedure is recommended only for some types of boilers. [2, 3]

Boilout begins with boiler filling with demineralized water. After that, boilout chemicals are dosed. Boiling chemicals consist of 100 % sodium hydroxide or, alternatively, 50 % caustic soda blended with trisodium phosphate. Then, after heating and pressurizing boiler to 5 bars, chemicals are kept in a boiler for at least 8 hours [3]. After the treatment, boiler is drained by opening all vents and drains. The boilout procedure is repeated until clear and largely solid-free water is obtained, usually it takes one or two times. [2]

To ensure proper result of boiler cleaning cleaning, there are couple of conditions that should apply when executing only weak alkaline boilout:

a) Boiler operates with demineralized water
b) Superheater, steam generator and economizer headers are found to be free of scale
c) Furnace wall tubes are found to have less than 0.1 mm thick scale
d) Drum is visually inspected and is found to have less than 0.1 mm thick scale
e) Operating pressure of the boiler is less than 40 bar

However, although the conditions above are met, it is always eligible to perform proper acid cleaning. Below the main stages of acid cleaning procedure are explained in more detail. [3]

2.2 Circulation piping and other arrangements

Acid cleaning can be performed for all boiler pressure parts including economizers, steam generators and superheaters, but in many cases, only economizer and steam generator are to be cleaned. Although pre-operational chemical cleaning is sensitive, technically demanding and relatively expensive procedure, by performing it well it is possible to achieve extensive savings. Efficient cleaning results from three main objectives. Firstly, chemicals which are fed must be evenly distributed in cleaning solution. Secondly, the solution must circulate properly in the pipeline to avoid acid concentration dropping, and also, to hinder the solution becoming saturated with iron. In case of rapid saturation, there may be scale remaining in the pipeline even though the cleaning solution has circulated long enough. The third objective is to ensure that cleaning solution flow does not exceed 0.5 m/s in any part of the boiler so that corrosion could be locally enhanced.

To follow the requirements, some temporary arrangements are needed. Temporary circulating pump or pumps are needed to keep the liquid flowing. These pumps take in water from bottom header drains, mud pockets and inspection connections, then pumping water to feedwater line, economizer drain and steam blowout line. To enhance circulation, it is possible to inject nitrogen or install restriction plates. In addition to temporary pumps, vent connections to drum and downcomers are needed. If also superheaters are cleaned, backflushing is needed to ensure proper flushing.

Degreasing and acid cleaning use large quantities of 60 – 95 °C demineralized water, which means that availability of sufficient water and heat sources must be ensured. Waste water amount classified as hazardous varies between 2 – 6 boiler volumes, but also several boiler volumes of non-hazardous water is generated. It means, that with respect to waste water treatment and sludge disposal, a water authority shall be consulted early in the cleaning process. [1-3]

2.3 Degreasing

Despite the chosen cleaning method, degreasing stage is usually applied. To clean boiler inner surfaces from preservatives and oils used in manufacturing, organic cleaning agent is dosed into circulation at 70 – 85 °C. After that, circulation is continued for 1 – 2 hours. The boiler does not necessarily have to be drained after degreasing, so it is possible to directly dose corrosion inhibitors and acid cleaning chemicals needed for next stage. There also are cleaners, who prefer draining between degreasing and acid cleaning. Draining can be advantageous, if degreasing waters are possible to sewer by separating these from other waste water streams; in many cases, degreasing waters become suitable for sewerage at least by settling. Nowadays, degreasing chemicals are chosen with consideration so, that sewerage of degreasing waters should not be a problem. From the acid cleaning point of view, cleaning result may be improved if acidic chemicals are added to the clean solution. [2]

2.4 Acid cleaning

Acid cleaning begins with filling boiler and superheaters with hot demineralized water, or chemicals can be added straight to degreasing solution. Temperature is then stabilized to a right level for chemical dosing. First chemical to dose is corrosion inhibitor, which protects base material from corrosion during acid cleaning. Inhibitors which are later introduced more specific, are mixtures containing organic compounds and sold with trade names, such as Stannine LTP or Armohib 28 A. The most appropriate compound must be chosen on a case-by-case basis. After inhibitor dosing, acid cleaning chemicals are dosed. Mixture consist of acid solution, and for citric and hydrochloric acids, sometimes also ammoniumbifluoride (ABF) for silica removal. Boiler parts to be cleaned are economizers, evaporator surfaces and superheaters. Due to the low chemical resistance of superheater materials and poor possibility to rinse superheater tube bendings, sometimes it is appropriate to chemically clean only water-wetted parts. Especially cleaning of hanging type superheaters is not recommended. [2, 4]

The dissolution rate of iron oxides increases proportionally to the cleaning acid concentration and exponentially due to increase in solvent temperature. It could be evaluated that dissolution rate doubles per 10 °C increase of temperature. As shown on figure 1, iron concentration increases in the beginning but begins then to level out after 2 – 3 hours of acid circulation. [2]

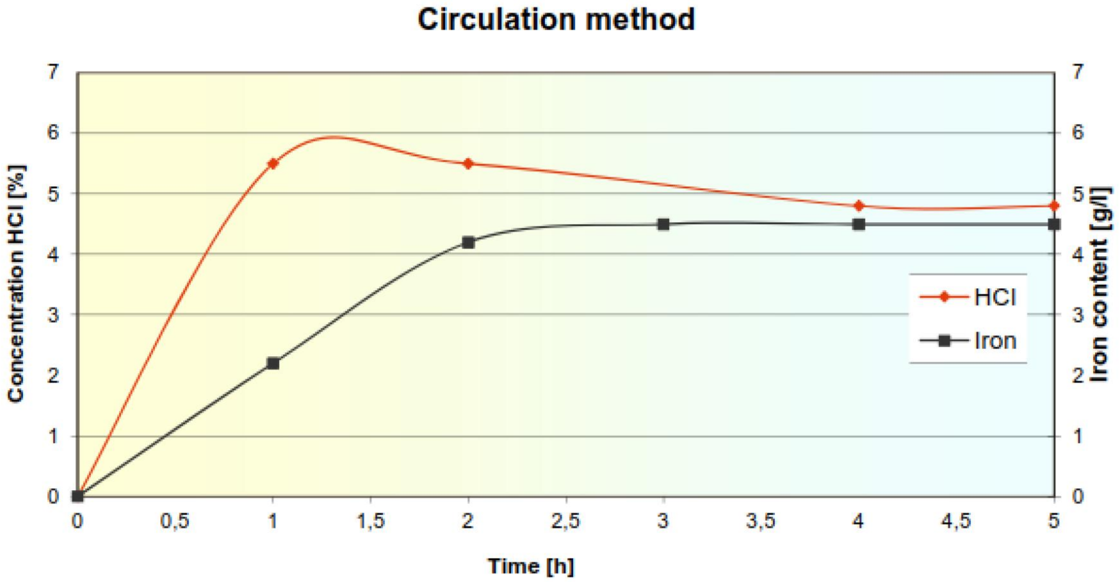

***Figure 1**. Iron dissolution rate as a function of the duration of the acid phase [3].*

During pre-operational acid cleaning, the cleaning solvent will be distributed fragments of mill scale remaining on the tube inner surface upon fabrication, and then the scales will slowly dissolve. Reaction time must be carefully considered, and it depends on particle size of mill scales, acid temperature and concentration. After stabilization of iron concentration, circulation is still continued for some time to remove the remaining of residual deposits. Practical experience has shown that dissolved iron after a certain time mostly consist of iron dissolving from ferritic materials [3]. For this reason, it is not possible to improve the cleaning result by prolonging the circulation time endlessly; after 2 – 3 hours, there is base material dissolving to an increasing extent and increasing metal concentrations in waste water.

Typically, there are three acid cleaning chemicals used in European countries Table 1). After the suitable solvent is chosen, acid cleaning stage, additive chemicals and their concentrations may be varied depending on the type of boiler deposits.

Table 1. *Typical temperatures and concentrations of cleaning chemicals [2].*

Acid	**Temperature**	**Concentration**
Hydrochloric acid	60 - 70 °C	6 % HCl + inhibitor (+ 0.25 % ammonium bifluoride)
Hydrofluoric acid	50 - 60 °C	1 % HF + inhibitor
Citric acid	80 - 95 °C	3 % CA + ammonium hydroxide for pH 3.5 + inhibitor (+ 0.25 % ammonium bifluoride)

Acid solution is circulated until iron concentration is stabilized. After the treatment, boiler is drained and flushed. Then the bottom drains are closed again to fill the boiler. Flushing water is circulated for 5 – 10 minutes and drained again and then checked, if water turbidity is maximum of 50 % higher than clean water turbidity. The company performing the cleaning measures acid and iron concentrations at steady intervals. Once increase in iron concentration levels off, circulation can be stopped. That occurs usually in 4 – 6 hours and then all oxides are dissolved. If the chosen solvent is citric acid (CA), boiler may not be drained after acid cleaning, which reduces the total amount of hazardous waste water generated during the process from 5 – 6 boiler volumes to 1 – 2 boiler volumes. [3, 5]

The choice between cleaning chemicals must be considered taking boiler design, construction materials and required surface cleanliness but also environmental loads, steam purity and the economic efficiency into account. Alternatives of acidic solvents are introduced more accurate in chapters 2.4.1, 2.4.2 and 2.4.3. The first decision to make is the need and possibility of clean superheaters, which are the most challenging part of the cleaning what comes to flushing cleaning chemicals after the procedure. Carbon steel is the most common metal, and because its relatively low cost, it is used in boilers, heat exchangers, waste heat steam generators as well as in most of pipings and tanks. It is highly vulnerable to corrosive attack and heat, leading the use of alloyed metals in some boiler parts, such as superheaters. A few percent of chromium, molybdenum, vanadium, titanium, boron, nobelium or nickel are added to superheater surface material to improve metal properties. These material choices must be clarified prior to cleaning. Also, the availability of water and steam must be considered. [2, 3, 6]

Waste water treatment possibilities may vary a lot locally. Quality requirements for sewage water may be strict, which means that the entire amount of waste water must be neutralized and precipitated, dumped or transported out of the plant area. Composition of waste water mostly depends on used cleaning chemical, cleaning method and materials used in the inner surface of boiler tubes. Table 2 summarizes the cleaning capacity of different chemicals, also for hydroxyacetic-formic acid (HAF) and ethylenediaminetetraacetic acid (EDTA), which are not widely used in Finland. Although composition of deposits in operational cleanings is known, composition of waste water may still vary within the different types of cleanings, because cleaning efficiency is different between the solvents and the cleaning chemicals may include environmentally harmful chemicals. Still, the power of solvents affects mostly operational cleanings during the boiler lifetime. If the chemical is unable to remove a substance from deposit, it is not present at least in high levels in waste water. For example, silica deposits are very challenging compounds to be cleaned, but with HF it is possible to try removing. In that case, somewhat high silica levels may be present only in HF waste waters. In case of hydrochloric (HCl) and citric acid, silica removal is possible only by adding ammonium bifluoride to the solution to first produce silica-removing HF. To remove copper deposits, copper complexing substance, such as thiourea, may be added to HCl solution. [6-8]

Table 2*. Deposit removal of iron oxide removal solvents [9].*

Solvents and deposit constituents	**HCl**	**HF**	**HAF**	**Ammoniated EDTA**	**CA (ammonium)**	**CA (sodium)**
Iron oxides	High	High	High	High	High	High
Copper, metallic	Low	Trace	Trace	Medium	Medium	Trace
Copper oxide	Medium	Trace	Trace	Medium	Medium	Trace
Nickel oxide	High	-	-	High	High	High
Zinc oxide	High	-	-	High	High	High
Aluminum oxide	Low	High	-	Trace	-	-
Chromium oxide	-	-	-	-	-	-
Calcium salts	High	Medium	Low	Medium	-	-
Magnesium salts	High	-	Low	Medium	-	-
Silica	Low	High	Low	-	Low	-
Carbonates	High	-	-	High	-	-
Phosphates	High	-	-	Medium	-	-
Calcium sulfate	Low	-	-	Trace	-	-
Organics	Trace	-	-	-	-	-

Finally, the experience and practices of the cleaner party finally determine the way of executing the cleaning process. The benefits may be great if the procedure is executed quickly and safely with professionalism.

2.4.1 Citric acid

Citric acid is weak organic acid, which is one of the commonly used acid cleaning solvents. Solutions of ammoniated citric acid find wide usage in removal of mill scale from newly fabricated equipment, as pre-operational cleaning is. The mechanism of dissolving metals and silicates differs from inorganic salts. Citric acid is an excellent chelating agent, which binds metals chemically by making them soluble. Citric acid, which is sold in dry salt bags, has couple of advantages compared to mineral acids, but also some challenging features related to waste water treatment. When planning the waste management options, principles how citric acid as an organic solvent removes the deposits from the metal surfaces are essential to understand. There are some chemical features that define the behavior of such an organic solvent and, for example, increase significantly the costs induced by waste water treatment. [9, 10]

The most advantageous feature is, that there is no need to drain the piping after acid treatment phase; it is possible to dose neutralizing and passivating chemicals directly to the acidic water. This means, that the total generated waste water is only 1 – 2 boiler volumes.

If high nitrogen and chromium concentration in waste water is not a problem for water treatment, waste generated in acid cleaning is usually drainable making water treatment easy and inexpensive. On the other hand, waste waters from citric acid cleaning can also be an embarrassing issue. What is more accurately discussed in chapter four, the precipitation of metals from waste water is challenging. Costs induced by waste water treatment can rise lot, if local waste water treatment plant does not allow to sewer waters. In addition to those drawbacks, citric acid is relatively expensive [3].

Citric acid is relatively safe to operate. Diluted citric acid solutions are neither irritant nor corrosive and are also used as a food additive. Low chloride content allows sensitive surface contact, which means that also superheaters can be cleaned. That is advantageous compared to other commonly used chemicals. The dissolution of iron oxides in case of citric acid is slow, but once dissolved the ions are sequestered by citrate. Solutions of citric acid are nontoxic, biodegradable and chloride free, making them useful also for austenitic steel superheaters. Cleaning of austenitic stainless steel surfaces is not allowed for hydrofluoric acid, which leads to citric acid being the only choice for some superheaters. Austenitic stainless steel is commonly used in superheaters, and the three mainly used materials are EN 10216-5: X7CrNiNb18-10, VdTUV Wbl 547 X8CrNi19-11 and VdTUV Wbl 546 X6CrNiNbN25-20 [2]. Some austenitic steel materials, and, couple of ferritic steel materials used in superheaters, can not withstand as high temperatures that citric acid treatment needs. Temperature limit for use may be as low as 70 °C, meaning that use of citric acid is not possible. As already mentioned, acid cleaning of hanging type austenitic stainless steel superheaters is not recommended, but there also are cleaners who do so. If superheaters are cleaned, the resistance of materials should be carefully checked. [6]

Dilute solutions of citric acid have been found to dissolve magnetite Fe_3O_4, but there is a saturation limit for iron in 3 % (or sometimes lower) by weight, in which a white granular precipitate, iron citrate, is formed. To avoid saturation, it is important to follow both consumption of the solvent and iron dissolution during the cleaning. On the other hand, saturation limit has generated interest towards the use of monoammonium and diammonium citrates instead of citric acid, as these have much greater capacities for iron removal. [10]

Organic solvents dissolve inorganic deposits in a way that is somewhat different from the mechanism by which mineral acids mostly remove deposits. Mineral acids remove metal oxides by creating low pH conditions whereby the metals are readily soluble and form well soluble salts, while in case of organic solvents metal oxides are removed at slightly higher pH values. Such weak acids require an elevated temperature and circulation to achieve deposit removal rates compared to those of mineral acids. [10]

Chelation is an equilibrium reaction between metal ion and complexing agent. This reaction is characterized by the formation of more than one bond between the metal and a molecule of the complexing substance and resulting to the formation of a ring structure, which incorporates the metal ion. The structural form of chelated metal is presented in figure 2.

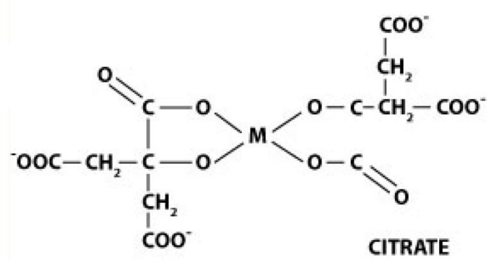

Figure 2. Metal chelated with citric acid [6].

Simple formation of stabile citratoferrate compound is presented below in equation (1), and is more accurately discussed in chapter 4.

$Fe^{3-} + C_6H_5O_6^{3-} \rightarrow C_6H_5O_6Fe$ (1)

In addition to citric acid, also ethylenediaminetetra-acetic acid (EDTA) is such an organic solvent. Most of the EDTA cases is currently in North America, and because of not having use in Europe, it is not included in this thesis work. [2, 6, 7]

Citric acid cleaning is carried out at high temperatures (usually 80 – 95 °C), which results in high steam consumption. After the cleaning, warm citric acid solution is led to tank truck for transportation. Even though the water cools down before putting it into truck, resistance of plastic waste container must be ensured. In some cases, also temporary storage is possible. If the temperature or concentration is too low or duration of the treatment is too short, some oxide scale may remain. [2, 6]

In most cleanings, additive chemicals are the reason for challenging waste treatment. For silica removal, sometimes the practice is to add ammoniumbifluoride (ABF, NH_4HF_2) to the cleaning solution. Usually silicates are formed during the operation, meaning that there should not be silica deposits to be cleaned in pre-operational acid cleanings. It also increases solution rate of magnetite and ferric oxide through the formation of hexafluoroferric ion [6, 10]. Oxidation potential of the following reaction is then lowered because ferric ions are more sequestered. That can complicate waste water treatment process, as ammonium bifluoride is toxic and contains nitrogen. Electric Power Research Institute (EPRI) has published a manual for boiler chemical cleaning waste management, in which reservations towards ammonium bifluoride are also expressed. It states that "ammonium bifluoride should not be applied if the boiler will be fired during the cleaning or if austenitic alloys are present in the cleaning loop". In acidic solutions, ABF forms hydrofluoric acid, which may lead that also hydrofluoric acid use with austenitic alloys is not reasonable. In addition to EPRI's guideline, recent finding in circulated fluidized bed boiler showed that the internal surfaces of sample tubes were uneven, when using citric acid with ammonium bifluoride, indicating general corrosion. One material had also local corrosion pits. It should be investigated more accurately, if use of hydrofluoric acid and citric acid with ammonium bifluoride should be limited. [2, 3, 9, 10]

Another additive is ammonia, which is mixed to the cleaning solution to neutralize it to the adequate level of 3.5 – 4.0. Citric acid capability to dissolve iron depends on pH, and if internal surfaces are rusty, the acid with low pH may saturate before all rust and scale have been removed. In higher pH values, saturation does not occur. Cleaning is possible without neutralization, but then pH of strong solution may be as low as 2.0 which may lead to worse cleaning result. By increasing nitrogen content of waste water, ammonia dosing makes waste water challenging to treat in hazardous waste treatment plants, which leads to balancing between ammonia dosing options. [2, 6]

As with the other cleaning solvents, inhibitor must be used during the cleaning. Appropriate and most often used inhibitors for citric acid are Stannine LPT and Lithsolvent CL 4. Stannine LTP is a trade name for the mixture of < 10 % dibutylthiourea and surface-active ingredients, while Lithsolvent is an aqueous solution consisting of thiocyanates, cationic and non-ionic surfactants. When inhibitor suitable for the situation is chosen, it should not cause additional problems with waste water treatment. [2, 7]

2.4.2 Hydrochloric acid

Hydrochloric acid (HCl) is corrosive and strong mineral acid commonly used in chemical cleanings. It dissolves metals on the tube inner surfaces by forming oxidized metal chlorides and hydrogen gas. To remove silicates and enhance iron dissolution, ammoniumbifluoride can be added also to hydrochloric acid solution. Commercial grades of hydrochloric acid, which is frequently called muriatic acid, are available at concentrations of 28, 32 and 37 weight percent, and are then diluted to concentrations of 5, 7.5 or 10 percent. Concentrations below 10 % used in chemical cleanings are so diluted that they are not classified as irritant, corrosive nor toxic by European Union. [2, 10]

Corrosion inhibitor for hydrochloric acid cleanings is the mixture of ethoxylate, formaldehyde, reaction products of oleylamine, propyl alcohol and acetic acid. Trade name for the mixture is Armohib CI-28, which is not recognized to cause any problems for water treatment. [2, 6]

Because of strong corrosive attack, austenitic stainless steel, titanium, zinc, aluminum and galvanized iron parts are not allowed to be cleaned with hydrochloric acid. In practice, such boiler parts are superheaters which are made of austenitic material. It has been shown [6], that at 65 °C, austenitic stainless steels are not attacked by inhibited hydrochloric acid; corrosion occurs after neutralization, when chloride ion causes cracking and steep-walled pitting in stressed areas. In neutral solutions, the chloride ion is adsorbed on the surface of ferrous metals, which destroys passivity by displacing oxygen. That type of penetration defects in the normally protective film and decreases the hydrogen overvoltage. After that, cracking progresses at areas stressed well below the yield point. [6]

As seen in equations (2) and (3), HCl is especially suited for dissolving ferric oxide, because of the driving force of the reaction

$$Fe_2O_3 + 6\ H^+ \rightarrow 2\ FeF_3 + 3\ H_2O \quad (2)$$

In acidic solutions, stable hexachloroferric ion will be formed

$$Fe_2O_3 + 6\ H^+ + 12\ Cl^- \rightarrow 2\ FeCl_6{}^{3-} + 3\ H_2O \quad (3)$$

Waste water treatment is significantly different than in case of citric acid. It is not common that municipal waste water treatment plant agrees to receive cleaning liquor from hydrochloric acid cleaning, but by neutralizing and precipitating metals the waste water it is possible to make the water fit into local sewage system. In that case, a large reservoir tank for 5 – 6 boiler volumes water must be built and placed on the plant site. On the contrary to citric acid, cleaning chemicals are relatively cheap. [2, 3]

Need for demineralized water is a lot higher than in case of citric acid, when only 2 – 3 boiler volumes are needed, because the need for emptying and rinsing before neutralization and passivation. Because of HCl effectiveness, the temperature needed is lower than with organic cleaning solvents being 65 – 75 °C. Despite of lower cleaning temperature, neither HCl is allowed for austenitic stainless steels due to risk of stress corrosion cracking. [2, 3]

2.4.3 Hydrofluoric acid

Hydrofluoric acid will be formed, when hydrogen fluoride dissolves in water. It is a strong mineral acid with the highest dissolving potential. During the cleaning, remaining scale dissolves slowly when the acid is distributed under the fragments of the scale. Because of its effectiveness, hydrofluoric acid is capable of dissolving silicates. Steam consumption is possible to keep at low level, because the cleaning temperature of 50 – 60 °C is high enough. [2, 6]

Hydrofluoric acid is classified as corrosive and toxic, and that is why HF is not commonly used in the USA. Over 70 % solution, as the acid is sold, it can cause immediate skin corrosion and severe throbbing pain, forcing that all the processes and transports must be performed with care. Hydrofluoric acid is a common solvent together with citric acid and hydrochloric acid in Finland, but in Sweden, the majority of pre-operational cleanings are done with 1 % diluted hydrofluoric acid. [11]

Corrosion inhibitors which are generally used with hydrofluoric acid are Bonderite S-AD 31A and Lithsolvent CL4. Bonderite S-AD 31A is trade mark of mostly organic compound diethyl-thiourea and sulfuric acid. Lithsolvent CL4, too, is practically completely organic compound including not any hazardous or harmful chemicals. [1 – 3]

Hydrofluoric acid can remove iron oxides and silica very effectively. Fluoride ion forms very stable compounds, complexes, with ferric ion, and rapidly dissolves deposits of magnetite (Fe_3O_4) and hematite (Fe_2O_3). Using HF, ferric ion attack is reduced compared to hydrochloric acid, meaning that the corrosion rate for metal surfaces is not that high and the surfaces meets more sensitive attack. Dissolution reactions for hematite and magnetite is depicted by equations (4) and (5). [10]

$$Fe_2O_3 + 6\ HF \rightarrow 2\ FeF_3 + 3\ H_2O \tag{4}$$

$$Fe_3O_4 + 8\ HF \rightarrow 2\ FeF_3 + FeF_2 + 4\ H_2O \tag{5}$$

Because of the ability of HF to dissolve and complex ferric ions, it offers the greatest advantage over HCl and other solvents, in which iron oxide is present in large amounts and ferric ion corrosion is a problem to solve. Abilities of other mineral cleaning solvents are based on sloughing off the deposits, while hydrofluoric acid forms complexes with deposits. This leads to that using HF the problems associated with sedimentation of undissolved deposits is avoided. [10]

2.5 Neutralization and passivation

The clean surface formed in acid cleaning may be easily corroded and oxidized again, when the acid cleaning chemicals have been drained and pipe surfaces come into contact with air. To protect clean surfaces from re-corrosion, these must be neutralized and passivated. First, small amount of rust-dissolving citric acid is dosed. Then, ammonium hydroxide (NH_4OH) is dosed to obtain pH value of the system fill water 9 – 10. To form a thin and protective oxide layer, oxidizing chemical will be blended shortly after having started the alkalization, as soon as pH has stabilized to high level enough. The temperature is kept under 40 °C. Usually sodium nitrite, $NaNO_2$, is used as an oxidizing chemical, but also hydrogen peroxide, H_2O_2, is commonly used. Sodium nitrite is light, odorless and powdery crystalline substance, which absorbs water from air. Because of a strong oxidative ability, sodium nitrite is used to reduce the rate of corrosion. With the aid of $NaNO_2$ or H_2O_2, the metal surface is passivated. The protective tight layer, which is formed, will prevent boiler for further corrosion for approximately four weeks. By protecting from corrosion, the layer helps permanent passivation layer to form more permanently after restoration of boiler. If sodium nitrite is used to oxidize the surfaces, it must be beware of not to dose oxidizing chemical to solution having pH under 9. That prevents process from formation of red, poorly cleaned sludge. The sludge may be hard to remove, and thus it may lead to an unsuccessful cleaning result. Then, toxic nitric oxide gas could also be formed. [12-14]

Sodium nitrite is problematic for waste water treatment plants, as it is classified to environmentally toxic compound. Also, it contains nitrogen, which is undesirable for treatment process. Because of these challenges, hydrogen peroxide as a passivation chemical is sometimes used. Still, in most cases it is not the simpler choice. The possible foaming in the boiler may be adverse reaction, if the surfaces to be passivated are not flushed properly. Proper flushing consumes high amounts of clean water, an also, it increases volume of waste waters if all the waste waters are mixed together. Passivation step is tried to do as soon as possible after the acid cleaning, and all type of extensions of the total process duration are wanted to minimize. [3, 7, 14]

In mineral acid cleaning, the boiler must be drained before passivation stage, but in case of citric acid the passivation solution is possible to dose immediately after cleaning.

2.6 Magnetite layer formation

Thin oxide layer formatted at the end of acid cleaning provides only a limited protection against corrosion. Stable oxide layer due to corrosion begins to form as soon as boiler pressure and temperature are increased. Thus, protective magnetite layer is formed for boiler, which is ready for steam process. Refractories must be dried prior to magnetite layer formation. [2]

Magnetite (Fe_3O_4) is one of the oxides of iron, which is formed during iron oxidation, also called passivation. The function of magnetite layer is both to protect base material, iron, from corrosion, and also to prevent impurities from coming into contact with iron. First, the boiler is filled with feedwater containing low silicate and sodium concentrations and pH over 9. Then the boiler is heated and slowly pressurized to 36 – 40 bars, continuously feeding alkaline. If pH drops to too low level, it indicates that there still is some residual acid left and the passivation process must be started from the beginning. During the pressure increase, boiler water is continuously drained keeping pH high enough. When iron concentration of boiler water is lowered to 0.5 mg/l and pH is stabilized to over 8, blowdowns can be stopped and pressure can be increased to the normal operating level. The formation of magnetite layer is controlled by taking pH, conductivity, total iron concentration and silicate concentration samples typically every two hours. Generally, the desired magnetite layer is formed within 12 – 24 hours after pressure level 36 bar has been achieved. Faultless magnetite layer will renew itself during the boiler operation, when it is damaged. [2, 15]

3. SEWERAGE SYSTEMS AND CLEANING WASTE WATER COMPOSITION

Boiler pre-operational acid cleaning comprises of different stages, which all consume large amount of water. Used cleaning water is waste containing elevated levels of metals used as construction materials, and other elements which may form fouling deposits on the inner surfaces of boiler tubes. Iron is generally the most abundant metal, but there also are high concentrations of other elements such as chromium, magnesium, nickel and zinc. Other water parameters, such as pH, total organic carbon (TOC) and total dissolved solids (TDS) vary depending on the type of cleaning chemical.

Local waste water treatment possibilities and restrictions vary by country, but also by municipality. These variations must be taken into account already in designing the cleaning procedure. One of the main objectives is to decide responsibilities of waste water treatment. In case of operational cleaning it is obvious that cleanings are the buyer's responsibility, but the responsibility of boiler pre-operational cleaning can be the seller. Anyway, usually the buyer is interested to know how to treat waste waters, how much waste water is generated and how much different treatment alternatives cost. What is interesting, the costs induced by waste water treatment can be as high as the costs of the whole cleaning itself.

Permissions for the drainage shall be in all cases obtained from the local waste treatment plant. This may sometimes require lengthy discussions and demonstrations showing that the chemicals used and the other contaminants present in the waste water do not pose a threat to the microbes in the treatment plant. Also, possibility to cause uncontrolled increase in concentrations of phosphorous, nitrogen and chemical oxygen demand must be investigated. [21]

A rough estimate of waste water produced is 0.5 m^3 for each one megawatt produced [9]. In practice, volume of cleaning wastes depends on the boiler size and the number of rinses necessary to properly flush the cleaning solution. As already mentioned, with citric acid, it is possible to perform all the stages in the same solution. In case of mineral acid cleaning, the tubes must be properly rinsed before neutralization and passivation. Examples from the realized cleanings may give more accurate view of the waste waters produced. For example, hydrofluoric acid cleaning executed in circulating fluidized bed boiler produced waste water volume of 600 m^3 with the cleaned volume of 145 m^3 boiler. 200 m^3 of the total 600 m^3 was waste waters containing mainly acidic cleaning chemicals, while 300 m^3 was less or more nitrogenous waters. The rest, then, 100 m^3 was relatively clean rinse waters without chemicals added. [16].

Waste water treatment processes and cleaning procedures are investigated with discussions and site visits. Table 3 summarizes the most important contacts during the work.

***Table 3.** Discussion and site visits during the work.*

Chemical cleaners	
Enerkem Oy	Discussions
Wistrand AB	Discussions
Hazardous waste treatment companies	
Fortum Oyj	Discussions; site visit
Lassila & Tikanoja	Discussions; site visit
Global Ecoprocess Services (EPSE)	
Kierto Ympäristöpalvelut	Discussions; site visit
Municipal waste treatment plants	
Tampereen Vesi	Discussions; site visit
Helsingin Seudun Ympäristöpalvelut (HSY)	Discussions; site visit
Other waste water treatment specialists	
Vesi-Ihminen	Discussions
Timo Karjunen	Discussions

3.1 Sewerage systems

When focusing on costs induced by acid cleaning waste treatment, understanding the function of municipal waste water treatment plants and their requirements are the most determinant. If the properties of waste water meet the restrictions set by sewerage waste, it is possible to drain it to municipal waste water sewerage system. In that case, induced costs are minimal because only a normal sewage fee will be charged. Sometimes an increased fee for industrial waste is charged, but typically in Finland this is only when combination of nitrogen, phosphorous and biological oxygen demand is over the limit value. For example, in year 2017 a normal fee for Helsinki region environmental services (HSY) was 1.39 €/m$_3$. [17, 18].

There are also sewerage systems of the factories, which are intended for the plant's own use. Processes in these type of sewerage systems are somewhat similar than in municipal treatment plants.

To define the properties disrupting the function of waste water treatment plants and thus making waste water not suitable for draining, the most sensitive stages of the treatment process should be known. Modern municipal waste water treatment plant consists of both mechanical, biological and chemical phases, and is illustrated in figure 3.

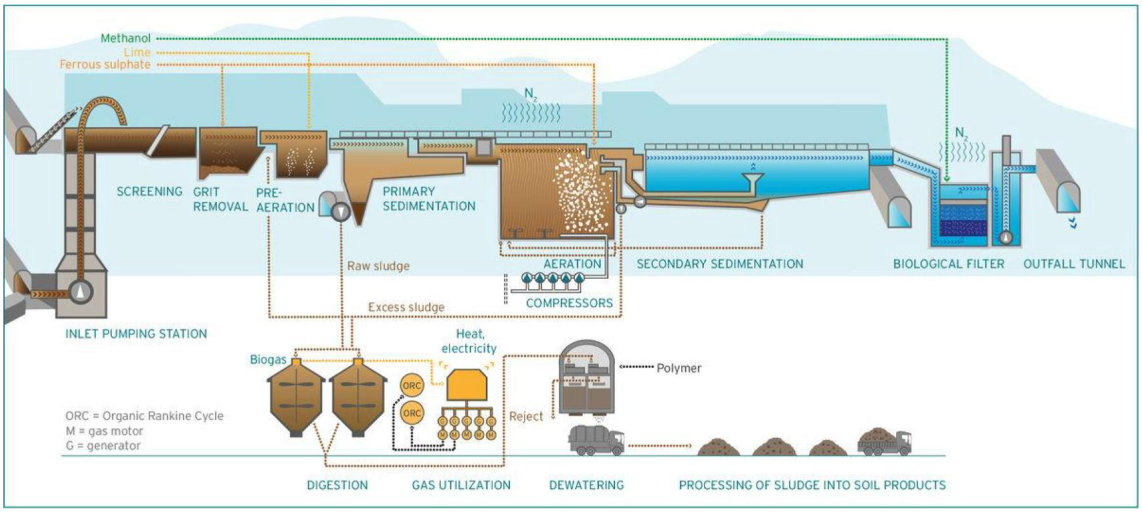

***Figure 3**. Modern municipal waste water treatment plant consists of both mechanical, biological and chemical phases [19].*

3.1.1 Mechanical treatment

There are basically two main stages by which water is purified. During the primary stage, solids are allowed to settle and then mechanically removed from waste water. The secondary stage uses biological and chemical processes to further purify wastewater. In the beginning, sewage from households and industry is pumped inside the process via one or two stations inside the treatment plant building. After that, the largest pieces of solid matter are removed by screening the sewage to ensure faultless operation of the equipment in upcoming process. The target is to have smell-free and somewhat dry sludge, but also keep the treatment costs of following stages low. Screening is followed by sand and surface sludge filtering, whose function also is to remove solid matter containing grease and oil having an interfering effect on biological treatment bacteria. [5]

Most treatment plants have pre-aeration stage for refreshing the water flowing upward. Pre-aeration aerates the waste water, thus reducing the oxygen demand. Also precipitating chemicals may be added. Today, most treatment plants do not need pre-aeration, but the function of aeration pool is to store water before preliminary sedimentation. Flowing waste water is then shared usually to five to seven lines. Preliminary sedimentation will improve the degree of solid separation and decrease the load of expensive biological treatment. Sedimentation is followed by biological process, which is the most sensitive phase what comes to acid cleaning wastes. [20, 21]

3.1.2 Biological treatment

The coarsest particles of waste water are removed during previously described stages of water treatment plant. In some countries, that is the required level of treatment. Still, at least in EU and U.S, secondary treatment is always done. Several secondary treatment processes exist, but activated sludge technique is today the most common suspended-growth method. It is possible to use activated sludge to oxidize nitrogenous or carbonaceous biological matter, or to remove nutrients. [19, 21]

Biological process consists of aeration tank and settling tank, which separates biological sludge from clear water. The process uses dissolved oxygen to promote growth of biological floc, which removes organic matter. The floc is an ecosystem of living biota, which needs nutrients from the inflowing clarifier effluent. During aeration, dissolved solids in the floc will be decomposed because of impacting oxygen. After that, the solids will be either biologically oxidized to carbon dioxide, or converted to additional biological floc of micro-organisms. Also, nitrogenous impurities in waste water are converted to biological floc, or oxidized by the floc to nitrites and nitrates. Biological oxygen demand of waste water will be decreased during the reactions. Today, in newly constructed treatment plants, nitrites and nitrates are processed further through denitrification process to nitrogen gas. The schematics of nitrogen gas utilization is showed in figure 3. [20, 21]

So far, most of BOD decrease is achieved. After biological process, the activated sludge flows to secondary settlement, where the sludge is separated from clean waste water with sedimentation. Thus, BOD value will be lowered even more. [21]

In most cases, vulnerability of bacteria in the activated sludge causes that usually waste waters from acid cleaning are not drainable. Local authorities give restrictions, which are especially meant for the industry. Helsinki Region Environmental Services Authority (HSY) has defined a list of chemicals or additives which are disruptive to nitrification process. This list must be taken on account already when choosing the cleaning chemicals. Certain agents are growth slowing or toxic for nitrification bacteria, and if such agents can react with active sludge, the functional capacity of bacteria will be lowered or bacteria may die. In that case, nitrogen content of treated water will rise. A good example of the toxicity of acid cleaning chemicals is thiourea, which is generally used for silicate removal. If thiourea contacts with bacteria, the nitrification process will be significantly weakened in couple of hours [22]. Especially the autotrophic organism of nitrification process is sensitive to most heavy metals and synthetic organic chemicals. Bacteria of denitrification zone are considerably more tolerable. In addition to chemicals, also fluctuation of pH may injure nitrification process. Bacteria typically adapt to prevailing conditions, but bacterial strain is not capable to be transformed at the same rate than pH or other circumstance changes. For that reason, tolerance for waste water pH is from 6 to 11. [21, 23]

3.1.3 Final treatment

The last stage of waste water treatment is biological filtration. The purpose is to enhance nitrogen removal after active sludge process. Waste water from final sedimentation flows through the filter, whose purpose is to provide a breeding ground to denitrification bacteria. During streaming through the filter, nitrogen in waste water is converted to nitrogen gas. After the biological filtration, water is sewered to the receiving environment. When planning the acid cleaning process, also geographical location of the plant must be considered. If sewerage to sea is possible, restrictions for waste water can be significantly more tolerable than in inland areas. Especially outside Finland, salt contents and conductivities of treated water can be multiple times higher. [12, 22]

3.2 Composition of waste water

The scope of the work is highly affecting on the composition of the waste waters. In case of power boilers, the whole boiler is typically cleaned (except hanging type superheaters, which usually are not cleaned at the plant site), but in case of recovery boiler this is not always the case, because in some cases boiler's large size restrict cleaning at the site. Nowadays most superheaters are austenitic, and as earlier mentioned, if those are cleaned there is large amount of heavy metals present in the waste water.

ln principle, the target of the waste water treatment must be that the waste is possible to be cleaned as much as possible already at the plant site. Generally, it is not allowed to sewer the waste waters directly to the municipal or plant site sewage system, but in good case, already with a light site treatment it may be possible to avoid expensive transport to the local hazardous waste treatment company. Before draining, at least pH, solids, organic matter, mineral acids as well as heavy metal concentrations must be typically defined [12].

From municipal sewerage systems point of view, there are two types of harmful substances: Those, whose concentrations are possible to lower during water treatment process, and other features, which stay stable through the treatment or accrue to the waste sludge. Water treatment plants can decrease the amount of solid matter, nitrogen, phosphorous and oxygen consuming organic substances. If these concentrations in waste water are higher than limit values, an increased waste water fee may be charged. Costs share for removable substances in HSY is divided between couple of features: solid matter 38 %, total nitrogen 35 %, biological oxygen demand 19 % and total phosphorous 8 % [12]. Industrial actors are charged based on this distribution. However, restrictions vary within the country based on the location in which the water will be finally sewered. Unlike the substances mentioned above, metals and heavy metals are not removable. These elements migrate unchanged through the treatment process and remain the sludge, which are then reused for soil or energy production. In the long run, the substances will accumulate to the sludge making it useless for further utilization. [19, 22]

Most of the problems with to chemical cleaning wastes are related to operational cleanings executed during the boiler life cycle. In that case, waste water contains mostly the same components, but in larger quantities. Stronger cleaning chemicals not only remove deposits accrued during the boiler usage, but also dissolve the outermost layer of the pipe coating, causing increased metal concentrations in waste water. On the other hand, harmful additives may be used to increase the efficiency of solvent. As public research data of pre-operational cleanings is very limited, information of waste water compositions is practically completely compiled from Valmet data. Still, couple of waste water compositions from different types of operational cleanings are collected together to boiler cleaning waste management manual published both EPRI (Table 4) and VGB PowerTech e.V [3, 9, 10].

Table 4: *Major elements in both hydrofluoric and citric acid waste waters [9].*

Analyte	**CA**		**HCl**		**HCl**	
	Spent	**First rinse**	**Spent**	**First rinse**	**Spent**	**First rinse**
pH	9.8	9.3	1.8		1.5	
Major metals						
Iron	6950	520	4140	86	5900	0.14
Copper	3.8	8.5	182	1.7	320	0.31
Nickel	4.9	0.49	26	0.25	210	0.031
Zinc	2.7	0.49	30	0.14	30	0.006
Minor metals						
Arsenic	0.17	0.018	<0.002	<0.002	0.004	0.004
Barium	0.32	0.097	0.47	0.051	1	0.006
Cadmium	<0.2	0.04	0.78	0.002	0.18	0.007
Chromium	5.7	0.77	6	0.045	3.5	0.011
Lead	0.19	<0.002	0.51	0.7	1.6	<0.002
Mercury	<0.0002	<0.0002	0.0003	0.0003		
Selenium	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Silver	<0.02	<0.02	0.098	0.0038	0.17	0.0063
Other						
Acidity	<10	<10	52000			
Alkalinity	21000	1050	<1			
Aluminum	12	1.2	25	0.48	<5	<0.05
Ammonia	8410					
Antimony	0.77	0.15	0.5	0.077	5.6	0.075
Beryllium	<0.1	<0.01	<0.1	<0.001	<0.1	<0.001
Boron	80	4	12	<0.05	6.2	0.23
Calcium	26	6.3	29	21	74	18
Chloride	<10	24	33000			
Chromium Vi			0.47		0.24	
Cobalt	0.95	0.09	1.5	0.013	1.6	<0.006
COD	15000		8000			
Fluoride	620	150	2100			
Magnesium	7.9	0.91	14	5	42	6.2
Manganese	47	3.4	27	0.9	31	0.004
Molybdenum	1.1	0.19	0.45	0.007	0.72	0.033
Nitrate	11	<1	19			
Nitrite	370	12	<0.02			
Phosphorous						
Potassium	<0.05	<0.05	<0.5	2.4	<5	3.2
Silicon	<0.02	1.2	15	2.2	22	6.7
Sodium	2110	85	390	13	160	35
Sulfate	<20	<5	50			
Thallium	0.41	<0.09	<0.9	<0.09	<9	<0.09
TOC	7050		890			
Vanadium	0.29	0.03	0.094	<0.003	<0.3	0.009
TDS	25000	1700	12000			
TSS						

Based on EPRI’s compilation of waste streams, there are some features that have significantly high values. Those are more accurately described the following sections. Noticeable findings are both metal concentrations and the amount of organic content in first flushing waters (first rinse drain), which are much lower than in spent solvent. Based on compositions of flushing waters, these may be possible to sewer.

3.2.1 Heavy metals

Biological process of waste water treatment plant is not capable to remove such large amounts of heavy metals that waste liquor has. These metals will thus accumulate in the sludge, which is then recycled to energy use. Cadmium, mercury and lead are the most harmful chemicals what comes to reusing the sludge, but still the most harmful components in the acid cleaning are chromium and nickel, because these concentrations in boiler chemical cleaning waste waters typically exceed the limit values multiple times. As seen in figure 3, in addition to chromium and nickel, also concentrations of iron, copper and zinc are highly elevated. Although iron is always the most abundant metal in waste waters, it is harmful for neither hazardous waste treatment plants not municipal waste treatment process and is allowed even in high concentrations.

Some of the nickel and chromium compounds are highly toxic to aquatic organisms, and depending on metal, the sludge of the treatment plant binds 20 – 80 % of the metal amount. It is not possible to remove all the metals during the treatment process. Especially the chromium and nickel limits for treatment plant sludge have been tightened during the years: As figure 4 shows, tightening of the limits has decreased metal concentrations in final sludge.

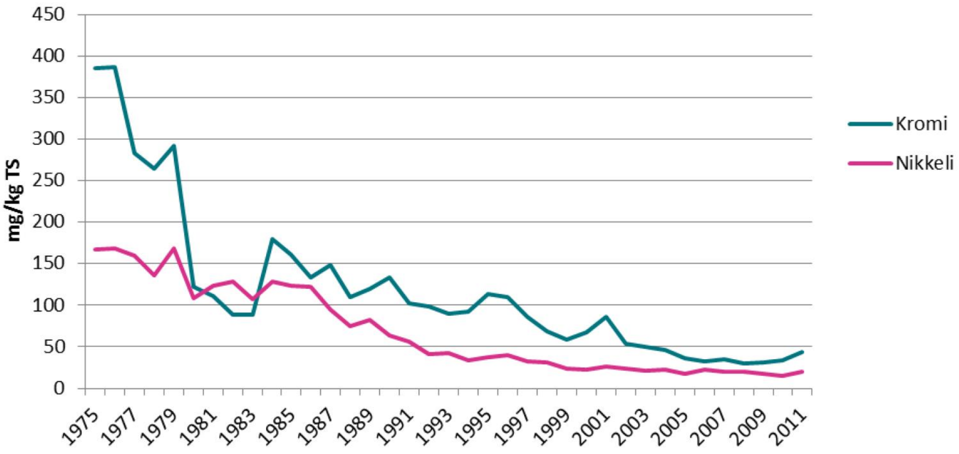

Figure 4. *Chromium (blue) and nickel (purple) content in the sludge of HSY treatment plant 1975 – 2011 [24].*

There are other metals which interfere biological process of treatment plant, inhibiting the function of micro-organisms. That type of metals are mercury, iron and copper. With biological treatment, small amounts of metals can be removed but compared to communal waste water, metal content is too high. For example, removal of nickel is poor, under 50 %, because nickel exists as complex compounds and does not bind easily to the sludge.

Also inhibiting metals tend to bound to the micro-organisms in the active sludge. For aquatic organisms, small concentrations can be toxic. Limit values and restrictions are more accurately specified in chapters 4 and 5. [12, 24]

3.2.2 Organic matter

Aeration during the sewage treatment process is designed to disperse a certain amount of organic matter. Oxygen-consuming substances in waste water may disrupt the function of treatment process, if the input stream exceeds the oxidation efficiency of the aerator. If the oxygen level in aerator decreases, biological sludge may be destroyed or problems in sludge settling can occur. Some bacteria may also overgrow.

To estimate oxygen consumption in waste water processes, biological oxygen demand must be defined. BOD describes the amount of dissolved oxygen, which is needed by aerobic biological organisms to break down organic matter. BOD value in the acid cleaning waste water varies depending on cleaning stage. In case of passivation solution, BOD_7 value may be over 1000 mg/l O_2, but in acid cleaning waters the value varies typically from 100 to 400 mg/l O_2 [25]. For comparison, BOD_7 value in European untreated sewage can be 600 mg/l, still having an average of 200 – 300 mg/l. [9, 26]

Another feature similar to BOD is chemical oxygen demand, COD value. It describes oxygen demand, too, but the demand to be measured is from chemical reactions, not from biological organisms. Thus, it reflects the oxygen demand caused by degrading organic substance. The effect of activated carbon injection can be seen in waste water compilation collected by VGB standard in table 4, in which relatively low COD values has been achieved. Waste water compilation in EPRI's manual shows, that organic content in organic solvents (citric acid and EDTA) is higher than in case of hydrochloric acid. Organic content may be the feature which disables sewage of citric acid waste waters. [9, 26]

Nitrogen is another element to be analyzed. In general, nitrogen concentrations in acidic waste waters are relatively low. Still, nitrogen added to the neutralization stage is the most demanding organic compound in the waste and it can be a major harm for hazardous waste treatment plant, if the waste is not possible to sewer. If the waste is treated with physical-chemical treatment including neutralizing, precipitation and filtering stages, nitrogen will stay in waste water because neither precipitation nor evaporation are possible. Sewage the cleaned sludge is not allowed, because the nitrogen concentrations of the waste water exceeds many times the limit values settled by treatment plant. In addition, nitrogenous wastes are often mixed with acidic waters in which heavy metal concentrations are increased. If any more advanced technology is not possible to use, water may be incinerated [27]. Still, only some treatment facilities have possibility to incinerate waters, so there may be alternative that the treatment company totally refuses to accept waste waters. For physical-chemical treatment, the limit value for ammonium nitrate content is approximately 400 mg/l. In most cases, 100 mg/l is possible to achieve by neutralizing waste water [25]. For comparison, concentrations in household wastes are approximately 40 mg/l [12].

Table 5. *Waste waters from boiler HF cleanings including lime and activated carbon addition [3].*

Plants	**A**	**B**	**C**	**D**	**E**	**F**
pH	8.2	8.3	6.1	9.5	8.2	9.2
COD (mgO2/l)	40	26	26	32	200	69
Fe (mg/l)	0.3	0.63	0.09	0.26	-	-
NH3 (mg/l)	4.1	18.1	2.6	2	8.6	0.7
Fe (mg/l)	10	18	2	11	2	22
TSS (mg/l)	1	-	-	10	4	34
Conductivity (µS/cm)	199	1260	121	144	122	340

Especially for organic content, it is important to check the specific features of local restrictions. Final disposal destination of treated water has an effect on limits for nitrogen and phosphorous. Although in most of sea areas in Finland nitrogen is the most important value to control, e.g. in the northern part of the Gulf of Bothnia, phosphorous content must be carefully considered. Typically, phosphorous is removed from waste water chemically, which increases chemical costs, while nitrogen removal is usually executed during the biological process.

3.2.3 Conductivity

There are differences between country and area restrictions for salts, whose concentrations lead to high conductivities, reflecting usually an elevated amount of dissolved solid substance. In case of hydrochloric acid cleaning, salt content of waste water may be high because of chloride ions. After sodium hydroxide or sodium carbonate neutralization, no precipitation of salts occurs and chloride concentration may stay too high disabling sewage. Chloride concentrations in waste waters may cause challenges only in hydrochloric acid cleanings. High concentrations will corrode the structures of sewers and pumping stations. In Finland, chloride limit for sewage water is 2500 mg/l, which is achievable in case of citric- and hydrofluoric acid cleanings. Instead of these, chloride concentrations in hydrochloric acid wastes may be as high as 20 000 – 30 000 mg/l, forcing the waste always to precipitate [28].

On the contrary to hydrochloric acid, hydrofluoric acid waste having high fluoride content is possible to get nearly salt-free by precipitating fluorides from the solution as calcium fluorides. In case of citric acid, the waste is usually nearly saltless. Sewage of salty waste waters is possible only on the coast, because the sewage system is not capable to remove all salt from water. Salts remain in the sewage water which is brought to the sea, and sewage of salts into lake is forbidden. If the neutralized water is precipitated, salt content in precipitation pool surface waters is relatively low. Chemical conductivity indicates the total salt content of waste water, and is at highest in hydrochloric cleanings. Conductivity of acid solution may be over 10 000 µS/cm, but in passivation solution only half of that. By neutralizing and precipitating the sludge, it is possible to lower the conductivity to approximately 500 µS/cm. In comparison, typical conductivity level for drinking water varies from 50 to 800 µS/cm. [12, 16, 25]

3.2.4 Cyanide

Cyanide (CN^-) limit for waste water is 0.5 mg/l. As well as being poisonous to aquatic organisms, it inhibits the nitrification bacteria. Cyanide anion will form toxic salts, such as sodium cyanide and potassium cyanide, and in acidic conditions also hydrogen cyanide (HCN) is formed. [12, 29, 30]

Cyanide is used as one of the key components in metal plating as an additional compound in plating path to facilitate anode corrosion. Metals, which are commonly plated in cyanide bath and are also used in boilers, include cadmium, zinc and copper. Because of toxicity of the cyanide compounds, there are alternative plating bath chemicals under development. Still, today usage of cyanide is common.

Cyanide-containing fraction of waste waters requires segregation from other waters. If cyanide is removed prior to other waste treatment operations, formation of HCN will be prevented. CN^- typically complexes metals from non-cyanide waste water, complicating further treatment processes. By removing cyanide from waste stream as early as possible, total treatment cost can be minimized. So far, there have not been such high cyanide concentrations that they would cause any problems. [29, 31]

3.2.5 Other physical properties

In Finland, pH limit for sewage water is 6 – 11. Neutralization of waste waters to get these within the boundaries is mandatory in Europe, but also to a growing extent in the rest of the world [12]. Acidic wastes have been found to be corrosive to sewers and pumping stations. Bases do not cause any problems for sewage system, but as previously mentioned, fluctuating pH may be harmful to treatment bacteria. In general, acidic cleaning solution and alkaline passivation solution are mixed together. Thus, the liquid is neutralized and pH is set. After the neutralization and precipitation processes, pH of the supernatant usually stays between the limit values. pH of the remaining bottom sludge can be acidic, but acidity does not hamper treatment process in hazardous waste treatment plant. If there is not possibility to neutralize or store cleaning liquids on the plant site, acid cleaning and passivation solutions must be transported straight to waste treatment plant. pH for acid cleaning solution varies between 2 – 3 causing then a safety hazards to the employees. In ammoniated citric acid cleanings, pH of the solvent may be 3 – 4. Also, passivation solution may be harmful because of pH of 9 – 10. [2, 3]

Total dissolved solids (TDS) is a measure of inorganic and organic substances in liquid. Those solids may be in molecular, ionized or micro-granular form. Solids are removed from sewage water at the early stage, but still, large amounts of solids add the amount of sludge generated from the waste water, leading to higher sludge treatment costs. In Finland, limit value for dissolved solids is not defined, but it varies from 300 mg/l to 500 mg/l. [12]

Sulfates in waste water must be accurately analyzed, because under certain circumstances, these may cause concrete corrosion. Volume of reaction products is larger than the volume for reactants, thus causing the concrete to swell and break down pipelines. Sulfate limit 400 mg/l for sewage water consist of total sum of sulfate, thiosulfate and sulfite. Acid cleaning waste waters generally have concentrations of 100 – 300 mg/l [12, 25].

High temperature (50 – 90 °C) of circulating cleaning water may force to use temporary container pools as an intermediate storage for water. In the pools, the water is allowed to cool to a desired level. The temperature resistance of tank of transportation vehicle is about 60 °C, meaning that especially with citric acid treatment the waste must be cooled prior to loading it into the vehicle. High temperature may also be disadvantageous to municipal water treatment process causing failure of to grease separation and therefore leading to blockages. Also, oxygen demanding reactions may be enhanced, which will lower allowed amount of COD and BOD coming in the treatment plant with waste waters. Temperature limit set by municipal treatment process is 40 °C, but in practice, higher values can be tolerated as waste water has time to cool off in the pipelines during the flow to the treatment process. [12]

3.3 Toxicity

Acid cleaning stage is usually followed by storage, in which the cleaning liquids are passed to temporary reservoir in order to sample the waste. After neutralization, and possible precipitation, the composition of waste water is defined. Both precipitated bottom sludge and possible drainable surface water are analyzed. When defining the possibility of waste water sewerage, and also, evaluating the treatment costs charged by hazardous waste treatment plant, the analysis results are determinant. There may be such synergies between waste harmful properties that individual factors do not reveal; for example, acidic or grease and oil containing waste water separately is not a problem for waste treatment plants, but oily and acidic waste is complicated to treat as grease will block the channels of physical-chemical plant and, on the other hand, acidic water must not be allowed to enter the grease separation equipment. As table 6 shows, typical laboratory analysis consists of both elemental and water quality analysis [9]. In most EU countries and North America, diluting the waste water prior to sewage is prohibited.

Table 6. *Common waste water properties to be analyzed [9].*

Property	**Unit**	**After acid cleaning**	**After neutralization**
pH		2.3	8.2
Conductivity	µS/cm	320	3000
Solids	mg/l	53	100
BOD_7	mg/l	18000	18000
COD_{Cr}	mgO_2/l	32000	31000
Fluoride (F)	mg/l	0.44	0.61
Chloride (Cl)	mg/l	< 0.1	< 0.1
Sulphate (SO_4)	mg/l	44	16
Nitrogen (N) total	mg/l	180	7200
Nitrate (NO_3)	mg/l	< 0.1	< 0.1
Phosphate (PO_4)	mg/l	< 0.1	< 0.1
Ammonium (NH_4)	mg/l	2.2	7200
Cyanide (CN) total	mg/l	<0.05	0.14
Arsenic (As)	mg/l	0.026	0.028
Mercury (Hg)	mg/l	<0.00010	<0.00010
Silver (Ag)	mg/l	<0.0020	<0.0020
Cadmium (Cd)	mg/l	<0.00020	<0.00020
Chromium (Cr)	mg/l	0.93	1.1
Chromium VI (Cr)	mg/l	< 0.1	0.59
Copper (Cu)	mg/l	0.040	0.19
Lead (Pb)	mg/l	0.0026	0.0017
Molybdeum (Mo)	mg/l	0.16	0.23
Nickel (Ni)	mg/l	0.48	0.57
Iron (Fe)	mg/l	690	830
Zinc (Zn)	mg/l	0.40	0.41
Tin (Sn)	mg/l	0.017	0.022
Cobolt (Co)	mg/l	< 0.01	< 0.01
Antimony (Sb)	mg/l	< 0.01	< 0.01
Phosphorous (P)	mg/l	0.067	0.076
Hydrocarbon oils (C_{10}-C_{40})	mg/l	0.16	<0.20
Hydrocarbon oils (C_{10}-C_{21})	mg/l	0.06	<0.20
Heavy oil fractions (C_{10}-C_{40})	mg/l		

To clarify whether waste water is toxic to bacteria in municipal water treatment plant, the specific toxicity test must be taken. Activated sludge oxygen-suppressing effect and biological degradability are tested to determine the toxicity to plant bacteria. Low BOD/COD-ratio is characteristic to acid cleaning wastes and indicates that organic matter in waste waters are poorly biodegradable or toxics in the water inhibit biochemical oxygen demand. Most acid cleaning wastes contains chemicals which inhibit nitrification, and in that case, a nitrification inhibition test is carried out after the cleaning procedure. [12, 22]

In addition to toxicity tests, the most common analysis are biological tests and aquatic toxicity. Flash-light bacterial and biological sludge analysis are used to define if the cleaning solution is acute toxic or lethal to treatment bacteria. Practice has shown, that cleaning solutions are toxic to bacteria when 100 % concentration is used, while with 10 % concentrations the effect disappears [16, 22]. Typical practice is to sewer cleaning waters in the daytime and at limited rate in order to get the wastes mixed with household wastewaters. In that way, the wastes become too diluted to cause harm for bacteria. [12, 22]

4. WASTE WATER TREATMENT TECHNIQUES AND LIMITATIONS

There are couple of alternatives to treat chemical acid cleaning waste. Costs induced by the technique selected can vary widely and depending on the method used, the costs can rise as high as the costs of cleaning procedure itself [1]. It would be better to consider water treatment methods early in the boiler delivery project, at the same time when choosing the cleaning chemicals.

Chosen cleaning chemical may be the most considerable factor affecting the choice of treatment method, because different types of acids are used. Cleaning solvents are typically divided into organic and mineral acids, whose methods to bind impurities from tube inner surfaces differs from each other. Generally, the stronger metal-binding force the chemical has, the more difficult these metals are to remove from waste water. Another significant factor in choosing the treatment method is local circumstances. For example, narrow plant site or safety requirements can require treatment technique which is done entirely outside the plant site.

On a larger scale, local circumstances are affected by environmental restrictions for sewerage and treating the hazardous waste water. When planning the cleaning in the country, in which there have been only a few or no earlier experience of acid cleaning water treatment, sewerage limits and hazardous waste treatment practices are important to decide early beforehand. Restrictions for different countries are compiled into table 7. Limits vary by country significantly, and for some chemicals there may be zero tolerance, meaning that the only alternative is to transport sludge to hazardous waste treatment plant. As the table 7 illustrates, the differences between the limits can be more than tenfold. For chromium and nickel, which are the most difficult substances to be removed, there are lower limits in Finland than for example in India. On the other hand, for copper, the limit in Finland is 2 mg/l, while in India it is 3 mg/l, in Germany 1 mg/l and in U.S. 0.5 mg/l [12, 32]. Still, the country limits are only indicative, as they vary also within the country. Besides sewerage limits, there are other quality parameters that are under monitoring. For these features, the limit values are not predetermined but the more value is exceeded the more difficult it is to get the permit for sewerage. In Finland, there are several features to be monitored in addition to the list in table 4, such as conductivity, biological and chemical oxygen demand and solids, while in some countries there are not any other control than the limits listed in table 4 Some areas outside Europe there is no continuous monitoring; once a permit for drainage has been granted, future drainage permit is ensured, even if the composition of the wastewater is changed. Restrictions are not totally accurate, as there may be local differences between different municipalities. For example, in Tampere main water treatment plant in Viinikka, bacteria of aeration process are generated so that the process can withstand the wastes coming from Tampere's biggest waste water producer Metsä board Tako carton factory. On the other side of the city, waterworks in Rahola most of the waste loads are household waters. As the table 8 illustrates, there are still not many differences between the general limits set by Finnish municipal water treatment plants. What is interesting, is that the limits remain the same whether the load is continuous or not. Pre-operational cleanings are one-time performances, which means that these types of loads alone can not cause long-term accumulation of heavy metals. The classification between one-time and continuous load is one of the most significant features what comes to total costs induced by waste treatment, and it is more accurately discussed later. [11, 33]

***Table** 7. Sewerage limits in different countries [12, 17, 18, 34, 35].*

mg/l	**HELCOM**	**Finland**	**Sweden**	**Germany**	**US (Texas)**	**China**	**India**
Antimony				0.5			
Arsenic	0.3	0.1		0.5	0.1	0.5	
Barium					1		
Cadmium	0.2	0.01	0.01	0.5	0.05	0.1	
Chromium, total	0.7	1	1	1	0.5	1.5	2
Chromium, VI	0.2	0.1		0.2		0.5	2
Copper	0.5	2	2	1	0.5	1	3
Cyanide	0.2	0.5	0.5	1		1	2
Lead	0.5	0.5	0.1	1	0.5	1	1
Mercury	0.05	0.01	0.01	0.1	0.005	0.05	0.01
Nickel	1	0.5	1	1	1	1	3
Selenium					0.05	0.2	0.05
Silver		0.2	0.1		0.05	0.5	
Tin		2		5			
Zinc	2	3	2	5	1	5	15
Fluoride		50				20	15
Phosphorous, total		50		50			
Sulphate		400	400	600			
pH		6,0-11,0	6,5-10,0	6,5-10,0	5,5-12,4	6,0-9,0	5,5-9,0
Temperature (°C)		40	50	35	65		45
Mineral oil and grease		100	50	300	100		

Table 8. *Sewerage limits in selected cities in Finland [12].*

mg/l	HSY	Kymen Vesi	Lahti	Tampere	Turku	Vaasa
Arsenic	0.1	0.1	0.1	0.1	0.1	0.1
Mercury	0.01	0.01	0.01	0.01	0.01	0.01
Silver	0.2	0.1	0.1	0.2	0.1	0.1
Cadmium	0.01	0.01	0.01	0.01	0.01	0.01
Chromium, total	1	0.5	0.5	1	1	1
Chromium, VI	0.1	0.1	0.1	0.1	0.1	0.1
Copper	2	0.5	2	2	2	1.5
Lead	0.5	0.5	0.5	0.5	0.5	0.5
Nickel	0.5	0.5	0.5	0.5	0.5	1
Zinc	3	2	2	3	2	2
pH	6,0-11,0	6,0-9,0	6,0-11,0	6,0-11,0	6,0-11,0	6,0-11,0
Temperature (°C)	40	30	40	40	40	40
Total solids	300-500					
Cyanide	0.5	0.5	0.5	0.5	0.5	0.5
Mineral oil and grease	100	100	200	100	100	200

In addition to differences between sewerage limits, tightening environmental requirements causes challenges with water treatment in hazardous waste treatment plant. Measuring technology has developed to so accurate, that small concentrations are possible to detect. That may lead in some cases to unnecessary tight requirements for removal efficiency in waste treatment plants. Usually, small concentrations like mercury, cadmium and salt traces come to the waste water from somewhere else outside the process than the cleaning solution or boiler surfaces. Removing of negligible concentrations is difficult and expensive, and it can be even more comlicated than removing the dissolved metals. For processing the waters clean enough, advanced technique as ion exchange or reverse osmosis must be introduced. The complexity of technology can be injurious for smaller treatment facilities, as they are not able to invest in new technology, which may raise prices through reducing competition and supply. [11, 33]

Waste treatment methods are affected also by the experience and habits of the cleaner. Acid cleaning wastes shall be handled as hazardous wastes, and even though they are neutralized, pH can vary substantially. Experienced cleaner can take into account the potential hazards in his own way of handling and use appropriate personal protection equipment. Still, waste transport to the toxic waste disposal plant shall be preferably done by the receiving party's personnel. [1, 2]

What comes to treatment of chemical cleaning wastes, pre-operational procedure's uniqueness and one-time performance should be taken on account. In addition to sewerage limits, there are significant differences in cost-effectiveness between one-time pre-operational and operational cleaning done at regular intervals. Already the authorization procedure for the on-site handling of hazardous waste can be more complicated that it would be better to rely on external authorized actor who completely carries out the process from start to finish, than managing waste treatment itself. [7]

Basically, the three alternatives to move wastes away from plant site are sewerage to local water treatment plant, on site-processing followed by dumping and sewerage, and transporting the waste to hazardous waste treatment plant for further processing. Table 9 summarizes the most common techniques, which are more accurately described in chapters 4.1, 4.2, 4.3 and 4.4.

Table 9. *Alternatives for waste water treatment.*

	Organic acid (CA)	**Mineral acid (HF, HCl)**
Municipal sewage treatment plant	Whole amount to sewage	Precipitation followed by surface water sewage
Hazardous waste treatment plant	Whole amount to hazardous waste treatment plant	Precipitation followed by bottom sludge treatment Whole amount to hazardous waste treatment plant
Industrial waste water treatment plant	Whole amount to industrial treatment plant	Precipitation followed by surface water treatment Whole amount to industrial treatment plant

4.1 Neutralization combined with drainage

Waste water sewage to the local treatment plant is the simplest and the cheapest alternative. In this method, all the waters are led to sewage treatment plant. Pre-operational acid cleanings for the entire boiler are one-time procedures, meaning that at least in Finland, plant sites do not need to apply for general industrial waste water permission. Instead of that, each chemical cleaning is considered separately on a case-by-case basis. In all cases permissions for the drainage shall be obtained from the operator of local treatment plant, which may require lengthy discussions and, possibly, a demonstration that the chemicals used do not cause any harm to the microbes in the biological treatment sludge. It should be also ensured that the waste do not cause an uncontrolled increase in P, N or COD concentrations. [2]

On the contrary to limitations for metals, treatment process is able to remove nitrogen, phosphorous, organic chemicals and solid matter, thus allowing bigger tolerances for waste. Another factor affecting the sewage of waste water is scheduling and reporting. If the information of waste water load does not come early enough to the treatment plant, there are no time to test the toxicity or composition of the waste. In that case, drainage typically is prohibited. Too high nitrogen, phosphorous, or BOD value is rather uncommon for boiler cleaning wastes, which means that the normal water treatment cost is charged. For example, in Finland the charge is 1.39 €/m^3 meaning that the cost of whole waste water amount is moderate [22]. Volume of waste water may be hundreds of thousands of cubic meters meaning that the capacity of treatment plant must be high enough. Especially in sparsely populated area, where the ratio between industrial and household waters is higher than other densely populated countries, it is important that the amount of household waste waters coming to the plant is large enough to dilute wastes from chemical cleaning. That is why the time slot for draining is typically limited to daytime. Diluting the wastes prior to sewage to meet quality limits is prohibited [12].

To neutralize water to a level of pH 6 – 11, generally used neutralizing chemicals are calcium hydroxide and natrium hydroxide. Calcium hydroxide is the most profitable what comes to price of chemical, but then great amount of the metal sludge is generated. In case of natrium hydroxide, volume of the metal sludge is smaller but price of the chemical is higher. Ideally, neutralized waste should have a pH of 6 – 9, but moderate variation may be tolerated depending on local conditions [3]. Precipitation can be enhanced adding a polymer to the solution. In most cases, neutralization requires a temporary neutralization tank, in which pH elevating chemicals are dosed. Sometimes, when storage is prohibited or there are no room for tank on the site, waste waters can be neutralized using on-line chemical dosing which means that the neutralizing chemical is injected straight to the outflowing water. In that case, neither settling nor precipitation of metals occur. [14]

Amount of adequate amount of neutralizing agent varies within solvents. pH of hydrochloric acid waste may be in some cases as low as 1.0 – 1.5, while in case of citric acid the pH may vary from 3 – 4 [36]. To neutralize hydrofluoric cleaning waste from 145 m^3 system, 1450 kg 48 % diluted natrium hydroxide and 2900 kg calcium hydroxide was needed. [2, 9, 36]

After neutralization stage, it is important to understand the chemistry of different cleaning solvents. Neutralization combined with drainage is usually carried out only for organic acids: citric acid and more often in United States used EDTA, which both form chelates with metals. In most cases, neutralization is followed by precipitation of metals, which reduces the volume of waste considerably as the surface water above the bottom sludge usually is drainable. In case of organic acid, precipitation is not possible as the molecule bindings between the chelating agent and the metal are too strong to break. This means that waste water will be drained or transported to hazardous waste treatment plant. Although volume of waste water generated when using organic solvents is only 1.7 – 2 boiler volumes, it is still quite much to treat at hazardous waste treatment plant. Hence, the costs induced by the treatment of wastes can vary significantly and sewerage all the wastes to communal or industrial treatment plant is preferred. When choosing citric acid as a cleaning chemical, it would be better to check already early in the project if the waste water generated is drainable. Sometimes defining of drainability is complicated and dependent on several factors. In addition to municipal water treatment plants, the co-operation with industrial water treatment plant may be possible. Especially with industrial sewers, the local conditions can affect the treatment possibilities so that the waste water is drainable unless municipal sewerage limits are exceeded. [2]

As explained in chapter 5, there is possibility to separate neutralization-passivation waste waters from acidic cleaning waters. Separating facilitates the treatment process, but it can also make passivation waters drainable. In mineral acid cleanings, the clean surface which is formed in the acid cleaning stage, may corrode again. For dissolving initial rust, iron-complexing citric acid may be used. For ensure permission for drainage, it can be possible to eliminate citric acid injection during neutralization-passivation stage. Drawback then is rustier boiler inner surfaces and the coloring, that resembles more yellow than pure grey, which is the normal cleaning result. According to the cleaner, eliminating citric acid addition does not have impact on final cleaning result. That cleaner has done elimination for several projects when sewerage limits are not negotiable. When leaving citric acid off, it becomes more important to do quick start-up after the chemical cleaning for avoid re-corroding. Even if passivation waters were mixed with acidic waters, eliminating citric acid injection still has beneficial effect on water treatment by decreasing the amount of organic content.

Unless direct drainage would not be possible due to too low capacity of municipal water treatment plant, cleaning liquids must be stored to decrease the speed of drainage. Smaller single dosages do not affect limitations for metals, because these will anyway accumulate to the sludge, but with smaller dosages it is possible to balance the nitrogen load of waste water. Nitrification bacteria in biological sludge tolerate small amounts of nitrogen and other oxygen demand increasing impurities, but high concentrations are toxic for bacteria.

Storage tank can also be used for store waters for toxicity sampling, which is needed when there is no certainty for waste suitability to sewer. [1, 7, 8]

4.2 Storage and precipitation combined with drainage

Cleaning with mineral acids, such as hydrochloric or hydrofluoric acid, the waste water generated seldom is drainable. To reduce iron and heavy metal concentrations, it is possible to store, neutralize and then let the waters to settle and precipitate. With precipitation, the amount of waste to be treated is possible to reduce significantly, because the surface water usually is drainable and only bottom sludge must be processed further.

As mentioned earlier, with current technology only precipitation of mineral acid solutions is possible. In Finland, there are couple of main facilities that offer sludge treatment services. [1, 2, 7, 13]

4.2.1 Storage systems

Need to storage of produced waste water must be considered on planning stage. Volume of storage or neutralization pond must be at least twice the volume of the boiler. Storage tank can be constructed by digging the pit on the plant site and then terracing the excess soil to the edges. As shown in the figure 5, the embankment is usually made of fine sand, on which 1–3 covering tarpaulins are placed. Sometimes, if terracing is not made of fine sand, the filtration cloth between the tarpaulin and the soil is needed. Another alternative is to use rental storage tanks, which will cause even higher costs. In addition to environmental permits and financial contribution, on-site storage pond requires space. Therefore, it is justified to find out early in the project which type of storage is suitable. Generally, acid cleaning is better to schedule during summer or autumn in order to the storage pond placed outside. [2]

If the volume of the system to be cleaned is 150 m^3, storage for 5 – 6 boiler volumes of waste water may be 300 m^3 [16]. The depth of the pool can then be, for example, 2,8 m. Metals are typically precipitated so well that the sludge transported to further processing may be 30 cm from the bottom of the pool, meaning that approximately 90 % of waste water generated become drainable [2, 7, 13].

Figure 5. On-site pond for storage, neutralization and precipitation [37].

There are three main reasons for letting the waters to stand in the storage containers. First reason to storage is to neutralize waters for precipitate metals. Secondly, laboratory sample which is possibly taken for define the possible treatment methods, needs to be analyzed, and it takes 1 – 7 days to receive results [7, 11]. During this time, waste waters are stored in containers. In the Nordic countries, the cleaning process, composition of boiler inner surfaces and local limitations are known so well that laboratory samples may not be needed [13, 59]. Thirdly, whether the treatment method for waters is drainage or processing in hazardous waste treatment plant, receiving capacity of the plant is limited. That causes the need to smoothen the waste load of treatment plants by intermediate storage. Sewerage limit for municipal water treatment plant is typically 100 m^3 per day, meaning that drainage takes couple of days and remaining waters must be wait for treatment in the containers [12]. Also, hazardous waste treatment plants have their maximum capacities, meaning that there are separate capacities for reception tanks and for treatment tanks. In Lassila&Tikanoja treatment plant in Lahti, the current volume of the reception tank is 200 m^3 while total volume of three precipitation containers is 100 m^3 [38]. In Fortum, physico-chemical treatment plant storage capacity is 200 m^3 [27]. Processing capacity in Kierto Ympäristöpalvelut is 100 – 200 m^3 having additional restriction of 20 m^3 per day for acids. [22, 27, 38, 39]

In large-scale boiler chemical cleanings, there is not possibility to store waste waters in mobile containers. An example from cleaning procedure in Stockholm, there was a boiler cleaning having volume of 440 m^3 to be cleaned. Storing was executed with the wooden storage pool of 52 m*33 m and 12 000 m^3. Obviously, this was the most expensive alternative, but the pipes, cables and other parts beneath the ground excluded the option that temporary pool could have been dig with embankment construction. The biggest possible portable container is approximately 300 m^3, and it usually is included the scope of the cleaning work. [11]

4.2.2 Precipitation and solubility

During the neutralization process, iron and heavy metals will precipitate as hydroxides. In some cases, also precipitation with sulfides is used. With sulfide precipitation, it is possible to achieve lower metal concentrations, but the method is more complex and usually too expensive to be utilized for waste waters produced during the pre-operational cleaning. When minimizing both amount of precipitated sludge and costs, the pre-clarification should be done with hydroxide precipitation and then move to sulfide precipitation. Still, mixing precipitation is not widely on-site precipitation method used in boiler chemical cleanings.

Precipitation is the process of forming solid phase. If supernatant liquid, the process is also called clarification. Precipitation begins when the process become over-saturated. In its simplest state, two reagents are mixed and solid matter is formed. Compared to crystallization, precipitation is slightly faster reaction. The most used clarification method, chemical precipitation, is used for separate metals from the solution. The semi-solid sludge formed is insoluble between pH 8 – 10. [40, 41]

Solubility S describes the maximum concentration of soluble substance in saturated solution at a certain temperature. Salts having solubility under 1 g/l are called slightly soluble compounds. Equations below illustrate salt dissolution in water (6), and how the solubility is obtained (7).

$$M_n + A_m(s) \rightarrow mM^{n+}(aq) + nA^{m-}(aq) \tag{6}$$

$$S = \frac{[M^{n+}]}{m} = \frac{[A^{m-}]}{n} \tag{7}$$

in which $[M^{n+}]$ describes concentration of cations in solution

$[A^{m-}]$ describes concentration of anions in solution

m describes coefficients of dissolved cations in reaction equation

n describes coefficients of dissolved anions in reaction equation

Solubility product constant K_s describes concentration of slightly soluble matter in saturated solution. If all concentrations in the solution are known, K_s is possible to calculate using the formula (8). If concentrations of ions in saturated solution are replaced by instantaneous concentrations, an ion product Q is obtained. If $Q > K_s$, the solution is oversaturated and precipitation of ions begins.

$$K_s = [M^{n+}]^m \, [A^{m-}]^n \tag{8}$$

Temperature rise usually increases solubility of organic salts, but in case of inorganic salt, solubility may even decrease. Value of solubility product constant is highly dependent on temperature, but in chemical cleanings, dependence on pH is more dominant factor.

As the figure 6 illustrates, each metal has substance specific pH range, in which precipitation is possible. The formed precipitate is totally insoluble from pH 8 to 10, but if pH is let move outside the boundaries, the formed precipitate begins to dissolve again.

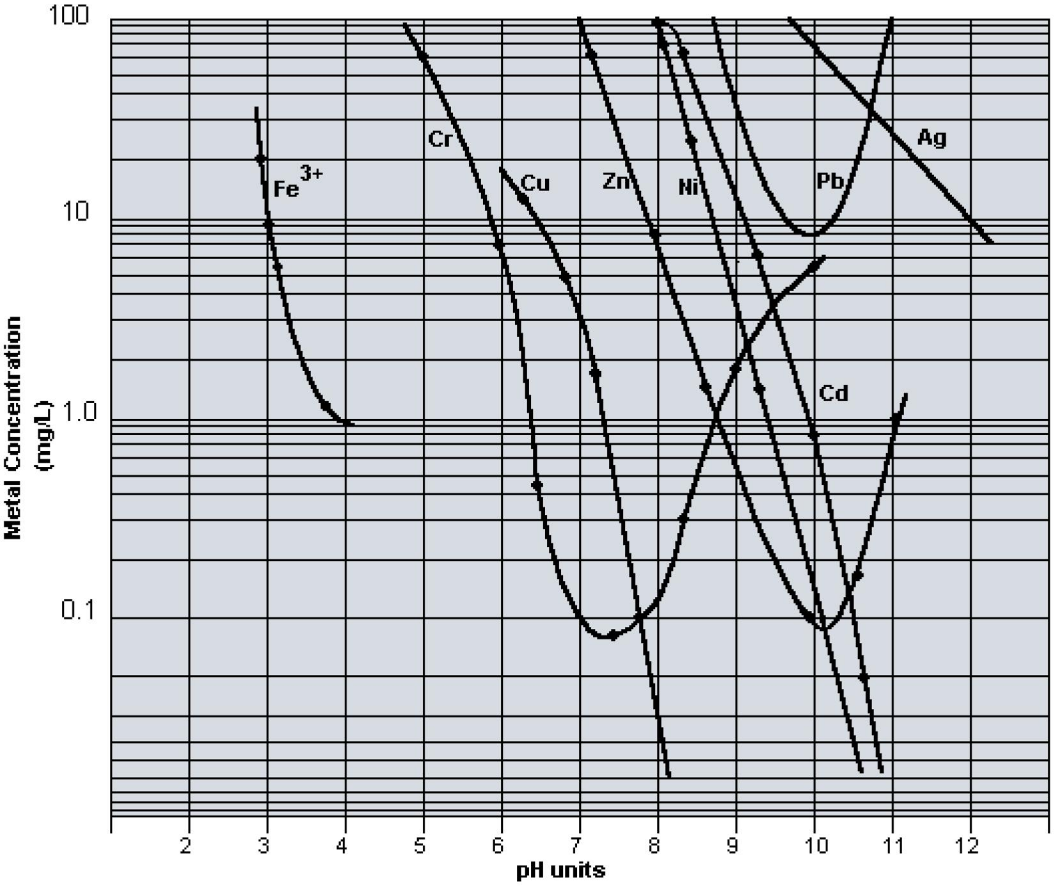

***Figure 6.** Precipitation of metal hydroxides as a function of pH [42].*

Precipitation of heavy metals in acidic wastes is under investigation by couple of industrial actors. There are possibilities to develop cleaning process and treatment methods so, that smaller heavy metal concentrations are achieved. These developments are described more accurately in chapter 5.

4.2.3 Treatment of bottom sludge

In most cases, disposing follows precipitation process, leading to keeping the volume of sludge to be disposed relatively low. However, there may be reasons that the whole waste amount is transported straight to the further processing. Due to lack of space or storing permission, precipitation may not be possible, or in case of small-scale cleaning the amount of water may be so low that precipitation is not worth doing. Depending on possible usage of precipitation, treatment costs and the amount of waste to be processed can vary a lot. As mentioned, there may be additive compounds present in the waste water that interfere precipitation. Sometimes the whole waste water must be further processed as the surface water, even after precipitation, is not drainable. For ensure precipitation, additive compounds must be exactly known. Only through understanding the chemistry of cleaning process, it is possible to design possible segregation for the chemicals which hamper precipitation. Bottom sludge treatment techniques are presented in chapter 4.4.

4.2.4 Citric acid treatment

While dissolving force of mineral acids is based on acidic dissolution of deposits, organic solvents have ability to chelate a deposited metal and bind it. As the acid spends during the cleaning, pH of organic acid solution tends to increase, sometimes near to neutral conditions. That enables metals to re-precipitate, which is naturally prevented by complexation of dissolved ferric and other metal ions by the organic acid. Relatively high pH value compared to mineral acids and ability to sequester metal oxides also at elevated pH, differentiate organic acids from inorganic. Organic chelating agents are solvents that require high pH throughout the cleaning and utilization a chelation reaction to remove all the deposits. Some solvents, as citric acid, can be used also at intermediate pH values in which both acidic dissolution and chelation may occur. [10]

Cleaning formulations involving citric acid based solvents normally contain a variety of other components. These include ammonia, fluoride, organic corrosion inhibitors, surfactants and sodium nitrite. High COD value makes the waste treatment difficult also for waste treatment plants. Citratoferrate (lll) ion has high stability, because three electrostatic bonds are supplemented in the complex by three dative covalent bonds. As the picture below illustrates, the free tridentate ligand, citrate ion with three negative charges, contains three unshared electron pairs meaning that these are capable of functioning as Lewis bases. Electron pairs enter in the empty outermost d orbitals of central transition metal, such as iron, significantly increasing the stability of complex. [6, 12]

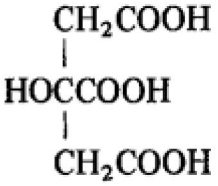

Figure 7. *Citric acid*

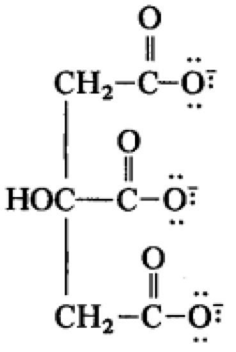

Figure 8. *Citrate ion*

Ferric hydroxide at pH 10 does not precipitate in the presence of three-fold excess of citrate, because concentration of ferric ion contributed by citratoferrate complex is only one-half compared to ferric hydroxide. Thus, it is important of not allowing the concentration of citric acid to dwindle during the cleaning procedure.

The general perception is that chelated organic acids do not precipitate, because bindings between the metal and solvent are too strong to break [3, 10]. Still, there are methods which the citrate metal complex is destroyed so that conventional alkaline precipitation of the metals can be used. One procedure is used at least in U.S., and the method is consisted first on an oxidation step whereby citrate is decomposed and the solubility of metal hydroxides is decreased. Oxidizers, which are used for this stage are ozone, hypochlorite and persulfate. Next, lime ($Ca[OH]_2$) is applied to increase pH to 12.5 to precipitate citrate as calcium citrate and metals as the hydroxides. Removal of ammonia is part of the procedure because it is not possible to remove it in other ways. After citrate has been precipitated, chemically bound ammonia will release. In this stage, stripping is applied to facilitate removal of ammonia. Without the addition of an oxidizing agent first, lime precipitation of metals and citrate may sometimes produce a slow settling floc, requiring filtration through granular carbon filters for its removal. For remove other organic substances, such as wetting agents, adsorbents may be used. [10]

Citric acid is the only organic solvent, which is currently used cleanings in Europe. In addition to citric acid, there are EDTA, which is widely used in the cleanings performed by U.S. Although in Europe, there are no generally known means for citric acid precipitation, in U.S. chemical cleaning specialists have managed to precipitate the citric waste waters so, that usually these are drainable [43]. The method based on lime injection followed by heating starts with mixing all the solvents and rinses together. After mixing, waste water is divided to three different treatment methods by iron concentration. For the waste having iron concentration below 1500 mg/l, the only stages of precipitation are lime adding three times more than the amount of dissolved iron, and adjusting pH to 12.5 with sodium hydroxide. For iron concentrations between 1500 – 5000 mg/l, lime must be added four times iron rate followed by heating to 65 °C for at least eight hours. If iron concentration is still too high, it is possible to continue heating until the dissolved iron concentration achieves 1 mg/l. Without diluting the wastes first, iron concentration reduction from over 5000 mg/l to 1 mg/l or below is not achieved. To enhance the precipitation, addition of approximately 660 mg/l cationic polyacrylamide polymer is possible. It is unclear if the method has been tested in Europe, but in Finland, it would be useful to try the precipitation method used in Valmet U.S. Sewerage limits in North America are rather similar than in Nordic countries, meaning that supernatant may be suitable for sewage also there [43]. Also for the method described above, there are some challenges. For the whole boiler chemical cleanings, execution of proper heating may be problematic due to the great amount of water needed. The more complicated issue is chromium content, which can not be reduced with the method. According to U.S. division, waste waters, which are anticipated to have high chromium content, are separated from other wastes before draining them in the same container, and transported to waste treatment company. Final disposal method for citric acid wastes having high chromium content is dumping to landfill, which is always the responsibility of treatment company However, that type of landfilling is not allowed in most of European countries. [43]

Many professionals in the area of chemical cleaning would prefer hydrofluoric acid over citric acid for environmental reasons [11, 14, 44]. Although citric acid itself is relatively harmless and environmentally safe compound, its cleaning waste usually is more problematic than separated treatment of precipitated surface water and bottom precipitate sludge from mineral acid cleanings, especially insoluble precipitate of HF waste. In Sweden, Denmark and Norway the usage of citric acid is minor. For environmental reasons, even the use of 0.1 % solution in passivation stage can be problematic. In other Nordic countries than Finland, roughly 98 % of the new boiler cleanings are done with hydrofluoric acid. Because of tightening waste organic content and metal limits, use of citric acid may be terminated also in Finland. For these reasons, research for new precipitation techniques is intense. In addition to the method used in U.S., recent studies on physical-chemical treatment of organic acid solvent solutions led to methods by which the citrate metal complex is destroyed with oxidizing chemicals so that conventional alkaline precipitation of the metals can be effectively done [44]. [11].

There are experience also for that alkaline citric acid waste will degrade readily through microbiological utilization of the citrate, when it is stored at pH 8.0 – 8.5 [10, 13]. If ammonia removing aeration is added to the citric acid waste cleaning procedure, it begins to remind those methods used in microbiological processes applied in sewage treatment plants’ extended aeration and activated sludge technique. In Finland, there is boron-based patented precipitation method already in small-scale use, but again, large-scale European experience is missing. Method based on boron precipitation is discussed in chapter 4.4.5. However, proposals for citric acid precipitation exist, but these are not yet commercial. [10, 13]

4.2.5 Hydrochloric acid treatment

While treatment of citric acid waste is a process that requires development and research, the treatment methods of both hydrochloric- and hydrofluoric acid wastes consists mostly of same stages, which based on metal precipitation followed by supernatant neutralization and passivation. Usually, waste waters from pre-operational hydrochloric cleanings contain no or only a few cleaning performance enhancing additive chemicals, as hydrochloric acid itself is effective enough to remove deposits. Ammonium bifluoride and thiourea, which are generally used additives in operational cleanings for hardly removable silica and copper, are still possible to remove from waste stream [10].

During the neutralization of hydrochloric acid with caustic soda solution, pH is raised to reduce corrosivity and to avoid classifying the waste as hazardous based on pH. Hydrochloric is applicable chemical to calcium hydroxide and calcium carbonate, with metals precipitating as hydroxides. The reactions during neutralization process can be seen in equations 9 – 12. Several pH targets have been used (8.0 – 11.0), but the final pH values are usually 9.0 or above. It is possible to add an adsorbent material, such as activated carbon, or lead the solution through a portable activated carbon filter to remove partially hydrophobic agents that may be present in inhibitors. [10]

$$FeCl_2 + Ca(OH)_2 \rightarrow Fe(OH)_2 + CaCl_2 \qquad (9)$$

$$2\ FeCl_3 + 3\ Ca(OH)_2 \rightarrow 2\ Fe(OH)_3 + 3\ CaCl_2 \qquad (10)$$

$$2\ HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2\ H_2O \qquad (11)$$

$$NH_4HF_2 + Ca(OH)_2 \rightarrow CaF_2 + H_2O + NH_4OH \qquad (12)$$

Due to excellent cleaning power of HCl and relatively easy waste treatment, the use of hydrochloric acid typically is connected with operational cleanings. In Nordic countries excluding Finland, the chemical is used roughly for 95 % of the operational cleanings [13].

4.2.6 Hydrofluoric acid treatment

Waste water treatment of HF follows mostly the same procedures than HCl treatment. It may not be allowed to drain the cleaning liquor, but by neutralizing and precipitating heavy metals off the waste water, supernatant of 5 – 6 boiler volumes becomes drainable. If the necessary permits have been applied, the sludge generated in neutralization can then be deposited to local landfill. Ease of waste treatment and disposal are significant advantages compared to other conventional cleaning solvents. Due to the low solubility of calcium hydroxide, the addition of lime can be utilized to precipitate the solvent as well as dissolved metals. During the calcium hydroxide neutralization, insoluble calcium fluoride CaF_2 will form. Because of low solubility of calcium fluoride, the sludge is possible to dispose to the landfill or transport to hazardous waste treatment plant. In case of landfilling, the moisture content must be lowered or it must be initially dry enough to be landfilled [10, 43].

After neutralization and metal precipitation, waste water contains little or no phosphorous, nitrogen nor salts, and fluoride concentration generally stays under 20 mg/l. Although handling of the solvent must be performed with special care, the cleaner may choose HF to avoid unexpected problems of waste water treatment. By choosing HF as a solvent, it is possible to avoid transportation of high amounts of waste water to hazardous waste treatment plant. Because of the ease of HF treatment, in Nordic countries HF is used as a main cleaning chemical for pre-operational cleanings. [2]

4.3 Final treatment of sludge

The fourth method to treat cleaning wastes is transport of sludge, or the whole cleaning solution, to further processing without precipitation first. Further processing options are physical-chemical treatment, evaporation, incineration and dumping. Also, other processing technologies are recently developed. In practice, it is not worth commissioning for boiler utilities to develop a new, or on the other hand high fixed cost-having methods, because pre-operational cleaning is largely one-time process. In European countries and especially in Nordic countries, the most common procedure is to transport wastes that are not drainable, to hazardous waste treatment plant. The main techniques remain the same, whether it is all the waste water to be treated or only semi-solid bottom sludge after precipitation. Treatment costs vary depending on waste volume and chemical composition. Renting a mobile treatment unit may also be a solution, if appropriate equipment offered by local actor is found. Possibilities for such on-site treatment by rental equipment must be investigated soon by boiler cleaning responsible and treatment company. Applicable alternatives of final sludge treatment are discussed in chapter 5. It is possible to dispose wastes with only a little advice of authorities, but in most cases further processing will be implemented in cooperation with some waste treatment expert. [3, 10, 11, 43]

Each of the wastes has special characteristics based on the solvent formulation. As an example, citric acid solutions are ammoniated to enhance cleaning process, which means that citric acid streams contain high levels of ammonia and pH is elevated. On the contrary to organic citric acid, pH of mineral acid wastes is lower, being 1.0 – 1.5 in hydrochloric acid. Then also the amount of neutralizing and other treatment chemicals needed vary being only for $Ca(OH)_2$ at least 3500 kg. All these chemical additions must be taken on account when planning appropriate disposal method. [3, 10]

As mentioned, to remove rust and thin oxide layer formed after acid cleaning, small amount of citric acid is dosed to the passivation solution of mineral acid cleanings. Although citric acid concentration in the passivation solution is only 0.5 – 0.75 %, lower than in citric acid cleaning stage, it complicates final treatment process [2]. As mentioned in previous chapter, citric acid forms easily complexes that are hard to broke. Even the treatment plants do not have a proper solution which could be able to break the complex. From municipal sewer point of view, the problem is citric acid, which chelates metals that are unwanted in the water. From the hazardous waste treatment plant point of view, the hardest feature to remove is not metals but high nitrogen content of waste water. The smaller the project, the easier this treatment problem is to solve. If there are only couple of ton waste water to be treated, it may be more profitable not to do precipitation but transport all the water to further processing. This is a common practice especially in superheater cleanings which are done at the factory, outside the plant-site. Water containing citric acid is hardly drainable, but sewerage of nitrogenous neutralization and passivation waters usually is not a problem. For that reason, it is important to consider if the amount of hazardous waste is possible to decrease by optimizing water storages and temporary pools for different waste batches [11]. For example, in Sweden it is not possible to drain citric acid wastes. If these wastes are transported to hazardous waste treatment plant, the price is higher than for waste which contains no citric acid. Price increases proportionally to the amount of acid concentration, which means that treatment price for passivation solution is still lower than for the citric acid cleaning solution having much higher acid concentration. In Finland, citric acid cleanings share of the total cleanings is higher than in many other countries, so treatment facilities are easily available and costs may be lower than in areas which the waste treatment plants rarely receive citric acid solutions. [11]

4.3.1 Physical-chemical treatment

The most widely used form of further processing of precipitated bottom sludge or waste water which is unsuitable for sewerage is physical-chemical treatment, which have couple of advantages compared to other treatment methods. The procedure has been developed to process non-organic acids, bases and solutions having high heavy metal concentrations. First stage is always neutralization, although executed already at the site. pH of the solution is increased to the level in which metals are precipitated, depending on technique with oxides, sulfides, borates or these mixtures. Some acidic or hexavalent chromium including wastes are reduced while cyanide compounds are oxidized prior to neutralizing. Precipitation process is performed more efficiently and possibly in more than one step than in case of on-site treatment, and also, citric acid waste may be treated in some levels. As already explained, treatment of citric acid waste is the most expensive stage of the treatment, especially because of its inconsistent behavior; sometimes the complexes are formed unexpectedly easily and sometimes these do not form at all [38].

An example of the challenges of citric acid treatment comes from national company Lassila & Tikanoja’s main treatment plant in Lahti, where almost all experience of trying to clean citric acid waste have been successful, but the failures which still have been, are caused by citric acid or its additives. Efficient buffering capacity having citric acid tends to form citrate complexes with nickel-, chromium- and copper compounds, and the complexes have proved to be difficult to broke even with physical-chemical treatment. [38]

After heavy metals are precipitated, filter press separates precipitate from surface water. Drainable surface water is led to further treatment, e.g. re-use for lime water or further on-site treatment, including sand filtering and an ion exchange system, after which the treated water is possible to drain to local water treatment plant. Slightly soluble heavy metal salts and -oxides are transported to final disposal. If metal concentrations are not high enough to commercial refining, the precipitate is used for environmental construction. The most decisive factor determining the complexity of final treatment is suitability for landfill, which may have significant effect on waste treatment total costs [14, 27]. Landfilling prices are only a fraction of the price of physical-chemical treatment [27, 38]. Refineries can accept the waste, if the chloride concentration is below 1 %. That disables wastes from hydrochloric cleaning to re-use. [10, 38, 43]

If off-site treatment in waste treatment plant is chosen, at least in European countries, it is best to favor physical-chemical treatment because its relatively simple operation and affordable price. In most cases, especially in case of pre-operational cleanings, the only treatment needed is physical-chemical process. Nevertheless, there are couple of issues considered. In addition to problems with chelated citric acid wastes, some additives, such as thiourea or degreasing- or inhibitor compounds, may disable the use of this method and force to use more complex treatment techniques. High hydrocarbon content is reflecting increased amounts of hydrocarbon oil and grease, being disadvantageous to the treatment process. Oily waste sludge seems to block physical-chemical plant cleaning channels, while treatment plant specialized on oily waste waters management can not withstand as high heavy metal contents as acid cleaning wastes have. Sufficient level of hydrocarbons is 0,5 mg/l, meaning that higher values may cause blocking for treatment equipment [38]. Still maybe the biggest disadvantage is the challenges with organic wastes, such as citric acid waste. Citric acid is ammoniated prior to use, which leads to high nitrogen content of the solvent. Nitrogen does not precipitate but remains in the water, and especially for the biggest hazardous waste treatment plants there are strict regulatory control and limitations for drainable water. Limitation to physical-chemical treatment is sludge ammonium nitrogen content of 400 mg/l, which is exceeded in most organic acid cleaning solutions [27]. In addition to disadvantageous complexing capacity, hydrogen is then released [38].

Based on the conversations with waste treatment professionals, there seems to be consensus among hazardous waste treatment facilities that waste waters coming from different stages of cleaning process are better to keep separate from each other [11, 14, 22, 27, 38, 43]. Table 10 compares acidic cleaning solution to passivation solution from four different acid cleaning waste waters.

Table 10. *Four acidic solutions compared with their passivation solutions (only the most significant features have been detected). [25].*

		HF solution	**Passivation**	**HF solution**	**Passivation**
pH					
Conductivity	µS/cm				
Solids	mg/l				
BOD 7 ATU	mg/l	150	5500	830	1200
CODCr	mgO2/l	680	8600	3000	1700
Fluoride (F)	mg/l				
Chloride (Cl)	mg/l				
Sulphate (SO4)	mg/l				
Nitrogen (N) total	mg/l	19	2400	<0.10	510
Nitrate (NO3)	mg/l				
Phosphate (PO4)	mg/l				
Ammonium (NH4)	mg/l				
Cyanide (CN) total	mg/l				
Arsenic (As)	mg/l				
Mercury (Hg)	mg/l				
Silver (Ag)	mg/l				
Cadmium (Cd)	mg/l				
Chromium (Cr)	mg/l	4.14	2.98	8.52	0.756
Chromium VI (Cr)	mg/l	<0.05	<0.05	<0.05	<0.05
Copper (Cu)	mg/l	0.045	0.26	0.43	0.04
Lead (Pb)	mg/l	0.028	0.002	0.077	0.001
Molybdeum (Mo)	mg/l	2.8	3.01	8.53	2.91
Nickel (Ni)	mg/l	2.03	2.21	2.23	0.494
Iron (Fe)	mg/l	4600	1800	2000	160
Zinc (Zn)	mg/l				
Tin (Sn)	mg/l				
Cobolt	mg/l				
Antimony	mg/l				
Phosphorous (P)	mg/l				
Hydrocarbon (C10-C21)	mg/l				
Hydrocarbon (C10-C40)	mg/l				

		HF solution	Passivation	HF solution	Passivation
pH		2.5	9.3	2.9	9.3
Conductivity	µS/cm	1200	430	11000	4200
Solids	mg/l		13	<2,0	3,2
BOD 7 ATU	mg/l	33	1300		1300
CODCr	mgO2/l	3700	1700	2800	2000
Fluoride (F)	mg/l	11000	13	10000	24
Chloride (Cl)	mg/l				
Sulphate (SO4)	mg/l	240	<1,0	250	0,87
Nitrogen (N) total	mg/l	110	710	110	750
Nitrate (NO3)	mg/l				
Phosphate (PO4)	mg/l				
Ammonium (NH4)	mg/l	24	830	29	790
Cyanide (CN) total	mg/l	0.058	0.021	<0.020	0.11
Arsenic (As)	mg/l	0.022	0.017	0.027	<0.00010
Mercury (Hg)	mg/l	0.00033	0.00015	0.00027	0.19
Silver (Ag)	mg/l	<0.0020	<0.0020	<0.002	<0.002
Cadmium (Cd)	mg/l	0.0028	0.0035	0.0077	0.0036
Chromium (Cr)	mg/l	2.5	2.4	9	1.2
Chromium VI (Cr)	mg/l		0.16		
Copper (Cu)	mg/l	0.5	0.23	0.54	0.3
Lead (Pb)	mg/l	0.083	0.001	0.0014	0.0021
Molybdeum (Mo)	mg/l	4.2	4.3	8.3	4
Nickel (Ni)	mg/l	2	2.1	3.2	2.1
Iron (Fe)	mg/l	1400	1300	1600	420
Zinc (Zn)	mg/l	1.2	0.23	0.22	0.015
Tin (Sn)	mg/l	0.069	0.055	0.11	0.042
Cobolt	mg/l				
Antimony	mg/l				
Phosphorous (P)	mg/l				
Hydrocarbon (C10-C21)	mg/l	0.13	<0.30	<0.20	0.09
Hydrocarbon (C10-C40)	mg/l	0.46	0.87	0.69	0.12

As the table 10 illustrates, nitrogen and ammonium concentrations as well as pH of passivation solution are higher than in acid cleaning solution. Also, lowered metal concentrations of passivation solution can be seen. Because of complexity of treating ammonia containing waste, but also high metal concentrations the solutions are further treated with different methods. If those wastes are mixed together in plant site, the treatment process becomes more difficult as there are more additives to be removed. In addition to that, treatment facilities hope that it is possible to track all the chemicals adding and stages by which the waste waters have gone through. Accurate chemical composition of the waste solution is easier to define, if the waters are managed to be as separated and simply [27, 38, 45]. Although the amount of nitrogen-containing waste water can be reduced with separation, there are still limitations. As mentioned previously, ammonium nitrogen content of 400 mg/l is the upper limit for physical-chemical treatment, because nitrogen neither precipitate nor evaporate [27]. In most cases, higher concentrations than 400 mg/l must be incinerated if incineration plant is available. If the waste waters are kept separate, only neutralization-passivation waste waters have such a high nitrogen content and the amount of waste to be incinerated will be significantly lowered [27]. In case of organic acid wastes, the whole waste water is neutralized to pasty-like sludge and then incinerated [27]. There are also facilities, whose treatment processes does not cover incineration but the physical-chemical process is modified so that the nitrogenous waste is possible to handle. Still the price is somewhat high. Recently, research is done in Finland to understand, which are those chemical reactions that could enable neuralization-passivation waters precipitation [7, 14, 38].

At least in Finland, all kinds of chemical cleaning waste waters will be accepted to the treatment plant but the price can vary from a few tens of euros to over 1000 €/m^3 [7, 27]. To such a one-time process combined hundreds of waste water cubic meters on-site precipitation for minimizing the amount of waste water is preferred first, but still, there are instances which include waste water transporting straight to the treatment plant without on-site precipitation, because troublesome storing and delay of disposal. [9]

4.3.2 Waste incineration

Incineration is waste water management technique used in off-site processes in hazardous waste treatment plants, that are intended to large waste amounts. In Finland, there are only one treatment company which is using incineration as an outsourcing service. In pre-operational cleaning, it is not profitable for supplier or customer to invest in such equipment, but it is useful to understand the factors affecting the treatment costs of processing plants. Due to cost and availability of incineration plants, the technique can not be automatically seen as a treatment option. [2, 11, 14]

In some industrial fields, smaller incinerators may be used on-site, but large-scale incineration of waste water is always off-site method, in which the waste is burned in conventional evaporators. Incineration is always the last possible alternative in case of other techniques have been found to be unusable. If the precipitate from on-site process or physical-chemical treatment is not good enough for landfilling, it must be stabilized to decrease its solubility and thus avoid incineration. Still, sometimes this is not possible. As previously mentioned, ammonia limit for physical-chemical treatment is 400 mg/l, which is usually exceeded in both alkaline waste from the final treatment stage and in ammoniated citric acid waste [27]. According to treatment company, if the percentage of organic matter is over 17 %, there is no other alternative than incinerate the waste [27]. Nitrogen limits in municipal waste water treatment plants are strict, and sewerage of waste waters from passivation step may be disabled. Nevertheless, according to the leading Swedish boiler chemical cleaning service provider, there are wide experience of sewerage of passivation waters [11]. In Finland, the suitability of passivation waste waters for sewerage should be more accurately investigated. Incineration of water is energy- and cost-intensive alternative to treat wastes, but only small amount of the wastes produced in pre-operational cleanings require such incineration. On the other hand, there are significant differences between the cleaning companies. Some facilities are used to do final treatment of all the citric acid waste by first neutralizing it pastry-like mass and then incinerate it, as others have invested in processing technique which reduces significantly the need of incineration. Investing in research and development seems to become profitable and interesting alternative among treatment companies, because of constantly demanding situation on the market. In general, it is possible to evaluate that the more organic matter the waste has, the more it takes resources to treat it at hazardous waste treatment plant. Moreover, stabilization, which can be done before incineration, is a complex process that would be better to be avoided. [7, 9, 38]

Besides incineration, in some countries located in warm areas on-site evaporation of the waste water may be useful way of reducing water content and volume. Evaporation requires either climate suitable for evaporation or an evaporation tower constructed for that purpose. These type of treatment alternatives are not applicable on large scale in Nordic countries. [27, 38]

4.3.3 Landfilling

Precipitation sludge having high moisture content, can be dried and landfilled into local landfill. The limits for dumps imported to local landfills are constantly tightening, and the sludge is more and more difficult to dump because too high amounts of soluble metals. When planning the waste treatment, local environmental requirements should be considered, because the limits can vary significantly by location and the type of the soil. Dumping, also, requires the temporary storage tank for both neutralizing and the determination of suitability for landfilling. Best choice would be that suitability can be determined already prior to chemical cleaning by simulating the upcoming wastes. By simulating the wastes beforehand, there may be no need for measurement tank. [10, 38, 43]

Solubility is the most important factor when defining the landfill suitability. In Finland, defining the initial state consists of laboratory analysis including total metal concentrations, solubility, TOC, pH and acid neutralization capacity (ACN). The sludge should not contain soluble fluoride. Besides these parameters, the way that the sludge is generated and raw materials used in the cleaning process should be known. After initial state definition, equivalence analyzes are performed. These are focused on the features characteristic for the waste; in case of chemical cleaning wastes, this may include leaching tests for ensure that the solubility of waste is at the low level enough. Limitations for landfilled waste are stated in landfilling regulation set by the Finnish Government 2013 [46]. In Valmet, there are no landfill suitability definitions performed, but leaching tests would tell if the cleaning waste is suitable for landfilling. Still limits for e.g. fluoride concentration may be too strict to be fulfilled even after drying. Third stage of defining the suitability is on-site quality verification at the dumping area for ensure waste acceptability. Landfill suitability of waste produced during hydrofluoric acid cleanings may be the highest, because precipitation of insoluble calcium fluoride. CaF_2 is completely solid powdery substance, which is relatively easy to landfill due to insolubility. [47]

Unlike other alternative sludge management techniques, landfilling may have potential to be commercially viable option for pre-operational boiler cleaning wastes in near future. The first stage in defining the costs of landfill is to determine landfill suitability of the sludge. This is done by local authority, and according to preliminary quotations, the price of landfill suitability specification and statement set by local waste treatment service provider cost approximately 600 € [38]. In case of dumping, there may be requirement that moisture content must be lowered by drying sludge in containers with filter press by some service provider, whose costs are still unknown. Rough estimation of the costs when investing in such on-site equipment is 200 000 €, which is high to be implemented [11]. However, all processes do not require drying. It would be important to contact local waste treatment company and find out, what to consider when planning the dumping of cleaning waste. Profitability of the pre-treatment and the whole dumping process is affected by the type of waste that treatment company wants it in to their site. If there is a requirement for low moisture content, on-site press filters are needed, but sometimes that is not mandatory. Landfill prices in Finland vary from 150 €/m^3 to 300 €/m^3, but there may be possibility to negotiate some discounts for large waste batches [48, 49].

Future prospects of dumping are highly depending on the development of pre-treatment techniques. Disadvantage for treatment technologies in use is, that metals in the final sludge are soluble due to high solubility product constants. When local circumstances changes, e.g. due to fluctuations in pH or weather, the sludge is exposured to moisture and harmful metals will spread to the environment. A potential alternative may be for example boron precipitation, which will be presented more detailed in chapter 4.4.5. The final sludge is then insoluble and may disposed to a conventional landfill. [2, 50]

Consultation of Valmet U.S. water chemistry specialist extended the knowledge of disposal methods used in North America. After metal precipitation, there are no transporting to hazardous waste treatment plants but the sludge is placed in disposal wells, which are always owned and coordinated by external facilities. As earlier introduced, citric acid waste is treated so that all the metals except chromium will precipitate. Practice is to separate the waste anticipated to contain high chromium content in a separate container and transport it to be dewatered and landfilled. Other waters are possible to sewerage. [43]

Although dumping can be profitable alternative or addition to physical-chemical treatment, tightening limits for landfilling may disable chemical cleaning waste dumping totally. Stabilization of soluble substances is the main challenge, and constantly tightening environmental limitations are driving force for developing new techniques for waste stabilization. One potential area of study is stabilization with ash, from which there are no exact research results. D. Dermatas and X. Meng have found out in their study, how heavy metals in contaminated soil would be possible to be stabilized and solidified with fly ash injection. Although the research is attended to contaminated soils, the method could be applicable also to heavy metal contaminated with waste waters [14, 51]. Another two references for ash stabilization are a patent ”Lime and fly ash stabilization of wastewater treatment sludge” and a study handling with methods of wastewater treatment sludge modified by lime, fly ash and loess [52, 53]. The study is from year 2003 and the patent from year 1991, but although researches in the field of ash stabilization have been published after that, specialist for chemical cleaning have not succeed to develop any working solution. That may suggest, that environmental limits are not yet so tight that utilization of fly ash to stabilize the heavy metals present in the waste would be profitable.

Waste ash stabilization is being exploited in Norway, where Langøya derelict mine is designated as a suitable site for the landfill of hazardous wastes. Those wastes are mixed with the liquid consisting of a strong acid mixed with fly ash. In Norway, chemical cleaning wastes from the surrounding area are treated in Langøya, but also imports from other countries are accepted. The original limestone quarry was designated as a suitable site for hazardous waste landfill owing to the characteristics that the rock formation is impermeable throughout the area. The quarry is located at a depth of 80 meters below sea level, and left open after the end of use. Sea water has not been observed to penetrate the site. [54]

Waste waters are possible to inject to the deep well by treatment company. Deep-well injection was a general technique in U.S., but for environmental reasons, today this technique is seldom used at least in Europe. Metals in the liquid waste are more mobile than in the sludges produced by physical-chemical treatment of boiler chemical cleaning wastes, and typically placed in landfills. In addition to environmental issues, there is complexed problems concerning indemnification agreements. Utilities may be liable for mismanagement of wastes by a contractor, and indemnification agreements are available from many contractors to allow the recovery costs caused by damage suits arising from their mismanagement of wastes under contract. Nowadays, such agreements are rarely granted. [9, 10]

4.3.4 Waste reuse or recovery

Cleaning wastes have been utilized for little or no beneficial purposes, which consist mostly of waste reuse for makeup to flue gas desulfurization (FGD) systems, land farming or metal recovery from sludges.

There are studies proposing that organic acids have beneficial purposes as a buffering agents in FGD systems [55, 56]. Due to decreased limestone consumption and increased scrubber flexibility and reliability, sulfur dioxide removal efficiencies can be improved and cost lowered. In 1986, adipic acid, which was used in United States Environmental protection Agency (EPA) studies for investigating the reuse alternatives of chemical cleaning waste, was reported to be already in use in seven utilities, and also, four were considering the use. Utilization of Adipic acid suggested the similar use of chemical cleaning wastes in FGD systems. Laboratory studies sponsored by EPRI evaluated the use of ammoniated citric acid, inhibited hydrochloric acid and some other cleaning solvents for this application. Residual metals precipitated in FGD system and leaching tests on process solids showed no metal species more than limits. On the other hand, ammoniated citric acid increased the extent of sulfur dioxide removal, which may be due to increased lime usage. The process is in use at a number of utility plants, and the negative results were not considered to be of a magnitude which would be sufficient to preclude this technique as a viable waste disposal alternative. Unclear is, how extensive the utilization in Europe is. [44]

Another waste reuse possibility is metal recycling. In pre-operational cleanings, amounts of deposits accrued on the waste water may be fractions of the amounts that have been generated in operational cleaning. Still, in the future the use of smaller amounts may be recoverable. In U.S., there are an example in which the annual savings of metal recycling were about 340 000 € already during years 1990 and 1991, when lime precipitation was used to produce beneficial lime flux, which enhances metal smelting process [44]. The study dealt with boiler operational chemical cleaning, meaning that metal concentrations have probably been considerably larger, but it still gives an indicative idea of how the recovery can be realized.

Land farming or disposal of reusable waste by spreading it on the ground was first used on the 1950's by food processors. Already then wastes could be sprayed over the soil surface and allowed to percolate into the ground. Natural nonclay soils, which allow such percolation to occur at an acceptable rate without ponding or runoff, have a natural capacity for biological assimilation and breakdown of the organics. In case of inorganic components, the wastes are hold by adsorption and ion exchange properties of the soils, which have beneficial effect as a fertilizer. In U.S., also chemical cleaning wastes have treated in this manner. Although there are several cases which ensure that percolation rates and ion exchange capability are both on an acceptable level, there are other comlicated issues to solve. Land farming of wastes requires a thorough evaluation of the potential toxic effect which are caused by bulk and trace constituents, such as arsenic. It should be still noted, that recent experience of that type of utilization in Europe do not exist. Today it is not practically available in Europe, and it must be modified to make it more environmentally acceptable and to get a comprehensive statement by the authorities. [9, 10]

4.3.5 Boron precipitation

One interesting method for metal precipitation is boron compound treatment followed by pH adjustment. The technique is developed and patented by Global Ecoprocess Services (EPSE), Finnish company having expertise of hydrometallurgical and chemical metal separation solutions for industrial- and mining waste producers.

According to EPSE's patent, the metal is brought to insoluble sludge by using a compound including boron and reinforcements and then adjusting pH. Formation of the precipitate requires precipitate agglomerates, which are formed during the former precipitation of the same metal, or an initial agglomerate is possible to bring outside the process. During the pH raise, metals are first precipitated as hydroxides, enabling boron compounds to stick to hydroxides. Based on experiments of the patent, formation of metal borates has been found to be combination of chemistry and hydrometallurgy, and such behavior has not been detected earlier. [38, 50]

The most significant advantage over other sludge treatment techniques is that the sludge generated during the precipitation process is so stable, that re-dissolution from already generated solid final sludge does not occur. The reaction product is highly insoluble, thus enabling it to be placed to conventional landfill instead of final treatment in hazardous waste treatment plant or disposing it to the landfill site intended to hazardous waste. With the method, low metal concentrations are achieved. [50]

According to meetings with waste treatment parties, several waste treatment service providers in Finland have been in contact with EPSE or already use EPSE's services- Still it is unclear, how the method will work in large scale usage. [38, 50]

4.3.6 Advanced techniques

In Finland, and, in other Nordic countries, amount of technologies that are profitable in practice is very limited. Clearly most of waste waters can be treated with physical-chemical treatment or incineration. Dumping is commonly used in U.S., but in Finland, landfilling itself and without any pre-treatment with physical-chemical plant is unusual. Heavy metal limits for landfilling are constantly tightening, meaning that it is not reasonable to try landfilling without any assistance of external treatment facilities. [7 ,11, 13, 14]

Because unprofitability of investment in the on-site treatment equipment of customer's or seller's own, and because the costs caused by hazardous waste transporting are raising, mobile waste processors are being developed by a few service providers. Kierto Ympäristöpalvelut and Lassila & Tikanoja both have their own equipment based on techniques, which are similar to the full-size equipment. So far, there has been no interest to any mobile solution for pre-operational cleanings due to both long performance interval and large single treatment waste amount. Based on discussions, the treating capacity of mobile equipment seems to be sufficient for pre-operational cleaning purposes, and the price might be acceptable. Still, placing mobile treating equipment to the plant site is another challenge. It is stated in The Finnish Waste Regulation, that handling and storage of hazardous waste are permitted only by a licensed processor [57]. Regulations make it time consuming and expensive to apply for a hazardous waste treatment and storing permit. It is still under investigation if it is profitable to take a trial treatment with mobile processor. Instead of boiler manufacturer, mobile processors owned by the cleaner may be an alternative. Preliminary co-operation between the cleaners and waste treatment facilities already exists, but such comprehensive treatment service is not yet on the market. Swedish mobile processor supplier Scanacon has specialized on mobile acid separators, and supplies also consultation of acidic waters treatment. Scanacon is an example of how water treatment process can develop to more on-site process in the future.

In addition to mobile processors, there are a few alternative techniques that are at the stage of development. Mostly such techniques can be viable off-site, but for some of the equipment, the possibility for long-term rental should be investigated. Reverse osmosis is a water purification technique, which is used to make demineralized boiler water by desalinating water. It separates a solute from a solution by forcing the solvent to flow through a membrane, which is in greater pressure than normal osmotic pressure. Size of the solute molecules is about the same than solvent molecules, and the separation process is based on pressure difference across the membrane [58]. High pressure reverse osmosis equipment has been shown to reduce total dissolved solids, heavy metals, organic pollutants and dissolved contaminants from waste waters. Investing in this type of osmotic equipment for treating the waste waters is not yet profitable, but it may become more viable [14]. Carbon filtering is a method of filtering, which uses an activated carbon bed to remove contaminants and impurities. Based on adsorption, carbon filters are most effecting at removing chlorine, volatile organic compounds and some chemicals. For example, removing thiourea with active carbon may be possible alternative, whose viability must be investigated. As mentioned in chapter 3, there are differences in active carbon usage between the cleaning facilities. It is typically used to lower organic content, but still, some do not use activated carbon injection at all. [3, 36]

5. BOILER CLEANING WASTE IN VALMET

In Valmet, principles of boiler chemical cleaning procedure usually follow the guidelines which are recorded in the process design manual. Chemical cleaning manual specifies the rules of the cleaning, which is performed by chosen cleaning authority. After technical specifications of the boiler are known, cleaning procedure and used chemicals are possible to define. In contrast to many other process design manuals, guidelines are not strictly defined for each stage of the operation. Possible waste water treatment alternatives are largely specified by local circumstances. [2]

Chemical cleaning procedure is planned case by case by the cleaner. Even though this study includes accurate suggestions how to enhance the cleaning process and water treatment, it is typically the cleaner who decide how the project proceeds, which are the chemicals to be used and how much these are needed. Finland's main cleaner is recently started co-operation with the consultant, who is specialized to water treatment. Objective for the project is to develop chemical cleaning procedure so, that local possibilities to waste water treatment and available technology are considered already during the planning of the cleaning. The final result might include the entity, in which the cleaner would provide the whole cycle from chemical cleaning to waste water treatment. In this case, investing in an on-site cleaning equipment owned by the cleaner might be viable alternative, meaning that the whole package is sold at a fixed price. [7, 14]

Because of variance in local circumstances, for two same type of waste water the treatment procedure can be different. Therefore, the costs induced by waste water treatment, varies. Although the volume of large scale boiler cleaning waste water may be over 500 m^3 and the cost of both cleaning and waste water treatment is 200 000 – 300 000 €, the impact on total boiler delivery price may not be relatively high. Large scale project for approximately 400 MWth, boiler volume can be 500 m^3 and the cost of the hydrofluoric acid cleaning procedure itself be below 300 000 €. Water treatment cost are still unclear, but the cost of treatment remains few percent of total boiler delivery price. [59]

Instead of total price, certainty of water treatment methods and its costs can increase competitiveness of the offer made by Valmet. There are two alternative possibilities to handle the costs. Sometimes, all the costs induced by waste water treatment are the manufacturer's responsibility, meaning that Valmet must plan, organize and implement waste water treatment. Another alternative, which is a more desirable option for boiler supplier, is that waste treatment and its costs lie with customer, meaning that after cleaning the seller does not have to take part in the future follow-up. However, there are cases in which the responsibility lies with the manufacturer, which does not encourage customer to help and operate cost-effectively [11]. Customer typically do not have any experience of such a water treatment processes and they may not have understood the waste water problem, especially during the once-time pre-operational cleaning, which do not play any role during normal operation. If an estimate of upcoming treatment cost is possible to provide by manufacturer, still being unaware of the extent of the used chemicals or volumes but having information of previous projects, pricing will be easier and more accurate. It also decreases the amount of work when drafting the tender, because less guesswork is needed.

5.1 Factors affecting the amount of costs

Based on the data of waste water compositions and treatment costs finished and currently ongoing cleanings, the purpose of this work is to evaluate cost for each option separately. Knowing the local drainage-, dumping- and other environmental limits, availability of hazardous waste treatment facilities, and circumstances on the plant site combined with composition and volume of waste water produced, the project-specific costs are possible to evaluate. Some factors that have proved to be important in terms of practical relevance are introduced below.

5.1.1 Location

Location of the plant site affects the costs of waste water treatment. Significant differences between West and East countries can be noticed when comparing the limits of drainage and procedures which are performed to dispose solid bottom sludge. While in Finland, the limits for example for dumping off the sludge into the local dump site is so strict that only possible alternative for further processing is transporting the waste to hazardous waste treatment plant, in U.S., dumping or waste reuse can be widely allowed [10, 43]. If power plant is located nearby or at the same plant site with another, bigger industrial process plant, there is possibility to cooperation. For example, most boilers which are built in connection with papermaking industry, are able to take advantage of the water treatment system of paper plant. Concentrations of heavy metals and other impurities in acid cleaning waste waters compared to water produced by industrial production are lower, meaning that the water treatment process is not as vulnerable as the process at municipal waste water treatment plants. E.g. in Rauma, there are various co-operation activities utilized at the plant site of UPM paper mill. A good example of co-operation between the industrial actors is an extensive utilization of paper mill heat production and waste water treatment plant designed for the mill. Waste waters from mill power plant, households and other co-operative companies are all treated at the industrial sewage system built for the paper mill. [60]

5.1.2 Amount of waste water

In some plants, there are shortages for demineralized water production capacity, hampering the choice of waste water treatment options and meaning that the whole cleaning procedure must be done on terms with water consumption. Flushing between the cleaning stages must be avoided, as well as using a high flushing requirement having hydrogen peroxide as a passivation chemical. In that case, citric acid may be the most suitable cleaning solvent because of the lowest water consumption. In hydrofluoric acid and hydrochloric acid cleanings, the total amount of fresh or demineralized water can be up to 12 – 14 boiler volumes, which may become a limiting factor of executing the cleaning [2, 3].

On the contrary to water shortages, in many countries there is sufficiently of water, but amount of waste water transported to treatment is the limiting factor. Distances may be long or treatment at the hazardous waste treatment plant may be expensive. As an example, in Finland, incineration of nitrogenous waste waters may cost up to 1000 €/m^3 [7]. Usually, flushing waters except the first flushing after acid cleaning, are drainable, enabling optimization of costs with planning storage pool layout and number of pools.

Figure 11 shows, how amount of waste water transported to further processing can be minimized in mineral acid cleanings executed in Valmet. In the best choice, flushing and degreasing waters are drained to the same container, which is then emptied. By keeping acid cleaning waters separated from other waste waters, it may be possible to sewerage both degreasing, flushing and passivation waters, which decreases significantly the need for hazardous waste treatment. There still are alternative methods for treating the waste water after neutralization and passivation. As shown on figure 9, some cleaners have used to sewerage the whole waste water amount, even though it consumes more flushing water between acid cleaning and passivation stages. Some others consume less water to rinse and thus do not so proper flushing, leading to dirtier passivation waters, which are not possible to sewerage. Although degreasing, flushing, acid cleaning and passivation are kept separated, existence of hexavalent chromium may disable precipitation. Formation of hexavalent chromium in the cleaning process is slightly complicated reaction, but using e.g. activated carbon or ion exchange techniques, hexavalent chromium may be possible to remove. [13]

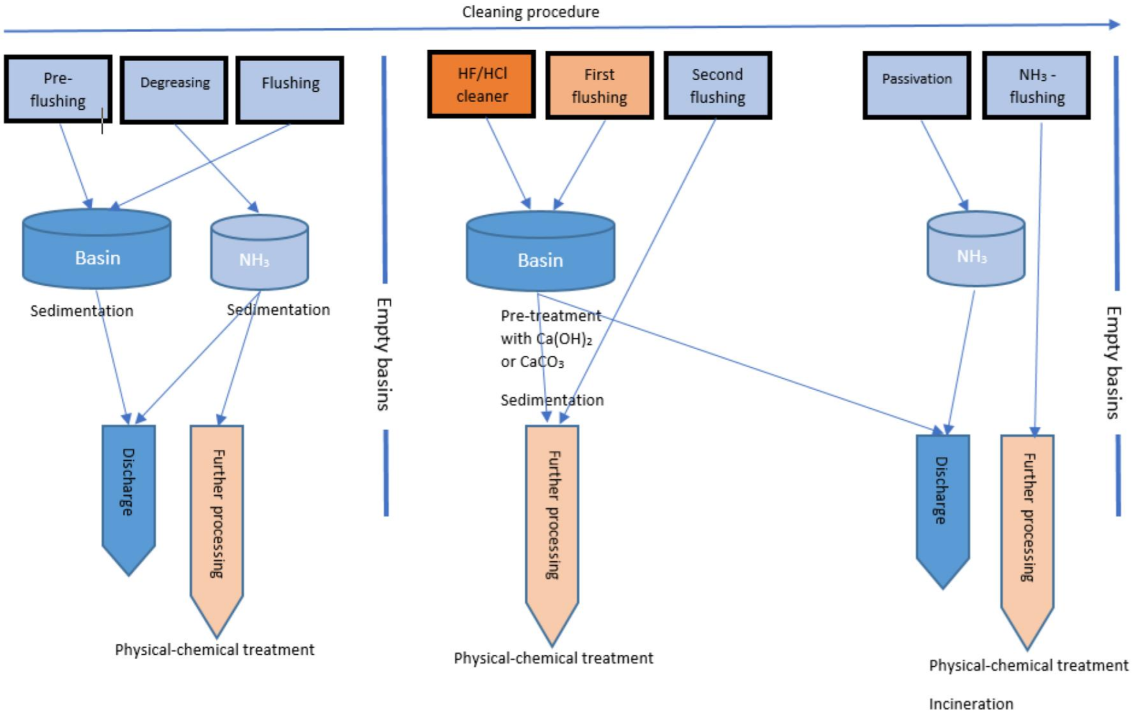

Figure 9. *Wastewater treatment of HF and HCl wastes produced in Valmet cleanings.*

Different alternatives of citric acid waste treatment have been shown on figures 10 and 11. Figure 10 illustrates, how the amount of waste water produced is minimized to 1 – 2 boiler volumes by omitting the flushing between degreasing, acid cleaning and passivation stages [2]. Then, all the waste waters except for pre-flushing water are led to the same basin, and must be transported to hazardous waste treatment plant. Because of high ammonia content, sometimes if physical-chemical treatment is not possible, incineration of the whole water amount at the treatment plant is the only way to treat the waste. As already stated, in Finland it is quite uncertain for the citric acid and ammonia containing waters that these are possible to sewerage. [2, 11]

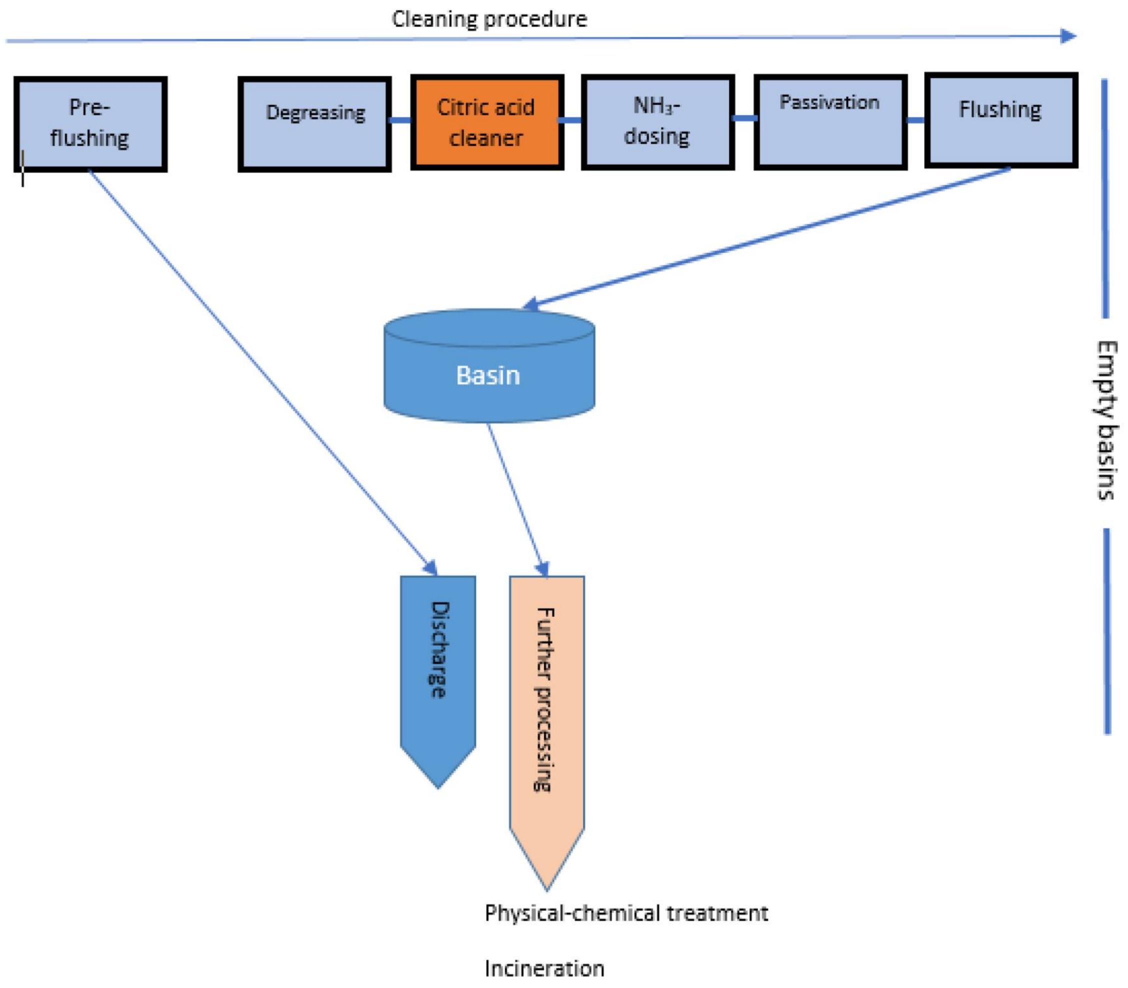

Figure 10. *All citric acid cleaning waste waters are led to the same storage basin.*

The differences between the treatment methods of citric acid and ammonia containing waters are big, and sometimes it may be reasonable to minimize the amount of acidic waste waters. If those waste waters are kept separated from nitrogenous passivation waters, citric acid wastes are possible to treat at physical-chemical treatment plant. It is still complicated to treat high ammonia content having passivation solution, but then the amount of further treatment needing waste water is minimized. Citric acid waste treatment with intermediate draining is shown in figure 11. Method decreases significantly the amount of acidic waste waters but usually, there is not possibility to empty citric acid containing waste waters immediately after the cleaning because of limited capacity at the treatment plant. For enable slower basin emptying, one basin for acidic wastes and another for nitrogenous passivation waters are needed.

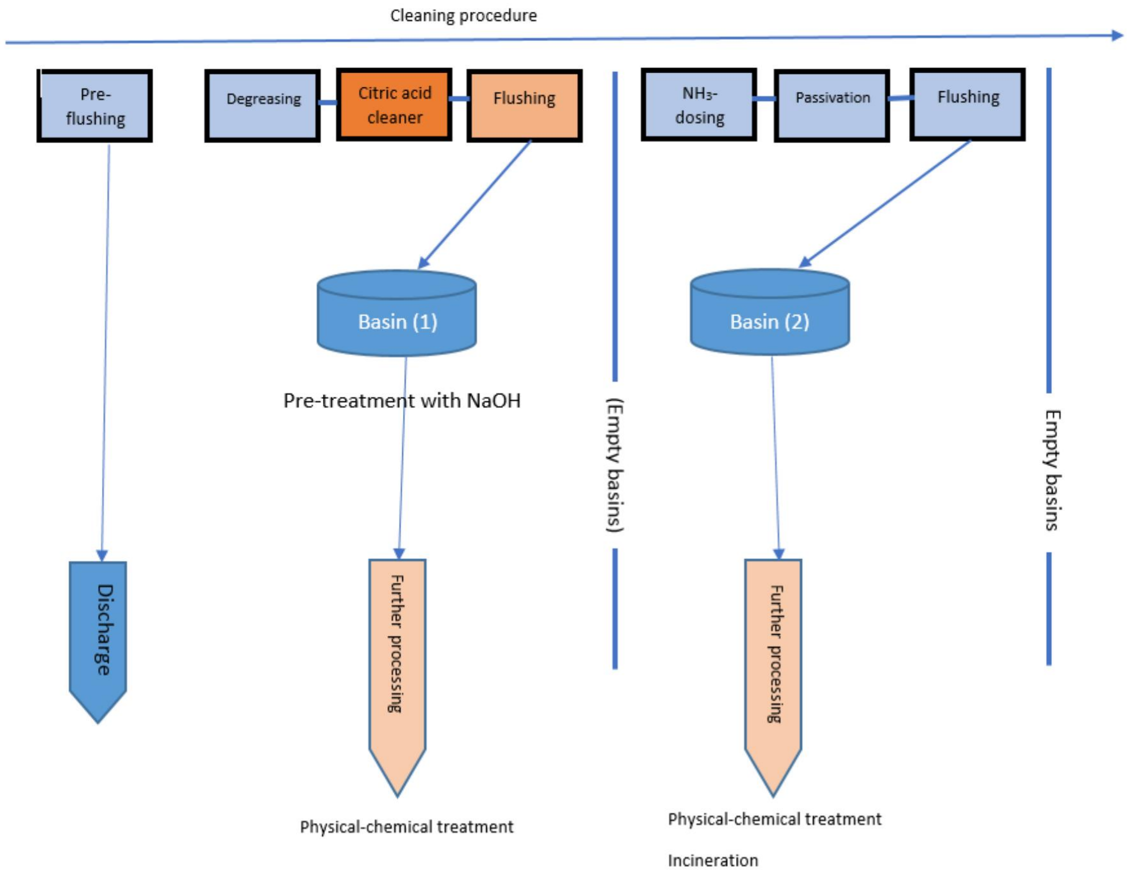

Figure 11. *Intermediate flushing after citric acid cleaning. Draining with two different basins is shown in parenthesis.*

In practice, the decisive factor in optimizing storage solutions is always local limitations. According to main cleaners in Nordic countries, Enerkem Oy and Wistrand AB, the effect of local sewerage limits is the biggest for citric acid waste waters [7, 11, 13]. In Finland, sewerage of citric acid waste waters having all the treatment chemicals in the same solution, is seldom possible if the activity is classified as continuous. One-time pre-operational whole boiler cleanings are not classified as continuous emission sources, which means that it is worth checking local sewerage possibilities first. Although instantaneous limits are exceeded, sewerage may be still allowed. According to the cleaner, one-time sewerage may be possible even despite the metal sewerage limits. What comes to operational cleanings and cleanings of individual parts performed at the factory site, emission source is classified as continuous and sewerage is seldom allowed. [7, 13]

In U.S., limitations for citric acid waste are approximately the same as in Nordic countries. What comes to other EU, the importance of optimize citric acid treatment options may not be currently as big, because usually sewerage is allowed. According to Finnish cleaner, many boiler cleanings in EU are done with citric acid, but on the other hand, another cleaner having wide experience of cleanings in Nordic countries but also around the world, says that nearly all the cleanings executed by them are done with hydrofluoric acid, and experience of citric acid cleanings outside Nordic countries is limited. [7, 11, 13]

5.1.3 Composition of waste water

In addition to amount of waste water, optimization of usage of storage basins greatly affects waste water composition. Nitrogen content of waste water is the most difficult part of acid cleaning waters, if the wastes are treated in hazardous waste treatment plant. Adding ammonia during the neutralization stage causes high nitrogen content, making optimization of waste water separation, which has been introduced in section 5.1.2., important. In addition to separation optimization, chemical choices should be carefully considered. It has been under investigation, if ammonia usage is possible to replace with another additive that raises pH, for instance with sodium hydroxide. The replacement is potential alternative only in case of citric acid, because with adding sodium hydroxide to the mineral acid solution, heavy metals will precipitate already in a boiler, which is not the objective. A recent study shows that ammonia probably has also other functions than only raising pH, but the results are not yet available [14]. Also scope of the cleaning affects composition, as the pipe materials of superheaters must include significant amounts of corrosion and high temperature resistance alloyed metal containing e.g. chromium, nickel and molybdenum. If superheaters are cleaned, waste water contains alloyed metals, which complicates the treatment process. Other boiler pressure parts contain mainly carbon steel, meaning that waste waters contain in addition to iron only traces of heavy metals. A common practice is to clean superheaters already at the factory, facilitating maintaining of good cleaning result and properly rinsing of tube bends, which are difficult to flush and dry when already installed.

High organic content of passivation water is significant difficulty, which may possible be decreased by eliminating citric acid injection during the neutralization-passivation stage. As mentioned in chapter 4, some cleaners have already taken eliminating in use in some of their HF cleanings. If passivation waters are kept separated from acidic waters, eliminating will facilitate the possibility to sewerage passivation waste waters by lowering organic content and especially COD value. Interesting difference between the opinions of main cleaners' is, that another cleaner has not tried to leave citric acid injection off, but they rely on general chemical cleaning standards set by VGB. In this guideline, citric acid injection is compulsory. There also are opinions for higher citric acid dosages that currently are used in Valmet cleanings. However, the beneficial effects of total citric acid elimination to water treatment should be more accurately investigated also in Valmet.

5.1.4 Planning and scheduling

Planning and scheduling of chemical cleaning have proved to be a significant cost-enhancer. Large amounts of waste water are produced within couple of days, which means that it should be prepared for storing of waste water prior to further processing to smoothen large flow rates. For example, Helsinki region environmental services has limited daily amount of cleaning waste water flow to 100 m^3, which means that cleaning waste waters from the boiler with volume of 100 m^3 needs temporary storage pool for from 2 – 3 days to almost two weeks. Another limiting factor is the capacity of the treatment devices in hazardous waste treatment plant, whose limitations of loads are approximately at the same level than in waste water treatment plants. If an advice of upcoming waste delivery is received e.g. less than a week before of days prior to need of service, the plant may have some unfinished treatments going, meaning that the capacity of treatment containers may be in use. Practice has shown, that in large-scale boiler commissioning, there is a risk that scheduling will be overlooked and there is not proper overview of who is the responsible part of the ongoing situation. Proper schedule for cleaning protects from business failures and unconsidered waste treatment solutions. It is possible that all the waters must be transported to hazardous waste treatment plant, just because of there are not any construction plan for container or time to wait until the drainage capacity tests have been done. [1, 7, 61]

Interruptions of information chain between the cleaner, builder and waste processor may pose expensive failures to the cleaning process. In pre-operational cleanings, planning the cleaning process usually follows the same guidelines because there are not any unpredictable accumulated deposits to be cleaned. Thus, the cleaner is able to define the used chemicals early in the process, but still, builder of the boiler may not know all the specifications that the cleaner has done. If incomplete information is transmitted to the municipal water- or hazardous waste treatment plant, consequences may be severe. [2, 7]

At the hazardous waste treatment plant, there are used to treat toxic compounds. They will get the water treated, but the costs will increase, because the optimization of treatment method can not be done as the composition of waste is not known. Instead, in municipal water treatment plants the process is so vulnerable that already the small amounts of nitrification process interfering substances can stop the process. Also, heavy metal concentrations above the boundaries are a major problem, because there are not any ways to remove these from waters. In addition to that, part of the heavy metal residues will accumulate to the treatment plant's residue sludge. The situation is well illustrated by an example from treatment plant in Finland, where the use of thiourea in practice stopped the activity of bacteria in the plant. The failure was a sum of many problems, but the main factor was that the staff of the plant has not been aware of the use of toxic thiourea, even though the cleaner had reported that the staff was informed. Even if the failure was detected immediately, the performance of nitrification process reduced significantly for several hours, because part of the bacterial strain was damaged. [12, 22]

5.2 Exploring the costs

One of the most hampering stage in determining the costs is to define the composition of wastes. Earlier, there has not been many analyses commissioned by Valmet on this purpose, because treatment costs or drainability are defined based on laboratory analysis ordered by external treatment company. In case of waste composition has been found to be permissible e.g. for drainage, the case is finished. If those limits have been exceeded, the waste has been transported straight to hazardous waste treatment plant without further analysis. The main stage for charting the factors affecting the treatment methods and costs was to meet several parties acting with waste water treatment. The parties are listed in table 8.

A representative of Enerkem Oy was first interviewed. Getting in touch to Enerkem’s manager and cleaner, was an important point because usually the cleaner knows best how the cleaning procedure in practice is, and which choices can affect waste management. Usually the further treatment of waste waters is ordered by the cleaner, which knows best which type of waste water the process produces. As a continuous service user, the cleaner may have lower treatment prices than random customer, which affects the contact prices for final treatment. As total volumes of the cleaning wastes produced in Enerkem’s processes is big relatively big, contract price for the cleaner is significantly more affordable than for Valmet. Thus, price information received from Enerkem was valuable and more truthful than possible price for Valmet. [7]

Another representative of the cleaning company to be interviewed was manager and cleaner of Wistrand AB, the most common cleaning party in Denmark and Sweden. Because there are differences in waste treatment procedures and costs between Nordic countries, and of course, between other countries, conversation with the cleaner having experience from all over the world was necessary. Guidelines for pricing between different cleaning facilities were then compared.

After cleaner’s representatives, five waste management parties were interviewed. Two visits headed to municipal waste water treatment plants, Viikinmäki plant owned by Helsinki region environmental services (HSY) and Viinikka plant owned by Tampereen Vesi. Three experts reported their experiences about the factors affecting water drainability, and the most sensitive stages were introduced in more detailed. In addition to that, there are operations and device managers to be interviewed. Acid cleaning waste waters have always been slightly problematic for municipal treatment plants, for which reason the staff of the company was interested to assist in finding additive chemicals that disable sewage.

The other three companies chosen were specialized in waste treatment services, whose expertise and equipment are needed when the cleaning waste water is not drainable. Represented facilities were Fortum Waste Solutions, Kierto environmental services and

Lassila & Tikanoja. The debate was focused on the treatment methods for different types of chemical cleaning sludges and their prices, but possible improvements in Valmet's cleaning procedure and waste management options were also discussed. Fortum Waste Solutions as a main waste treatment company in Finland has comprehensive experience of treating acidic cleaning waste sludges, while Kierto Environmental services is newer treatment service provider. Kierto's processes proved to be smaller-scale but more adaptive and profitable for Valmet, which has led Enerkem to choose Kierto Oy as a most commonly used treatment company.

Lassila & Tikanoja (L&T) was the third waste treatment company to be interviewed. With L&T, there have not been that much co-operation with Valmet, and the operations and processes in L&T were more unknown to Valmet. During the discussions, L&T treatment processes were introduced, and the possibilities of cooperation were considered. During the conversation, it turned out that there is a new technology under development and already in use in some processes. The technique was explained in the section 4. The company which offers the new technology turned out to be EPSE, whose boron precipitation method was tested, if it would be suitable for acidic chemical cleaning wastes. Valmet offered to L&T and EPSE possibility to test the method to citric acid waste generated during superheater cleaning. If cooperation with L&T will be realized and EPSE's technology turns out to be appropriate, L&T may become competitive alternative to Fortum and Kierto Oy being slightly different service provider for Valmet. Although Enerkem has consider using Lassila & Tikanoja as a waste treatment company and couple of waste deliveries have already been, the boron precipitation method is not used earlier and may bring new trends and ideas. [38]

5.3 Sludge treatment offer

Previously, the details for factors affecting cleaning waste water treatment costs are presented. Each of these features are affecting the process and the scope of treating, but when binding contract for waste treatment, all the factors can not be accurately determined; there are some decisive factors for pricing. Finding the contract making policies by discussing with service providers, was an important result of this work, even if the accurate costs was not possible to determine. [2]

Because of one-off process and large scale, it became clear that there is not possibility to define the cost for waste water treatment without specific information of composition of the waste generated. In Kierto Oy, there are two alternative information to be attached to the quotation. By delivering a sample of waste to be imported is the simplest alternative, if the costs are not needed to know beforehand and there are time and possibility to store wastes as long as the cost information is obtained. When the sample has been analyzed, consumption of treatment chemicals is defined by making a test experiment. After that, the company minimizes their own risk and gives the final price for treatment. Another possibility is to give an accurate analysis of the cleaning procedure. This analysis includes used boiler materials and cleaning chemicals with the percentages of chemical content, and volume of waste water generated [39]. It has proved difficult to predict at the boiler's contract stage which type of pre-operational cleaning will be used, and thus accurate definition of costs has not been possible to do. There may be requirements set by the buyer, which cleaning chemical is to be used or which additive chemicals are not allowed to use. Sometimes the requirements are uncommon and even unexpected, making the procedure more complicated. Still, cost evaluations for different alternatives of cleaning procedures can be specified.

Based on this thesis and earlier experience, in EU, especially in Nordic countries, the more accurate view of available cleaning chemicals and the amount of waste water generated can be shaped. Contacting the water treatment specialist having experience of local waste water management procedures already at the contract stage may facilitate launching the chemical cleaning procedure also in practice.

In most cleanings, practicalities related to waste treatment are handled by the cleaner, in Nordic Countries usually Enerkem or Wistrand. On larger scale, the customer chooses if responsibility of waste treatment belongs to customer itself or the builder, and the responsible party will then decide if waste treatment practicalities with the third party (municipal or industrial sewer, or hazardous waste treatment plant) are managed by customer or by the cleaner representative. By customer means, that responsible party finds the treatment company and contacts it directly. As mentioned earlier, because the cleaner usually has continuous contact with the treatment plant the contract prices for them may be lower than for the builder. The advantage of including waste treatment in cleaning contract is that the cleaner can accurate enough describe the composition of waste produced already beforehand, as he has used to do different types of chemical cleanings and based on earlier waste deliveries, the third party knows which type of wastes the cleaner will produce, meaning that the contract for sewerage or hazardous waste treatment may be done in an early stage. Then there is no need for sampling and intermediate storage. If the builder contacts directly to the waste treatment company, samples for waste waters produced must be sent prior to transportation to the treatment plant in order to define waste composition and then used treatment chemicals and treatment costs. When waste water sample has taken, the waste must be stored until the treatment permit comes and the contract is possible to do. Storing at the large plant site may be difficult and containers are expensive. Rental storage container for large amount of waste, 3000 m^3, can cost approximately 10 000 € if rented for storage for couple of days, forcing operators minimize the storing time. In the Nordic countries, laboratory analysis result can be possible to expedite to be completed within a day, but most of the Europe this may take 3 – 5 days [11]. In some plant sites, storage is prohibited and then the only alternative is to try to reach consensus on the price of treatment without customer side storage. [7, 11, 13, 14, 38, 39]

5.4 Cleaning and water treatment procedure

There are several proposals for re-considering common practices in the cleaning procedure. One of the most prominent consensus is, that on the waste water treatment point of view, the waste waters from acid cleaning stage and neutralization-passivation stage are better to keep separated from each other. Still, the final decision is set by the cleaner and nowadays in many Valmet cleanings, the waters are not kept separated. [1, 2, 7, 11]

Characteristic for the cleanings executed by Valmet are, that locations and scope of the procedure may vary significantly. Some of the cleaning projects may include only superheater cleaning which is done within one or two days at the factory, but typically chemical cleaning covers the whole boiler. Newly executed CYMIC boiler cleaning covers pre-operational hydrofluoric acid treatment of the whole boiler including also superheaters. Volume of the parts to be cleaned was 500 m^3, while the amount of waste water approximately 3000 m^3. Waste water management implemented in this project reflects the most typical way of operation and is thus a good example. Cleaner Enerkem set three pieces of tarpaulins in the bottom of three precipitation pools constructed by Valmet, after which the whole waste water let set for two days until precipitation of metal hydroxides has occurred. Disposal of metal sludge was the cleaner's responsibility and the price was the cleaner's contract price with one of the Finnish main treatment company, being somewhat under 300 000 €. As usual, surface water was allowed to sewer to municipal sewer system [59].

Figure 12*. Chemical cleaning of Valmet’s superheater executed by Enerkem Oy.*

From waste water treatment point of view, four different situations in the waste water are possible to recognize. The first split is done based on location; the treatment may be done in Nordic countries or U.S., or alternatively somewhere else, for example in other part of the Europe. The second division is made on the basis of the scope of cleaning. As seen in figures 12 and 13, small-scale off-site cleaning is possible to do also inside. Cleaning equipment needs little space, and storage of waste can usually be executed with 1 m^3 plastic container. The rough division is illustrated in table 11.

Table 11. *Different types of waste treatment situations in pre-operational cleaning.*

Located in Nordic countries or U.S.	**Located outside Nordic countries or in U.S.**
- Besides citric acid and EDTA, mineral acids (HF/HCl) are often used - Sewerage limits are respected - Citric acid wastes are not possible to sewer → acidic waters are better to keep separated from nitrogenous waters - Hazardous waste treatment costs are relatively easy to define based earlier experience	- Citric acid is the chemical most commonly used - Despite sewerage limits, citric acid waste waters are practically always drainable - Heavy metal sludge disposal alternatives vary by location and those must be accurately clarified during the boiler commissioning - Sufficiency and quality of the clean water must ensure
One-time cleaning of the whole boiler executed at the plant site	**Partial cleaning placed at the factory site**
- The cleaning is counted as one-off process → industrial water sewerage contract is not needed - Looser sewerage limits for one-time process possible sewerage of citric acid waste waters also in Nordic countries and probably in U.S. - Because of large amount of waste water, alternatives for final disposal of heavy metal sludge must be investigated early in the project	- Partial cleanings at the factory are classified as continuous process → strict limits for sewerage - Despite smaller amount of waste water, citric acid waste is seldom drainable - Waste water amounts are relatively small, from a few cubic meters to a few dozen m^3 - Waste waters from superheater and evaporator cleanings contain higher concentrations of heavy metals

Figure 13. *Chemical mixing pool.*

5.5 Sampling and waste water characterization

In most of the cases, municipal waste water treatment plants do not pay additional charge for chemical acid cleaning wastes, meaning that acid cleaning waters practically always fall under the normal waste water charge. Instead, other industrial waste treatment services will charge the price based on waste quality and quantity. Both excursions and interviews were good ways to get access to professionals, and through that, the treatment costs. However, an importance of the composition analyses in pricing revealed already in the early stage of discussions with water treatment specialists. As a result of the consultations, more accurate information of needed laboratory analyzes were given, as the effects of different waste water constituents for the processes of both municipal waste water treatment plant and hazardous waste treatment plant process were explained. Due to the lack of analysis of waste composition, it was decided to make new measurement data for small scale acid cleanings suitable for the situation, by incorporating the most significant waste water features into the analyzes. After the measurements, more accurate evaluation of pricing and treatment methods were possible. Data collecting will continue after the thesis work to get also waste waters from whole boiler pre-operational cleanings analyzed. Especially citric acid waste analyses will be important.

During this work, waste water properties to be analyzed are standardized. If any part of analysis is considered useless it can be omitted in the future. Still the sampling stages must be remained the same. First two analyzes which are executed during the work, are both small scale citric acid cleanings executed by Enerkem. For citric acid cleanings, the samples were taken from two different stages; first one from the end of acid circulation stage prior to dosage of neutralization and passivation chemicals, and the second at the end of the treatment from neutralized solution before sewage waters to sewer. First case to be sampled was superheater cleaning at Lahdesjärvi factory in March 2018, producing approximately 3 m^3 amount of waste water. Material of the inner tubes was mostly stainless carbon steel, which means that the waste waters are consistent for the most part with whole boiler cleanings. As mentioned, two samples were sent to the laboratory Eurofins to be analyzed, but there were also Fortum who took the sample from neutralized water. Fortum was intended to sample and make experiments for possible treating methods which may replace incineration. In Lahdesjärvi project, waste waters were not let to cleaner's responsibility, but Valmet contracted waste water treatment services itself. This made it possible to co-operate with Lassila & Tikanoja and let them try EPSE method for treating the waters. Another analysis package to be taken was recovery boiler power upgrading service project delivered by Valmet. In that project, conventional boiler wall tubes were cleaned, meaning that composition of waste waters coming from this small-scale cleaning responds very well to the real whole boiler cleaning.

6. RESULTS AND DISCUSSIONS

As mentioned, the composition of cleaning waste proved to be an important factor affecting the treatment costs. It is possible to make a rough estimation of the composition prior to cleaning, if earlier analysis data from different types of cleanings are available. In this section, previously collected results are presented together with the composition data collected during this thesis work.

6.1 Composition of waste water

Compositions of waste waters from whole boiler pre-operational cleanings are collected in appendix A. Four different hydrofluoric acid chemical cleaning cases in Europe may be seen. All four cleanings are commissioned by Valmet using Enerkem as a cleaner. For comparison, composition data from Wistrand's HF cleanings gathered during the work are presented in appendix A. Waste water compositions from small scale cleanings executed in Finland are seen in appendix B. On the basis of previous chemical cleanings and discussions, an indicative table of waste water compositions was made. As precise estimation of waste water treatment costs can seldom give, an indicative summary of water compositions may help planning the waste water treatment methods. The default is, that all waste water is drained to one container.

Table 12. *Estimate of waste water composition from HF cleanings.*

HF				
		Unprocessed	**Surface water**	**Bottom sludge**
pH		9 - 10	9 - 10	9 - 10
Conductivity	µS/cm	3000 - 4000	50 - 500	not relevant
Solids	mg/l	< 50	< 10	50 - 5000
BOD 7 ATU	mg/l	1000 - 4000	< 300	not relevant
COD Cr	mgO2/l	1000 - 4000	< 300	not relevant
Fluoride (F)	mg/l	< 10	< 10	< 200
Chloride (Cl)	mg/l	< 10	< 10	< 10
Sulphate (SO4)	mg/l	50 - 300	50 - 300	50 - 100
Nitrogen (N) total	mg/l	500 - 4000	500 - 4000	not relevant
Ammonium (NH4)	mg/l	500 - 1000	500 - 1000	not relevant
Phosphorous (P)	mg/l	< 1	< 1	< 1
Cyanide (CN) total	mg/l	< 0.5	< 0.5	< 0.5
Arsenic (As)	mg/l	<0.05	<0.05	< 0.6
Mercury (Hg)	mg/l	< 0.2	< 0.2	< 0.2
Silver (Ag)	mg/l	< 0.005	< 0.005	< 0.005
Cadmium (Cd)	mg/l	< 0.005	< 0.005	< 0.005
Chromium (Cr)	mg/l	0.5 - 4	< 0.005	20 - 70
Chromium VI (Cr)	mg/l	< 0.2	< 0.2	< 1.5
Copper (Cu)	mg/l	< 1	< 3	< 6
Lead (Pb)	mg/l	< 0.05	< 0.005	< 0.05
Molybdeum (Mo)	mg/l	2 - 5		
Nickel (Ni)	mg/l	0.2 - 3	< 0.05	< 25
Iron (Fe)	mg/l	100 - 5000	< 1	< 15000
Zinc (Zn)	mg/l	< 0.03	< 0.005	< 3
Tin (Sn)	mg/l	< 0.1	< 0.005	< 0.1
Cobolt	mg/l	< 0.01	< 0.001	< 0.01
Hydrocarbon oils (C10-C21)	mg/l	< 0.5	< 0.5	< 0.5
Hydrocarbon oils (C10-C40)	mg/l	< 1.0	< 1.0	< 1.0

***Table 13.** Estimate of waste water composition from CA cleanings.*

CA		Unprocessed
pH		8 - 9
Conductivity	µS/cm	1500 - 3000
Solids	mg/l	20 - 100
BOD 7 ATU	mg/l	10000 - 20000
COD Cr	mgO2/l	20000-30000
Fluoride (F)	mg/l	0.2 - 1
Chloride (Cl)	mg/l	< 0.5
Sulphate (SO4)	mg/l	10 - 20
Nitrogen (N) total	mg/l	4000 - 8000
Ammonium (NH4)	mg/l	5000 - 7000
Phosphorous (P)	mg/l	0.1 - 1
Cyanide (CN) total	mg/l	< 0.2
Arsenic (As)	mg/l	< 0.1
Mercury (Hg)	mg/l	< 0.0005
Silver (Ag)	mg/l	< 0.005
Cadmium (Cd)	mg/l	< 0.05
Chromium (Cr)	mg/l	0.5 - 4
Chromium VI (Cr)	mg/l	< 1.5
Copper (Cu)	mg/l	< 0.2
Lead (Pb)	mg/l	< 0.005
Molybdeum (Mo)	mg/l	0.2 - 4
Nickel (Ni)	mg/l	0.5 - 1.5
Iron (Fe)	mg/l	< 2000
Zinc (Zn)	mg/l	0.1 - 0.5
Tin (Sn)	mg/l	< 0.1
Cobolt	mg/l	< 0.1
Hydrocarbon oils (C10-C21)	mg/l	< 0.2
Hydrocarbon oils (C10-C40)	mg/l	< 0.5

Table 14. *Estimate of waste water composition from HCl cleanings.*

HCl		**Unprocessed**	**Surface water**	**Bottom sludge**
pH		9 - 10	9 - 10	9 - 10
Conductivity	µS/cm	3000 - 4000	50 - 500	not relevant
Solids	mg/l	< 50	< 10	50 - 5000
BOD 7 ATU	mg/l	1000 - 4000	< 300	not relevant
COD Cr	mgO2/l	1000 - 4000	< 300	not relevant
Fluoride (F)	mg/l	< 10	< 1	< 10
Chloride (Cl)	mg/l	20000 - 30000	< 1000	not relevant
Sulphate (SO4)	mg/l	50 - 300	50 - 300	50 - 100
Nitrogen (N) total	mg/l	500 - 4000	500 - 4000	not relevant
Ammonium (NH4)	mg/l	500 - 1000	500 - 1000	not relevant
Phosphorous (P)	mg/l	< 1	< 1	< 1
Cyanide (CN) total	mg/l	< 0.5	< 0.5	< 0.5
Arsenic (As)	mg/l	<0.05	<0.05	< 0.6
Mercury (Hg)	mg/l	< 0.2	< 0.2	< 0.2
Silver (Ag)	mg/l	< 0.005	< 0.005	< 0.005
Cadmium (Cd)	mg/l	< 0.005	< 0.005	< 0.005
Chromium (Cr)	mg/l	0.5 - 4	< 0.005	20 - 70
Chromium VI (Cr)	mg/l	< 0.2	< 0.2	< 1.5
Copper (Cu)	mg/l	< 1	< 3	< 6
Lead (Pb)	mg/l	< 0.05	< 0.005	< 0.05
Molybdeum (Mo)	mg/l	2 - 5	2 - 8	< 1
Nickel (Ni)	mg/l	0.2 - 3	< 0.05	< 25
Iron (Fe)	mg/l	100 - 5000	< 1	< 15000
Zinc (Zn)	mg/l	< 0.03	< 0.005	< 3
Tin (Sn)	mg/l	< 0.1	< 0.005	< 0.1
Cobolt	mg/l	< 0.01	< 0.001	< 0.01
Hydrocarbon oils (C10-C21)	mg/l	< 0.5	< 0.5	< 0.5
Hydrocarbon oils (C10-C40)	mg/l	< 1.0	< 1.0	< 1.0

6.2 Analysis based on compositions

As seen in appendix A, precipitation of neutralized hydrofluoric acid solution makes surface water drainable. In both the precipitation cases, B and E, sewerage limitations are met for almost all the substances. Especially levels for nickel, total chromium, copper and molybdenum must be carefully checked. In case E, large amount of waste water forced to build five different precipitation pools which all were sampled. It is easy to notice that the customer had responsibility for the storage of waters, and Valmet had not accurate knowing, which type of waste waters have been led to each storage pool. Local remarkably high values can be seen in each analysis, and water compositions of different pools differs from each other significantly. Especially fluoride content, and through that also conductivity, varies greatly. In the future measurements, mixing must be ensured and if there are several precipitation pools, the order of fulfilling and time should be marked up. In addition to that, future sampling should be unified by taking the same batch of analyzes each time.

As mentioned in earlier sections, another finding is, that neither sewage point of view nor hazardous waste point of view, it is not useful to only neutralize the water without precipitating it. Neutralized waste water is not good enough sewage but still levels of organic constituents are elevated causing problems in hazardous waste treatment process. If sewage treatment plant of the factory is available, only neutralizing may be a useful alternative as the sewage treatment process is sufficiently effective.

When comparing waste waters from the cleanings executed by two main cleaner's waste water compositions, significant differences between passivation waters can be seen. One method produces water in which both nickel, molybdenum and chromium concentrations are much above the sewerage limits, while another cleaner's waters, using their way of processing the waters, are drainable. Conductivities for these drainable waste waters are considerably lower not being more than 100 µS/cm, while passivation waters produced by the other varies between 400 – 500 µS/cm to 4000 µS/cm. Another noticeable detail is degreasing waters, which are only left for settlement in the basin and disposed to sewer. No dissolved metals are foreseen, and degreasing waters are drainable. Furthermore, degreasing water may include heavy oil fractions and hydrocarbon oils, and by mixing them with acidic-, neutralized or passivated waters may result in complex mixture of different types of additive chemicals.

As mentioned earlier, EPRI has compiled 12 different types of chemical cleaning waste compositions in U.S. published in chemical cleaning manual [9]. Although results are old and for operational cleanings only, comparison between different cleaning chemicals is possible to do. Also, the features which are problematic nowadays, have remained the same. Significantly elevated values for nickel, copper, silica, chloride and total dissolved solids can be noticed, but concentrations for copper and silica are highly case dependent and are not comparable to pre-operational cleanings. In addition to these, there are two waste streams which have hexavalent chromium concentrations of 2.6 mg/l and 3.0 mg/l. Any neutralization or precipitation have not been done for wastes in EPRI's publication, but such values can not be allowed anymore, because hexavalent chromium tends disturb the precipitation reaction of mineral acid waste. Another difference between Valmet and EPRI waste is amount of nickel in citric acid wastes. In most EPRI's cases, nickel content exceeds the sewerage limits, but despite that the waste is still sewer or drained in the surrounding nature. Nickel amounts of EPRI's citric acid wastes were even 13 mg/l, being remarkably high for any type of sewerage.

In addition to EPRI, also VGB PowerTech e.V. has published a compilation of waste water analyses for several chemical cleanings. Other than metal concentrations are measured, and it can be noticed in table 3, that e.g. COD values are significantly lower than in EPRI's compilation or Valmet's cleanings. That is probably because of activated carbon injection, which is performed for neither EPRI's nor Valmet's cases.

6.3 Small-scale cleanings

There are totally three small-scale cleanings to be analyzed. Alloyed metals present in superheaters makes cases J and K to produce slightly different waste waters, as metals have been dissolved more. In superheaters analyzed, chromium and molybdenum were the metals alloyed with carbon steel. Chromium concentrations of 3.2 mg/l and molybdenum 3.7 mg/l exceeds multiple times the sewage limits in Finland. Although there is not any sewerage limit for molybdenum presented by municipal waste water treatment plants in Finland, based on limitations in waste landfilling, it can be evaluated molybdenum to have largely the same restrictions than chromium. If the limit of 1.0 mg/l is obtained, both chromium and molybdenum concentrations in waste waters are exceeded over three times. On the other hand, those concentrations differ only a little from those in whole boiler cleanings. From this, it may be concluded that there is not much difference between slightly alloyed metal cleaning and carbon steel cleaning.

Increased metal concentrations are the only feature which is caused by the scope of cleaning. Still, another factor that has strong effect on waste water composition is the type of solvent. All three small-scale cleanings were done with citric acid, which has details that make waste waters easy to be recognized. As an organic chelate, organic content of citric acid waste water differs from mineral acid wastes significantly. When comparing BOD and COD values, over 10 000 mg/l for BOD and 20 000 mg/l for COD are achieved. For neutralized and passivated HF wastes, BOD values vary from lower than 100 mg/l (case E) to 3400 mg/l (case A). Such values can easily disable water sewerage. In addition to absolute numbers, BOD/COD fraction is followed. According to the instructions set by Swedish Nature Conservation Office, BOD/COD-fraction lower than 0.43 indicates wastes poor degradation causing possible difficulties for treatment process. Neither BOD nor COD analysis were taken in Wistrand's analyses, reflecting that those are not seen as ones of the most important values.

It is possible to notice high organic content of citric acid wastes through an elevated value of total nitrogen content. Nitrogen content of neutralized and passivated HF wastes varies approximately between 100 mg/l and 600 mg/l, while in case of CA waste analyzed contents are 4000 mg/l and 6000 mg/l.

Conductivities for small-scale citric acid cleanings are around 2000 µS/cm, which is approximately at the same level than in neutralized and passivated hydrofluoric acid waste water.

6.4 Cost caused by waste water disposal

In this chapter, waste water treatment costs have been evaluated for a common sized boiler of 150 m^3 having pre-operational cleaning with most common cleaning chemicals in Finland; citric acid, hydrofluoric acid or hydrochloric acid. Sludge disposal practices vary significantly between the countries, but in this section only the methods having large-scale use are noticed. Such techniques are physical-chemical treatment and incineration. In addition to waste water treatment, there is base price for chemical cleaning defined case-by-case and set by the cleaner. As an example, cleaner's base price includes cleaning chemicals, planning prior to cleaning, labor costs, equipment, and also installation of the circulation piping. In case of delays for reasons beyond the cleaner, additional costs may be charged according to the separate price list.

6.4.1 Neutralization combined with drainage

Today, drainage is possible only for organic acids. Costs induced by neutralization and drainage are lower than other treatment techniques. Most often used way of citric acid cleaning is cleaning without draining between the stages, but still there are also other practices. Amount of waste water, which needs treatment is 1.75 – 4 boiler volumes, depending on number of intermediate drains. If all the chemicals are dosed to the same solution, the amount of waste water may be only 1.75 boiler volumes producing approximately 260 m^3 waste water. If degreasing and acid cleaning are carried out in the same solution but neutralization and passivation chemicals are dosed after intermediate drain, amount of waste water may increase to 4 boiler volumes, producing 600 m^3 waste water.

Neutralization of citric acid waste to pH 8.5 – 9.0 is usually performed with 18 % or 25 % ammonia water. 25 % ammonia consumption for 150 m^3 boiler with intermediate drain is 400 kg. Amount of neutralization chemical needed are affected on the chosen cleaning procedure: in case of drained piping, ammonia is needed less than in case that there is no intermediate drain, because then the circulating and acidic piping waste water has significantly low pH. However, neutralization is included in delivery by default and price for both the performance and chemicals are included in the cleaning offer.

Small-scale cleanings having waste water amount of 5 – 50 m^3, may be possible to drain without intermediate storage. Then neutralizing chemical is dosed straight to the outlet pipe. For larger water amounts, rental storage pool or on-site terraced tray covered with rental tarpaulins must be used. According to the cleaner, at least three workers are needed to terrace and spread the tarpaulins, meaning that if each man-hour cost is 50 – 100 € the total cost of building the pool may be a few hundreds of euros. Price of each new tarpaulin is 4000 – 6000 €, but in most cases, those are reusable. Usually the whole costs induced by storage pool construction are included in the offer. In Sweden, the rental price of container for 3000 m^3 waste water may be 10 000 €. Because of limited capacity of treatment plants, such a high amount of waste water may need storage for couple of weeks. [11]

As mentioned earlier, neutralization combined with drainage is the most profitable alternative. In Finland and other Nordic countries, waste water in which sewerage limitations are met, belongs to normal sewerage fee. In Finland, the fee varies slightly between the regions. For Helsinki region environmental services (HSY), the fee was 1.39 €/m^3 and for Tampereen Vesi 1.66 €/m^3 in year 2017. Swedish average charge is 1.40 €/m^3, while in United Kingdom and United States differences in charges between the states are bigger, having rough averages of 2.58 €/m^3 and 1.91 €/m^3. [12, 33, 35]; [17, 18] In Helsinki region, total price for sewerage is then 360 – 580 €.

6.4.2 Storage and precipitation combined with drainage

Most often used waste water treatment technique for mineral acidic waste waters is storage and heavy metal precipitation followed by surface water drainage. Treatment costs consist mainly of neutralization chemical, construction or rental of precipitation pool, surface water draining and the bottom sludge disposal. In case of mineral acid, flushing may be done between degreasing, acid cleaning and neutralization-passivation stages. Compared to neutralization and drainage without intermediate flushing, the amount of waste water increases from 1.75 – 4 to 5 – 6 boiler volumes, meaning total volume of 900 m^3.

After the cleaning procedure, waters are lead to the storage- or precipitation containers, which are also used as an intermediate storage of drainable water. Amount of waste water in mineral acid case is bigger than citric acid case, which means that the customer must construct or rent several containers. For 150 m^3 boiler, neutralization of mineral acid waste water requires e.g. 1500 kg of 48 % natrium hydroxide and 2900 kg lime.

Degreasing waters are possible to let settle separately, because after a settling of few hours those are drainable [11]. As figure 11 shows, if also nitrogenous passivation waters are kept separated from acid cleaning waters, the amount of the waste water transported to hazardous waste treatment plant decreases and incineration of the bottom sludge is avoided. Decreasing of hazardous waste is possible, as by separation, the combination of both nitrogen- and metal-containing waste water is avoided. Depending on case separately kept passivation waters may be seweraged or transported to hazardous waste treatment plant, in which high nitrogen content will complicate the treatment process. In case of all the waters are led to the same precipitation container, the volume of bottom sludge requiring final treatment is approximately 90 m^3. Still, price is dependent on the shape of bottom of the basin; narrow basin will produce less bottom sludge to be further treated. The most used method for sludge disposal is treatment in physical-chemical treatment, but if there are no means for treat the waste physical-chemically, incineration may be the case in some bigger treatment plants. If nitrogenous passivation waters are kept separated, produced waste water probably is possible to treat fairly easily with no extra effort. High nitrogen content may disable the use of physical-chemical treatment, and what is more, separated passivation waters may be drainable.

Introduced already earlier sections, there are three alternative sludge final treatment providers. Valmet has experience of both Fortum, Kierto and Lassila & Tikanoja services, but today for economic reasons, Kierto's services are the most used in Valmet.

Hydrofluoric acid sludge disposal costs are somewhat unclear, but company A's price is approximately 300 €/ m^3. For 90 m^3, treatment cost of 27 000 € is obtained. According to experience of cleaners, the most expensive disposal prices in Nordic countries are in Finland. In Denmark, price for hydrofluoric acid treatment is approximately 200 €/m^3. Disposal prices separately for different disposal facilities in Sweden are not accurately known, but these vary from 50 – 100 €/ m^3. In Norway, waste transporting to other countries is more profitable than inland treatment. [7, 11, 13]

For chemicals, which are less commonly used in pre-operational cleanings, A's prices are for hydrochloric acid 320 €/m^3 (2017) and for nitric acid/hydrofluoric acid mixture 900 €/m^3. For EDTA, there has not been earlier experience in European countries and if interest for EDTA cleanings increases, treatment options must be investigated. Transportation costs will be more accurately specified in chapter 7.3. [11, 13, 27, 39]

There has been recently a lot of research and development work with respect to precipitation of citric acid waste water. Until this day, only experimental tests exist and solutions in practice are not yet available for purchase.

6.4.3 Final treatment of sludge

There are two different types of waste water streams, which are transported straight to the hazardous waste treatment plant without on-site pre-treatment; mineral acidic waste waters which volumes are so low that on-site precipitation is not worth executing, e.g. superheater cleanings executed at the factory, and citric acid wastes which are neither precipitated nor drained.

Differences between the prices of waste treatment facilities can be seen. A's contract price (2017) to cleaner for citric acid cleaning is 230 – 240 €/m^3, while B's price is 200 – 290 €/m^3 and C's 800 €/m^3. For amount of 260 m^3, total price varies from 50 000 € to 75 000 €. [11, 13, 27, 39]

Acid-proof tank truck is needed to transport waste waters. In case of precipitated sludge, the amount of waste to be transported is lower than if no precipitation is performed, and then the waste has had time to cool down prior to loading it to the vehicle. If citric acid waste water is led straight to the truck, also heat-resistant transportation container is required. Although B’s treatment price for citric acid waste may be lower than A’s, there are transportation costs which may make B the most affordable option. According to the realized costs, B’s transportation fee is 67 – 124 €/t depending on the distance. In A, there are vacuum truck, whose total transportation costs consist of the charge of truck 125 €/h according to working hours plus an assistant fee of 55 €/h and 2,5 €/km transportation fee. For small-scale superheater cleaning having waste water amount of 17 m^3 and transportation inside Tampere, total transportation costs were 100 – 1500 € of the total 5300 €. At the fees of A, transportation within the same city covers almost one third of total treatment costs. [7, 11, 13, 27, 39]

7. FUTURE PROSPECTS

Currently, the most predominant topic for research is behavior of citric acid and properties of the chelates, which are formed during citric acid cleaning. Understanding the chemistry behind the precipitation of the cleaning solutions, treatment techniques are possible to develop. Investigation is done by couple of parties, but the results obtained are not public. Although Valmet's main target is not to develop new waste treatment techniques, it is important to stay involved in development and consider developing the process based on the results. Small scale pilots are worth of commissioning. For example, one possible experiment may be testing the method for citric waste water precipitation used in U.S.

7.1 Technology

Alternative methods for heavy metal precipitation from mineral acid sludge are being developed. Besides patent for boron precipitation, there are some patented methods and researches for treating metal sludges from acid cleaning without dumping or exporting these to a hazardous waste treatment plant. An article relating treatment of chemical cleaning sludge by first neutralize it with calcium hydroxide followed by high temperature treatment and then reduce sludge to metal alloy with coke, has been published [62]. Another patent issued in U.S. is introducing method for cleaning sludge treatment, in which the waste is neutralized and then evaporated enabling metal salts to dissolve at temperature of ~500 °C [63]. Still, only a small fraction of developed methods has been found to be viable. [3, 43, 44]

Waste water treatment plants which are constructed for the needs of industrial production factories, typically have been designed to stand high concentrations of heavy metals and organic compounds. In addition to municipal and third-party plants, another alternative to chemical cleaning water treatment is co-operation with local industrial factory, which means utilization of factory treatment process also with acid cleaning waters. There has already been some experience for co-operation in Valmet projects, but it has limited to the plants which are located on the same plant site each other. It would be worth exploring if the transportation of waste water to the nearest co-operative industrial factory is viable alternative. Like in many other cases, permits for authority must be first checked.

One difference between the disposal methods in EU and e.g. U.S. and Asia are landfill practices. Statement of dried waste landfill capacity should be investigated and opinions of landfill facilities enquired. Prior to projecting the investigation, it might be best to contact with the cleaner and try to find locally the best practice. In U.S, for example, sludge dumping is common practice having significant treatment cost-lowering effect. Even though there are several issues to be clarified, possibility to achieve savings makes landfilling worth of research also in Finland. New techniques, such as method for treating the sludge to an insoluble form, may facilitate landfilling to fulfill environmental requirements.

Instead of introducing new waste water treatment solutions by the supplier of boiler delivery, the development seems to go in the direction of aligning the chain of the cleaning delivery. Such development project presented in chapter 5, in which the cleaner company together with water treatment expert, will develop the entity of services covering both the cleaning procedure and waste water disposal at a fixed price. If successful, the process becomes more effective as the number of middlemen decreases, as cleaner can utilize the knowledge of composition of waste water and both local available technology and sewerage limitations. Then, investing in cleaner's own treatment equipment may be viable alternative. Although having not enough resources to provide the waste treatment of cleaner's own, including waste disposal to the contract significantly increases the amount of certain cleaner's waste deliveries to treatment plant, which decreases the contract price between the cleaner and hazardous waste treatment plant.

Because of tightening environmental restrictions and increasing transportation costs, need for on-site treatment techniques will increase. Although chemical cleaning waste generated during boiler commissioning may be demanding destination to be utilized, there are different types of large-scale portable treatment equipment under development. Some contractors have portable equipment, which is profitable enough for also one-time cleanings. On-site processing is preferred for waste amounts over 100 m^3. On-site processes need authorization procedure and transportation the equipment to the plant site, which slows down the implementation of on-site techniques for one-off processes, in which the benefits compared to off-site treatment are not so big than continuously done cleanings.

7.2 Global overview

Certainly, tightening of the requirements set for both hazardous- and municipal waste water treatment plants push treatment solutions to develop. To a lesser extent, it is possible to rely on possibility to sewer. Tightening of sewerage limits and sewage control by authorities bring changes especially to other than Nordic countries and North America, where the changes have already taken place. Instead of the difficulty of obtaining authorization of sewerage, regulations set by hazardous waste disposal affects also in Nordic countries and U.S. Hazardous waste treatment services are driven to invest in new equipment to introduce new techniques by which local limitations for disposed waste are met. As well as in U.S., two out of three Swedish treatment services use landfilling as a waste final disposal (one third utilizes the energy of the waste), meaning that regulations for landfilled waste are determining. Current situation in Nordic countries and U.S. is, that a fraction of waste producers manages waste treatment themselves. Allowing waste producers to dispose wastes without continuous control is disappearing; smaller and smaller waste amounts are wanted to be traced by local authorities. As well as waste treatment facilities, also possibility to transport neutralized and dried waste straight to the local dumping area decreases.

7.3 Valmet point of view

There are couple of future assignments that this thesis entailed. Because composition data gathered during the work remained incomplete in some areas, data collecting should be continued using the same analysis package than in small-scale cleanings. For collecting, cleaning projects in the near future must be defined.

Another issue that could be put into practice is an experiment with a new citric acid waste treatment method introduced by Valmet U.S. division. It would be possible to share knowledge with some of Valmet cleaners and give them a chance to make an experimental treatment to waste waters by using this method. The content of treated water remains to be seen as there is no certainty how to further dispose possible high chromium contents, which will remain in the waste.

During the thesis work, two cases of co-operation have arisen. Lassila & Tikanoja and EPSE communication related to determining the possibilities of EPSE process and to investigate, which type of waste waters and at what price they are then capable to treat it. Current situation is, that it is possible to utilize EPSE process with mineral and organic acid cleaning waters, but because of unprofitability, not for small-scale cleanings. For Valmet, it is important to keep in touch with both the treatment techniques used by Valmet waste disposal contractors, and also, with trends in environmental limitations and laws.

If the concept of chemical cleaning package including acid cleaning, storage, waste water and sludge final disposal will be reality soon, it may be reasonable to specify the effects in Valmet point of view. Responsibilities of both boiler supplier and end customer will be then decreased, and also, the total boiler delivery price may be lower. By centralizing the cleaning process and water treatment for the same operator may also facilitate keeping acidic and high ammonia- and organic content having waste waters separated from each other. In that case, the cleaner may have established waste water treatment plan and sufficient amount of storage tanks or storage pond building capacity. However, future goal for water treatment may be to get rid of passivation waters treatment in hazardous waste treatment plants by separating them and, if needed, eliminating citric acid injection during passivation stage. In addition to these, intermediate drain between the acid cleaning and passivation stages would decrease the amount of ammonia water needed to neutralization.

Treatment of chemical cleaning waste waters may get a new perspective on co-operation with Kierto Oy. Communication within Kierto and Valmet during the thesis work made Kierto to ask Valmet to join the circular economy pilot funded by Ministry of Employment and the Economy. Kierto’s target is to develop more effective solutions for metallic waters re-use. By utilizing Kierto's knowledge and existing treatment processes, they will create four demonstrations of material efficiency service model for Valmet. Role of Valmet as a co-operative company will be to supply samples of process waste waters for test use and to participate development discussions during the pilot. Being a part of the pilot facilitates measuring and analyzing of upcoming waste streams, as waste water sampling is to be continued. [39, 45]

If the project succeed, Valmet will get suggestion for more efficient utilization cycle for metallic waters by producing cleaner water for sewage. As well as water treatment, both recovered metals and acids would be possible to re-use. Then, it could be also possible to get the knowledge of how remaining sludge would be possible to get stabilized to the form which is suitable for landfill. Treatment method of EPSE is also based on stabilization and, through that, to improve possibilities of waste landfilling. It is to be followed, to which type of suggestions those development projects will do. [39, 45]

8. SUMMARY

Chemical cleaning of boiler tubes is an essential stage of boiler commissioning, in which hazardous waste treatment and environmental challenges are combined with cleaning costs, which vary between the cleaning method, boiler location and waste water treatment possibilities. By optimizing both the cleaning and waste water treatment, savings are possible to achieve. On the other hand, only a rough calculation of waste treatment costs and solving the issues which are affecting waste treatment choices to customer, may have a facilitating effect during sketching the tender and pricing.

The purpose of this work was to study the backgrounds of cost share for the waste water treatment. Roughly, there are three main parties affecting the performance of the cleaning and its costs; Municipal water treatment plants, hazardous waste treatment plants and the cleaner company, which operates the cleaning procedure. Both waste composition, treatment techniques and treatment costs between different cleaning techniques have been compared with each other. In addition to current costs, also future trends and cost optimization have been evaluated.

Couple of main factors affecting the treatment costs can be identified. Scheduling and planning of waste water treatment is the first factor to be taken on account. On the basis of local sewerage limits, hazardous waste treatment possibilities, practicalities for landfilling and experience of customer, used chemicals and waste water amount produced can be evaluated. Treatment capacity of both municipal and hazardous waste treatment plants are largely affected by the length of preparation time and plant-site storage possibilities; acidic or heavy metal containing waste waters coming without warning are seldom drainable, but by communicating well in advance, toxicity measurements and appropriate time for draining is possible to make. To avoid unpredictable events, choice of both solvent and cleaning method should be planned together with the cleaner, customer and boiler supplier. Fluent communication with customer personnel is important also for sharing information of additive chemicals and other treatment complicating compounds present in waste waters.

The difficulty of obtaining an accurate price information was clarified already early in the project. Main reasons for these challenges are both lack of waste water composition data and treatment price dependence of customer-specific contract prices. For these reasons, clarifying the treatment cost share and function of different treatment techniques became more important than accurate price information. Treatment costs consist mainly of hazardous waste treatment, which means that waste disposal is a balancing case between two different alternatives: sewerage to local sewer or treatment in hazardous waste treatment plant. The default operating model for waste waters should be seweraged to municipal or industrial treatment plant, while hazardous waste treatment should be seen as a clear second alternative after sewage when wastes have been found to be unsuitable for sewerage.

Waste waters produced by the cleaning process are possible to divide to different type of water streams. First waste waters to be produced are the waters from first flushing, degreasing and flushing after degreasing, and these contain only low amounts of both metals and organic content, while slightly more complicated features in some cases to be removed are oil and grease. For most of the cases, these degreasing and flushing waters are drainable after a short sedimentation, because any of the sewerage limits is not exceeded significantly.

Another waste stream is acidic cleaning water, including first flushing waters after circulation of solvent. Characteristic to acid cleaning waters are high iron and heavy metal content, while organic content including nitrogen is not the problem. Wastes from these stages are seldom drainable, and are transported to further treatment. In case of mineral acid is the solvent, by precipitating the waste it is possible to get surface water drainable. Then, only bottom sludge of 20 – 30 cm from the bottom of the precipitation container must be transported to hazardous waste treatment plant, in which physical-chemical treatment is the most common alternative. Metals in organic solvent waste waters do not precipitate as they are tightly chelated, and these types of wastes have high organic content. Treatment techniques are still under development, but currently many of citric acid wastes must be expensively incinerated or transported to some other plant, as these are not possible to treat with physical-chemical plant with reasonable effort.

Third type of waste is the waters generated during neutralization and passivation. After ammonia addition, both pH, nitrogen content and amount of organic matter are significantly elevated. Alkaline neutralization and passivation waters do not include metals to a significant extent, which is why they should be kept separate from acidic cleaning waters. Absence of metals can enable sewerage, which is one of the biggest possibilities to optimize the treatment process; sedimentation followed by sewerage of neutralization and passivation waters is already in use for some actors. If sedimentation and sewerage is found to be impossible, waste must be transported to further treatment. High organic content having nitrogenous wastes can be problematic for hazardous waste treatment plants. At worst, the only alternative is incineration, which raises treatment prices significantly. Thus, it would be important to minimize the amount of neutralization-passivation waste waters.

For organic acid wastes, optimization of storage container placement, number and size may be even more important factor than with mineral acids, which have possibility to precipitate the metals. Sewerage as a default option must be maintained by clarifying local sewerage possibilities early in the project. In case of sewerage is prohibited, the choice of waste treatment company strongly affects costs, as the citric acid treatment techniques in the hazardous waste treatment plants differ significantly between each other. Due to metal-chelating ability of organic acids, waste treatment is considerably more difficult than for mineral acids. There are treatment facilities having equipment which is capable of treat citric acid waste, but still some do not have any other alternative than incineration. In that case, the costs can be 2 – 3 times higher than in case of mineral acid. If any assurance of treatment possibilities does not exist, keeping both degreasing-, acid cleaning- and neutralization-passivation waters separated by executing an intermediate rinse between the stages should be considered.

Important result of this thesis work was to define the factors from which the project-specific waste water treatment costs consist of. Networks and relationships created during the work will help to define case-by-case treatment costs when more accurate information of pipe material, local limitations and practicalities are known. Cleaning progress is highly influenced by the cleaner's choices, but by being aware of the possible alternatives for cleaning chemicals, cleaning techniques, waste storage optimization and treatment gives readiness for advice and questioning these choices. Thesis work significantly strengthened data and experience sharing between Valmet and both sewage plants, hazardous waste treatment facilities and professionals of water treatment. Earlier study on this field is limited and is poorly applicable to Finnish practicalities of water treatment.

In addition to keep different types of wastes separated, several treatment costs defining chemical features can be identified. Too high nickel and chromium content is common reason to disable sewerage, and sometimes in operational cleanings also copper can cause problems. In addition to metals, BOD value and conductivity must be taken into account. What comes to treatment costs caused by hazardous waste treatment, the most significant information is to roughly know, which kind of pre-treatment processes the waste waters have gone through on cleaning site. The worst case from the perspective of the treatment plant is, that all the wastes have been led to the same container and the cleaning chemicals and additives are not known. In practice, the only individual hazardous waste treatment cost increasing factor is high nitrogen content, which can rise costs significantly by disabling physical-chemical treatment. Some processes are able to perform physical-chemical treatment except nitrogen ammonium content, but there also are facilities who are forced to incinerate the waste having ammonium nitrogen amount of 5000 mg/l or over. In that case, costs will be 1000 – 1200 €/m^3.

Today, waste treatment contracts are not fixed but composition and batch size dependent. Basically, there are couple of waste treatment service providers in Finland, and their treatment prices seem to differ from each other. In addition to size dependent treatment charge, there are transport costs also having high dependence on both batch size and transport distance. For citric acid, treatment prices lie most of the cleanings 200 – 300 €/m^3, but there also is particular company, which charges 800 €/m^3. With the prices around 300 €/m^3, treatment of hydrofluoric- and hydrochloric acid is slightly more expensive than citric acid. Transportation cost vary from 67 €/t to 124 €/t, and there is also tarpaulin set in the bottom of precipitation pool having a price of 6000 € each. Total treatment cost for

3 – 20 m^3 partial chemical cleaning waters lies 3000 – 7000 €. In case of pre-operational cleaning for entire boiler, total costs for 150 – 300 m^3 boiler may vary from 200 000 – 300 000 €.

In Denmark and Sweden, treatment prices are somewhat lower than in Finland. In Sweden, there are couple of companies having approximate costs of 50 – 100 €/t. In Norway, transporting waste abroad may be in most cases more affordable than treating it in Norway.

In the future, more attention should be paid to keeping up with the upcoming changes. In addition to optimization of waste storage and precipitation of also wastes from another stage than acid cleaning, there are several main trends, which both force to change operation models and enables new techniques. The most intense area of study is citric acid precipitation, which is currently undergoing a lot of research. Precipitation to produce irreversible metal precipitate has already proved to be economical and efficient alternative to both mineral and organic acids, and its future use must be noticed. Another North American technique based on pre-oxidation followed by lime addition is capable to remove ammonia with air-stripping. By using this method, also citric acid waste is possible to precipitate. It is still unclear, if chromium content can be lowered.

Supply chain integration is another type of trend, which means that boiler manufacturer only order one unit consisting of chemical cleaning and water treatment. This type of solution may harmonize operating models and lower waste treatment prices. While the number of individual customers of waste treatment services decreases, delivery sizes will increase enabling lower contract prices and on-site treatment techniques. Interest towards off-site treatment equipment and its growth in the market has been rapid, and they will start to be profitable even in individual on-off deliveries. Current limit for profitability is estimated to be 100 m^3.

Only by keeping in touch with the contacts in the area of both municipal- and hazardous waste water treatment plants and other specialists, it is possible to optimize the process of chemical cleaning and stay involved in technical development. Progress of water treatment outside Europe, such as in Asian countries, will drive to review the current processing options worldwide.

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APPENDIX A: WASTE WATER COMPOSITIONS

		A			B				
		HF solution	Passivation with CA	Passivation	Degreasing	HF solution	Passivation	Surface water	Bottom sludge
		9614-1	9614-2	9614-3	9729-1	9729-2	9729-3		
pH									9
Conductivity	µS/cm								
Solids	mg/l								
BOD 7 ATU	mg/l	150	3400	5500	340	830	1200		
CODCr	mgO2/l	680	6000	8600	490	3000	1700		
Fluoride (F)	mg/l								5.4
Chloride (Cl)	mg/l								1.1
Sulphate (SO4)	mg/l								68
Nitrogen (N) total	mg/l	19	360	2400	0.32	<0.10	510		
Nitrate (NO3)	mg/l								<5.0
Phosphate (PO4)	mg/l								
Ammonium (NH4)	mg/l								
Cyanide (CN) total	mg/l								
Arsenic (As)	mg/l							<0.002	0.52
Mercury (Hg)	mg/l							<0.001	
Silver (Ag)	mg/l							<0.005	
Cadmium (Cd)	mg/l							0.002	<0.025
Chromium (Cr)	mg/l	4.14	1.86	2.98	0.009	8.52	0.756	<0.005	53
Chromium VI (Cr)	mg/l	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05		
Copper (Cu)	mg/l	0.045	0.22	0.26	0.017	0.43	0.04	<0.02	5.9
Lead (Pb)	mg/l	0.028	0.001	0.002	<0.001	0.077	0.001	<0.005	<0.50
Molybdeum (Mo)	mg/l	2.8	1.84	3.01	0.139	8.53	2.91		
Nickel (Ni)	mg/l	2.03	1.49	2.21	0.028	2.23	0.494	0.015	22
Iron (Fe)	mg/l	4600	1700	1800	400	2000	160		13000
Zinc (Zn)	mg/l							<0.02	2.6
Tin (Sn)	mg/l							<0.005	

		C			D		
		HF solution	Passivation	Neutralized HF solution	HF solution. reheater	HF solution. boiler	Passivation. boiler
		4045	4046	4047	3269	3270	3271
pH		2.5	9.3	10.7	3	2.9	9.3
Conductivity	µS/cm	1200	430	3800	15000	11000	4200
Solids	mg/l		13	2800	<2.0	<2.0	3.2
BOD 7 ATU	mg/l	33	1300	360			1300
CODCr	mgO$_2$/l	3700	1700	2600	3200	2800	2000
Fluoride (F)	mg/l	11000	13	11000	13000	10000	24
Chloride (Cl)	mg/l						
Sulphate (SO$_4$)	mg/l	240	<1.0	220	320	250	0.87
Nitrogen (N) total	mg/l	110	710	97	140	110	750
Nitrate (NO3)	mg/l						
Phosphate (PO4)	mg/l						
Ammonium (NH4)	mg/l	24	830	23	28	29	790
Cyanide (CN) total	mg/l	0.058	0.021	0.46	0.021	<0.020	0.11
Arsenic (As)	mg/l	0.022	0.017	0.05	0.044	0.027	<0.00010
Mercury (Hg)	mg/l	0.00033	0.00015	<0.00010	0.00046	0.00027	0.19
Silver (Ag)	mg/l	<0.0020	<0.0020	<0.0020	<0.002	<0.002	<0.002
Cadmium (Cd)	mg/l	0.0028	0.0035	0.0016	0.0074	0.0077	0.0036
Chromium (Cr)	mg/l	2.5	2.4	0.41	13	9	1.2
Chromium VI (Cr)	mg/l		0.16	<0.0050			
Copper (Cu)	mg/l	0.5	0.23	0.49	0.55	0.54	0.3
Lead (Pb)	mg/l	0.083	0.001	0.022	0.0011	0.0014	0.0021
Molybdeum (Mo)	mg/l	4.2	4.3	2.5	8.7	8.3	4
Nickel (Ni)	mg/l	2	2.1	1.7	1.8	3.2	2.1
Iron (Fe)	mg/l	1400	1300	580	1000	1600	420
Zinc (Zn)	mg/l	1.2	0.23	0.06	0.18	0.22	0.015
Tin (Sn)	mg/l	0.069	0.055	0.041	0.1	0.11	0.042
Cobolt (Co)	mg/l						
Antimony (Sb)	mg/l						
Phosphorous (P)	mg/l						
Hydrocarbon oils (C$_{10}$-C$_{21}$)	mg/l	0.13	<0.30	<0.05	<0.02	<0.20	0.09
Hydrocarbon oils (C$_{10}$-C$_{40}$)	mg/l	0.46	0.87	<0.05	0.36	0.69	0.12
Heavy oil fractions	mg/l	0.34	0.59	<0.05	0.26	0.5	<0.05

		Precipitation pool surfaces							
		Pool 1	Pool 1	Pool 1	Pool 1	Pool 2	Pool 2	Pool 2	Pool 2
pH		10.4	10.2	9.8	8.9	10	9.7	9.5	8
Conductivity	µS/cm	520	510	530	540	100	99	100	100
Solids	mg/l	1.5	2.6	4.6	5.1	<1	1.3	1.3	1
BOD 7 ATU	mg/l	220	230	200	210	10	11	11	9.5
CODCr	mgO_2/l								
Fluoride (F)	mg/l	1100	1100	1100	1200	210	220	210	270
Chloride (Cl)	mg/l								
Sulphate (SO_4)	mg/l								
Nitrogen (N) total	mg/l								
Nitrate (NO3)	mg/l								
Phosphate (PO4)	mg/l								
Ammonium (NH4)	mg/l								
Cyanide (CN) total	mg/l								
Arsenic (As)	mg/l								
Mercury (Hg)	mg/l	0.00003	0.00002	0.00002	0.00002	<0.000010	<0.000010	<0.000010	<0.000010
Silver (Ag)	mg/l	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
Cadmium (Cd)	mg/l	0.00017	0.00018	0.00017	0.00021	0.00002	0.00003	0.00002	0.00004
Chromium (Cr)	mg/l	0.0063	0.0069	0.012	0.0049	0.0056	0.033	0.0061	0.005
Chromium VI (Cr)	mg/l								
Copper (Cu)	mg/l	0.0028	0.0031	0.0026	0.0046	0.0001	0.0029	<0.000010	<0.000010
Lead (Pb)	mg/l	0.0005	0.00036	0.00045	0.00059	0.00039	0.00045	0.00028	0.00043
Molybdeum (Mo)	mg/l								
Nickel (Ni)	mg/l	0.014	0.014	0.015	0.02	0.0015	0.014	0.0015	0.0018
Iron (Fe)	mg/l	0.2	0.16	0.93	0.37	0.13	5.7	0.22	0.14
Zinc (Zn)	mg/l	0.0072	0.0037	0.0048	0.0044	0.0046	0.0063	0.0036	0.004
Tin (Sn)	mg/l	0.0025	0.0005	0.0024	0.002	<0.0002	0.0002	<0.0002	<0.0002
Cobolt (Co)	mg/l								
Antimony (Sb)	mg/l								
Phosphorous (P)	mg/l								
Hydrocarbon oils (C_{10}-C_{21})	mg/l								
Hydrocarbon oils (C_{10}-C_{40})	mg/l								
Heavy oil fractions	mg/l								

		Precipitation pool surfaces							
		Pool 3	Pool 3	Pool 3	Pool 4	Pool 4	Pool 4	Pool 5	Pool 5
pH		11.8	11.4	11.5	10.6	10.2	9.6	4.2	4.2
Conductivity	µS/cm	86	62	44	710	710	720	24	22
Solids	mg/l	8100	1300	6.2	10	4.5	3.1	5.4	3.7
BOD 7 ATU	mg/l	55	93	180	160	160	160	2.1	4.6
CODCr	mgO_2/l								
Fluoride (F)	mg/l	11	6.1	5.2	1500	1500	1500	82	81
Chloride (Cl)	mg/l								
Sulphate (SO_4)	mg/l								
Nitrogen (N) total	mg/l								
Nitrate (NO3)	mg/l								
Phosphate (PO4)	mg/l								
Ammonium (NH4)	mg/l								
Cyanide (CN) total	mg/l								
Arsenic (As)	mg/l								
Mercury (Hg)	mg/l	0.00043	0.00008	<0.000010	0.001	0.00009	<0.000010	<0.000010	<0.000010
Silver (Ag)	mg/l	0.0004	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
Cadmium (Cd)	mg/l	0.0013	0.00019	0.00005	0.00009	0.0001	0.00005	0.00007	0.00009
Chromium (Cr)	mg/l	4.2	0.51	0.0028	0.0091	0.0071	0.0045	0.17	0.17
Chromium VI (Cr)	mg/l								
Copper (Cu)	mg/l	0.39	0.055	0.0013	0.0006	0.0006	0.001	0.014	0.014
Lead (Pb)	mg/l	0.011	0.0022	0.00042	0.00037	0.00033	0.00044	0.00081	0.00076
Molybdeum (Mo)	mg/l								
Nickel (Ni)	mg/l	1.9	0.27	0.01	0.015	0.013	0.016	0.12	0.13
Iron (Fe)	mg/l	850	110	0.45	0.38	0.36	0.24	60	58
Zinc (Zn)	mg/l	0.15	0.031	0.0042	0.018	0.0055	0.0042	0.028	0.029
Tin (Sn)	mg/l	0.073	0.012	0.0002	0.0009	0.001	0.0002	0.0011	0.0003
Cobolt (Co)	mg/l								
Antimony (Sb)	mg/l								
Phosphorous (P)	mg/l								
Hydrocarbon oils (C_{10}-C_{21})	mg/l								
Hydrocarbon oils (C_{10}-C_{40})	mg/l								
Heavy oil fractions	mg/l								

		E		F		G	
		Superheaters		Superheaters		Wall tubes	
		Passivated CA solution		CA solution	Passivation	CA solution	Passivation
pH		9		2.4	8.9	2.3	8.2
Conductivity	µS/cm	1820		270	2200	320	3000
Solids	mg/l	52		27	3.7	53	100
BOD 7 ATU	mg/l	11000		13000	11000	18000	18000
CODCr	mgO_2/l	22800		22000	20000	32000	31000
Fluoride (F)	mg/l			0.29	0.39	0.44	0.61
Chloride (Cl)	mg/l						
Sulphate (SO_4)	mg/l			26	25	44	16
Nitrogen (N) total	mg/l	4000		22	6300	180	7200
Nitrate (NO3)	mg/l						
Phosphate (PO4)	mg/l						
Ammonium (NH4)	mg/l			<1.5	5200	2.2	7200
Cyanide (CN) total	mg/l			<0.05	0.2	<0.05	0.14
Arsenic (As)	mg/l	0.19		0.012	0.013	0.026	0.028
Mercury (Hg)	mg/l	<0.0004		<0.00010	<0.00010	<0.00010	<0.00010
Silver (Ag)	mg/l					<0.0020	<0.0020
Cadmium (Cd)	mg/l	<0.01		<0.00020	0.00024	<0.00020	<0.00020
Chromium (Cr)	mg/l	3.138		3	3.2	0.93	1.1
Chromium VI (Cr)	mg/l				1.3		0.59
Copper (Cu)	mg/l	<0.1		0.039	0.11	0.040	0.19
Lead (Pb)	mg/l			0.0054	0.0045	0.0026	0.0017
Molybdeum (Mo)	mg/l			3.3	3.7	0.16	0.23
Nickel (Ni)	mg/l			1.3	1.4	0.48	0.57
Iron (Fe)	mg/l			590	610	690	830
Zinc (Zn)	mg/l	<0.246		0.13	0.15	0.40	0.41
Tin (Sn)	mg/l			0.035	0.038	0.017	0.022
Cobolt (Co)	mg/l	0.187					
Antimony (Sb)	mg/l	<0.1					
Phosphorous (P)	mg/l	0.61		0.11	0.2	0.067	0.076
Hydrocarbon oils (C_{10}-C_{21})	mg/l	4.2		0.06	0.11	0.16	<0.20
Hydrocarbon oils (C_{10}-C_{40})	mg/l	0.2		0.19	0.32	0.06	<0.20
Heavy oil fractions	mg/l						

		H	HF				w/o CA
		First flush	Degreasing	Second flush	Surface water	Third flush	Passivation
pH		6.8	7.3	7.2	8.1	6.5	10.1
Conductivity	µS/cm	10.9	3.5	1.7	97.3	36	73.6
Solids	mg/l						
BOD 7 ATU	mg/l						
CODCr	mgO2/l						
Fluoride (F)	mg/l				8.9		
Chloride (Cl)	mg/l						
Sulphate (SO4)	mg/l						
Nitrogen (N) total	mg/l						
Nitrate (NO3)	mg/l						
Phosphate (PO4)	mg/l						
Ammonium (NH4)	mg/l						
Cyanide (CN) total	mg/l						
Arsenic (As)	mg/l	<0.00050	<0.00050	<0.00050	<0.00050	<0.00050	0.056
Mercury (Hg)	mg/l						
Silver (Ag)	mg/l						
Cadmium (Cd)	mg/l	<0.00010	<0.00010	<0.00010	<0.00010	<0.00010	0.00011
Chromium (Cr)	mg/l						
Chromium VI (Cr)	mg/l	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	0.0059
Copper (Cu)	mg/l	0.027	0.011	0.0033	0.0019	0.0031	0.036
Lead (Pb)	mg/l	<0.00050	<0.00050	<0.00050	<0.00050	<0.00050	<0.00050
Molybdeum (Mo)	mg/l						
Nickel (Ni)	mg/l	0.004	0.009	0.001	0.051	0.0015	0.025
Iron (Fe)	mg/l						
Zinc (Zn)	mg/l	0.0064	0.015	<0.0050	<0.0050	<0.0050	<0.0050
Tin (Sn)	mg/l						
Cobolt (Co)	mg/l	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010
Antimony (Sb)	mg/l						
Phosphorous (P)	mg/l						
Hydrocarbon oils (C10-C21)	mg/l						
Hydrocarbon oils (C10-C40)	mg/l						

		I		J	
		HF + passivation		HF Only passivation	
		HF	Passivation	Passivation 1	Passivation
pH					
Conductivity	µS/cm				
Solids	mg/l				
BOD 7 ATU	mg/l				
CODCr	mgO_2/l				
Fluoride (F)	mg/l	8.2			
Chloride (Cl)	mg/l				
Sulphate (SO_4)	mg/l				
Nitrogen (N) total	mg/l				
Nitrate (NO3)	mg/l				
Phosphate (PO4)	mg/l				
Ammonium (NH4)	mg/l			720	
Cyanide (CN) total	mg/l				
Arsenic (As)	mg/l	0.22		0.09	0.072
Mercury (Hg)	mg/l				
Silver (Ag)	mg/l				
Cadmium (Cd)	mg/l	<0.00010	0.00043	0.00032	<0.00010
Chromium (Cr)	mg/l				
Chromium VI (Cr)	mg/l	<0.0010	0.076	0.033	0.027
Copper (Cu)	mg/l	<0.0010	1.1	3.6	1.6
Lead (Pb)	mg/l	<0.00050	0.0074	0.019	0.016
Molybdeum (Mo)	mg/l				
Nickel (Ni)	mg/l	0.0039	0.58	0.79	0.34
Iron (Fe)	mg/l				
Zinc (Zn)	mg/l	<0.0050	0.34	0.42	0.26
Tin (Sn)	mg/l				
Cobolt (Co)	mg/l	<0.0010	0.04	0.012	0.0089
Antimony (Sb)	mg/l				
Phosphorous (P)	mg/l				
Hydrocarbon oils (C_{10}-C_{21})	mg/l				
Hydrocarbon oils (C_{10}-C_{40})	mg/l				
Heavy oil fractions	mg/l				

		K
		CA solution
pH		
Conductivity	µS/cm	
Solids	mg/l	
BOD 7 ATU	mg/l	
CODCr	mgO_2/l	
Fluoride (F)	mg/l	
Chloride (Cl)	mg/l	
Sulphate (SO_4)	mg/l	
Nitrogen (N) total	mg/l	
Nitrate (NO3)	mg/l	
Phosphate (PO4)	mg/l	
Ammonium (NH4)	mg/l	
Cyanide (CN) total	mg/l	
Arsenic (As)	mg/l	0.01
Mercury (Hg)	mg/l	<0.0005
Silver (Ag)	mg/l	<0.005
Cadmium (Cd)	mg/l	<0.001
Chromium (Cr)	mg/l	2.5
Chromium VI (Cr)	mg/l	1.5
Copper (Cu)	mg/l	0.17
Lead (Pb)	mg/l	0.029
Molybdeum (Mo)	mg/l	
Nickel (Ni)	mg/l	0.97
Iron (Fe)	mg/l	
Zinc (Zn)	mg/l	0.31
Tin (Sn)	mg/l	0.092
Cobolt (Co)	mg/l	
Antimony (Sb)	mg/l	
Phosphorous (P)	mg/l	
Hydrocarbon oils (C_{10}-C_{21})	mg/l	
Hydrocarbon oils (C_{10}-C_{40})	mg/l	
Heavy oil fractions	mg/l	