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**DEVELOPMENT OF A BOILER WATER LEAK DETECTION METHOD FOR
RECOVERY BOILERS UTILIZING ALL-VOLATILE TREATMENT OF BOILER
WATER**

Master's Thesis

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TIIVISTELMÄ

Lappeenrannan-Lahden teknillinen yliopisto LUT
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Kattilaveden vuodonvalvontamenetelmän kehitys haihtuvien alkalien kattilavesikemialla operoitaville soodakattiloille

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Tämän diplomityön tavoitteena oli parantaa soodakattiloiden käyttöturvallisuutta kehittämällä vuodonvalvontamenetelmä, jolla voidaan paikantaa kattilavesivuodot kattilan höyrystinosasta. Tutkimuksessa keskityttiin soodakattiloihin, joissa käytetään kattilavesikemikaaleina pelkästään haihtuvia alkaleja, sillä tällöin perinteisesti käytetyillä vuodonvalvontamenetelmillä ei voida erottaa onko vuoto höyrystinosassa vai jossakin muussa osassa kattilaa.

Soodakattilan toimintaa, vesikemiaa ja vuodonvalvontamenetelmiä tarkasteltiin kirjallisuudesta ja sopivaksi menetelmäksi valittiin kattilavesivuodon seuranta merkkiainekemikaalin massataseen avulla. Merkkiaine annosteltiin jatkuvatoimisesti kattilaveteen, josta sen pitoisuutta analysoidaan jatkuvatoimisella analysointilaitteella. Yhdessä syöttövesi- ja ulospuhallusvirtausten kanssa voidaan merkkiaineelle tällöin muodostaa massatase, josta voidaan laskea kattilavesivuodon suuruus ja seurata sitä siten jatkuvasti

Menetelmää testattiin suomalaisella sellutehtaalla haihtuvien alkalien vesikemialla operoivalla soodakattilalla. Merkkiaineen annostelun ei havaittu heikentävän kattilaveden ja höyryn laatua ja menetelmän avulla voitiin havaita 1,9 kg/s suuruinen vuoto kahdeksassa tunnissa.

Merkkiaineen käyttöön perustuva tiiveydenvalvontamenetelmä todettiin toteuttamiskelpoiseksi haihtuvia alkaleja käyttäville soodakattiloille. Menetelmän avulla voidaan tunnistaa jo pienetkin vuodot, joihin liittyy tulipesäräjähdyksen vaara, turvallisesti valvomossa työskennellen. Menetelmää käyttämällä voidaan siten varmistaa, että kattila ajetaan viiveettä ja henkilöturvallisuutta vaarantamatta alas aina kun kattilassa on vuoto, joka voi saada aikaan tulipesäräjähdyksen. Nyky menetelmillä vaaralliset vuodot voivat jäädä havaitsematta pitkäksi aikaa ja tulipesäräjähdyksen sattuessa voi kattilahuone olla siten miehitetty, joten menetelmän käyttöönotto parantaisi merkittävästi pelkästään haihtuvia alkaleja käyttävien soodakattiloiden käyttöturvallisuutta.

ABSTRACT

Lappeenranta-Lahti University of Technology LUT
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Development of a boiler water leak detection method for recovery boilers utilizing all-volatile treatment of boiler water

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The goal of this thesis was to improve the operational safety of recovery boilers by developing a boiler water leak detection method, that can locate leaks in the steam generator part of the boiler. Focus of the study was set on boilers utilizing all-volatile treatment of the boiler water, as the conventional leak detection systems used in these cases are unable to detect if the leak is located in steam generator, or in other parts of the boiler.

Boiler operation, water chemistry, and leak detection methods were investigated through literature, and a suitable detection method was chosen to be a tracer chemical mass balance monitoring. In tracer method a continuous dosage of substance is administered into boiler water and its mass balance is continuously analyzed, together with feedwater and blowdown flows of the boiler. A continuous trend for a leak flow could then be calculated from the mass balance of the tracer element in the boiler water.

The method was tested in an all-volatile treated recovery boiler at Finnish pulp mill. During the field trials it was determined that addition of tracer chemical did not adversely affect the quality of boiler water or steam, and leak sizes down to 1.9 kg/s were able to be detected in eight hours.

The tracer method for leak detection in boiler utilizing all-volatile treatment was found to be plausible. The method can detect even small leak sizes, that may induce a risk of furnace explosion, in a reasonable time frame while working safely from the boiler control room. By utilizing this method, the boiler can be shutdown without delay and without risking the operational safety of mill personnel, in the case of leak situation. Conventional methods may leave critical leaks undetected for crucially long time, which may lead into a furnace explosion while the operational personnel are still inside the boiler room. Introduction of tracer method as part of the boiler automation could therefore significantly improve the operational safety of boilers utilizing all-volatile treatment of boiler water.

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SYMBOLS AND ABBREVIATIONS

Roman characters

m	Mass	[kg, ton]
\dot{m}	Mass flow	[mg/s, kg/s]
M	Molar mass	[g/mol]
t	Time	[s, h]
w	Mass fraction	[mg/kg, μ g/kg]
V	Volume	[l, m ³]

Greek characters

Δ	Delta (difference)	[-]
ρ	Density	[kg/l]

Subscripts

ave	Average
BD	Boiler blowdown
D	Tracer dosage
fw	Feedwater
L	Leak
reg	Regression model
s	Steam

Abbreviations

AVT	All-volatile treatment
BLRBAC	Black Liquor Recovery Boiler Advisory Committee
BW	Boiler water

CEN	European Committee of Standardization
CHA	Cyclohexylamine
Cl ⁻	Chloride
CO ₂	Carbon Dioxide,
CT	Caustic treatment
DDA	Dodecylamine
DEAE	Diethylethanolamine
EPRI	Electric Power Research Institute
ETA	Ethanolamine
FBRC	Finnish Recovery Boiler Committee
Fe ₂ O ₃	Iron(III)oxide, rust
Fe ₃ O ₄	Iron(II,III)oxide, magnetite
FFA	Film forming amines
IAPWS	International Association of the Properties of Water and Steam
Mg	Magnesium
Morph	Morpholine
N ₂ H ₄	Hydrazine
NH ₃	Ammonia
N ₂	Number
ODA	Octadecylamine
OH ⁻	Hydroxyl ion
OLA	Oleylamine
OLDA	Oleyl propylene diamine
ppb	Parts per billion, µg/kg
ppm	Parts per million, mg/kg
PT	Phosphate treatment
SiO ₂	Silica

SO^{2-}	Sulphate
SS_{res}	Sum of square residuals
TOC	Total organic carbon

1 INTRODUCTION

Leak detection is important safety aspect of steam boiler operation, as boiler water leaks may subject both the operational personnel and the boiler plant to severe risk. In the worst case, tube failure can lead to an explosion as leaking water expands rapidly in the boiler furnace. Leaks in lower parts of recovery boilers are especially dangerous due to risk of smelt-water explosion. For this reason, leaks in critical parts of the boiler caused by tube failures require immediate emergency shutdown procedures for safety of personnel and mill property (Vakkilainen, 2005).

In the 21st century in Finland, there have been documented nine serious boiler water leaks in recovery boilers throughout, out of which three led to a furnace explosion, as leaking water entered the hearth. A unifying factor for these three cases was that the leak sizes were substantially large, up to 20 kg/s or more. In other cases, the leaks were smaller, and actions were taken before the leaks had time to grow. Another major boiler explosion in Europe due to boiler water leak occurred in 2014 on Zellstoff Pöls mill in Austria. In this occasion the explosion led to such significant structural damage, that a new boiler had to be built from scratch, which led to a 21-month partial downtime in the mill operation (Karjunen 2017).

The integrity of boiler tubing can be monitored during operation by measuring concentrations of non-volatile matter in the steam generator's boiler water, together with feedwater, steam, and blowdown flows. If dosing of non-volatile matter and water flows are undisturbed, a continuous decrease in concentration of analyzed non-volatile matter could indicate a leak in boiler tubing. Out of the mass balance of the dosed non-volatile matter, an equation can be made for calculating the leak size, even if dosages and flows are altered. Suitable substances are, for example, sodium and phosphate, since sodium phosphate is commonly used to adjust pH of boiler water (Karjunen, interview 2020).

Some plants have abandoned the use of sodium phosphate for boiler water pH adjusting. Instead, the pH is adjusted with the same volatile chemicals as for the pH adjustment of feedwater. These chemicals are volatilized, and partly decomposed, during boiler operation, so their concentrations in boiler water cannot be used for continuous monitoring of boiler tube integrity

as described above. Other methods for leak detection are still applied, such as water-steam mass balance monitoring, but these methods are unable to detect if the leak is in a critical part of the boiler or not. (Karjunen, interview 2020).

This inability to detect the most critical leaks, those located in the steam generator, poses a significant flaw for the leak detection of boilers utilizing all-volatile treatment (AVT) of boiler water. The goal of this study is to solve this by developing a leak detection method that can accurately detect these critical leaks in AVT boilers while they are still of small size, so that required actions can be made before they cause significant damage. One such method could be the use of a non-volatile tracer chemical that can be dosed into boiler water and monitored similarly to how it can be done in phosphate treated boilers. However, there is little to no studies to be found on effects of tracer chemicals on the stability of the boiler water treatment chemicals utilized in AVT boilers.

The study considers the basic concepts of recovery boilers and their water-steam cycle, leading to boiler water leaks and their detection methods. The target is to establish a suitable leak detection method and prove its capability and accuracy through field trials.

LITERATURE REVIEW

2 RECOVERY BOILER

This section covers the introduction of recovery boiler and the water-steam cycle. The function of recovery boiler and essential sections of water-steam cycle are discussed to provide necessary information for establishing the basic concepts required for further studying the boiler water leaks and their detection. The major focus of this section is set on the water-steam cycle of the boiler, as it is relevant for understanding the circulation of water and impurities in and out of the boiler.

2.1 Function of recovery boiler

Recovery boilers are steam boilers specialized for burning black liquor, which is a side stream of pulp industry, consisting of inorganic cooking chemicals and organics removed from the wood mass. The main functions of recovery boiler are recovery of cooking chemicals from black liquor and generation of steam for electricity production and other processes around the mill. Inorganic cooking chemicals in the black liquor mainly consist of sodium carbonate and sodium sulphate. The sodium sulphate is reduced to sodium sulfide by the reducing environment of the recovery boiler furnace (Vakkilainen 2005). A typical design and main components of modern recovery boiler is presented in Figure 1.

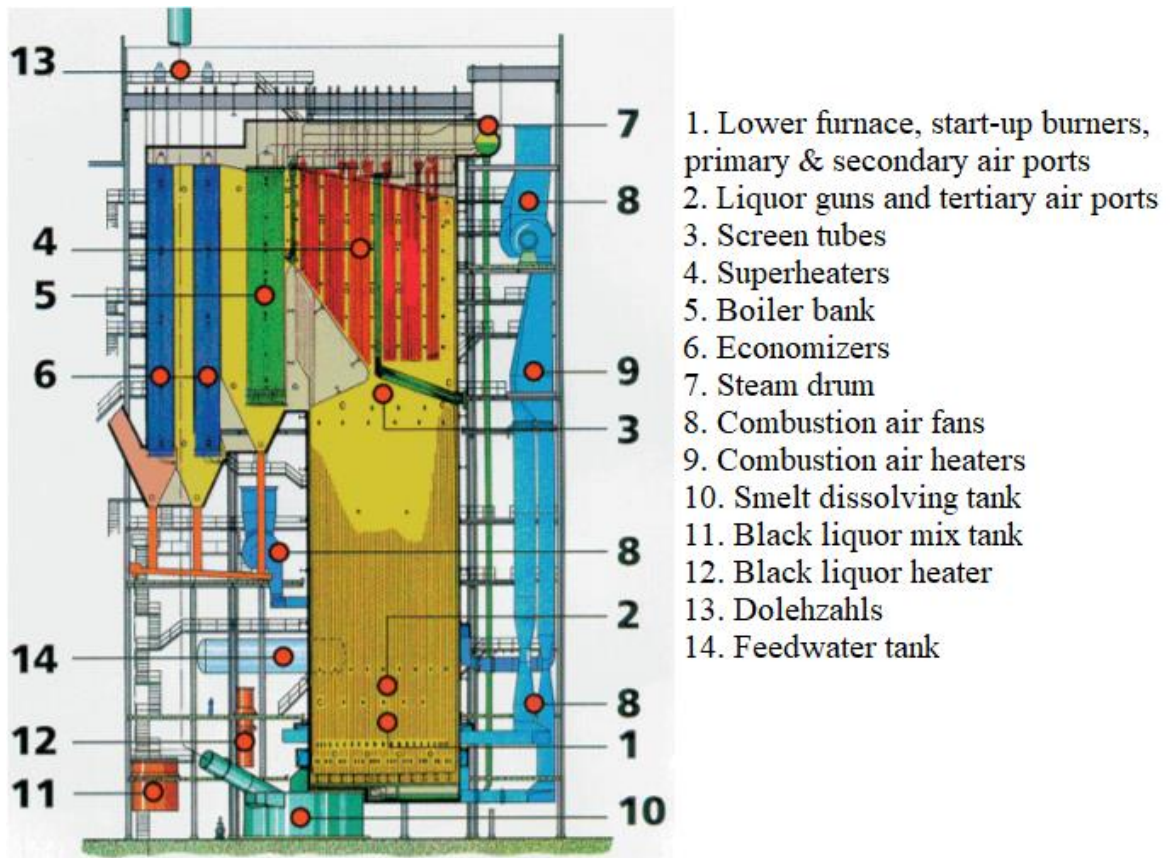


Figure 1. Typical design of modern recovery boiler (Vakkilainen 2005)

The main structure of recovery boiler consists of heat transfer surfaces, flue gas channel, and the furnace at which black liquor is combusted. Black liquor firing is performed by spraying as droplets into boiler furnace from higher elevation. On the way down, water and volatile organic compounds are vaporized from the droplets, and leftover inorganics and char fall to the furnace floor. The char is then combusted in the furnace under precisely controlled conditions. The inorganics melt in the furnace and form a smelt, that is then removed from the boiler through smelt spouts. The smelt is then dissolved to water in the dissolving tank, producing green liquor, which is transferred to a causticizing plant for further processing (Vakkilainen 2005).

2.2 Water-steam cycle

Heat released in black liquor combustion is used for steam generation in the boiler. The heat transfer surfaces of the boiler consist of furnace wall tubing, boiler bank, superheaters, and economizers. Evaporative surfaces where steam generation occurs are wall tubing and boiler bank. Superheaters are used to heat the steam to higher temperature to increase the heat transfer efficiency and power production. Economizers are placed in the last section of flue gas channel and are used for preheating the feedwater before it enters the evaporator. (Vakkilainen 2005).

Water-steam cycle of recovery boiler begins from low pressure feedwater which is pressurized and pumped from feedwater tank to the boiler. First the feedwater enters economizers, where it is heated close to boiling point, water then flows from economizers to steam drum. From steam drum the water flows down the downcomers and enters the boiler wall tubing from the bottom. Inside the wall tubing and boiler bank, part of the water evaporates, forming steam bubbles into the stream. water-steam mixture re-enters the steam drum, where steam is separated from water by gravitation, screens, and cyclone separators. Steam travels through superheaters, where it is heated to higher temperature, and leaves the boiler (Vakkilainen 2005). Figure 2 below presents the design of water circulation system in recovery boiler.

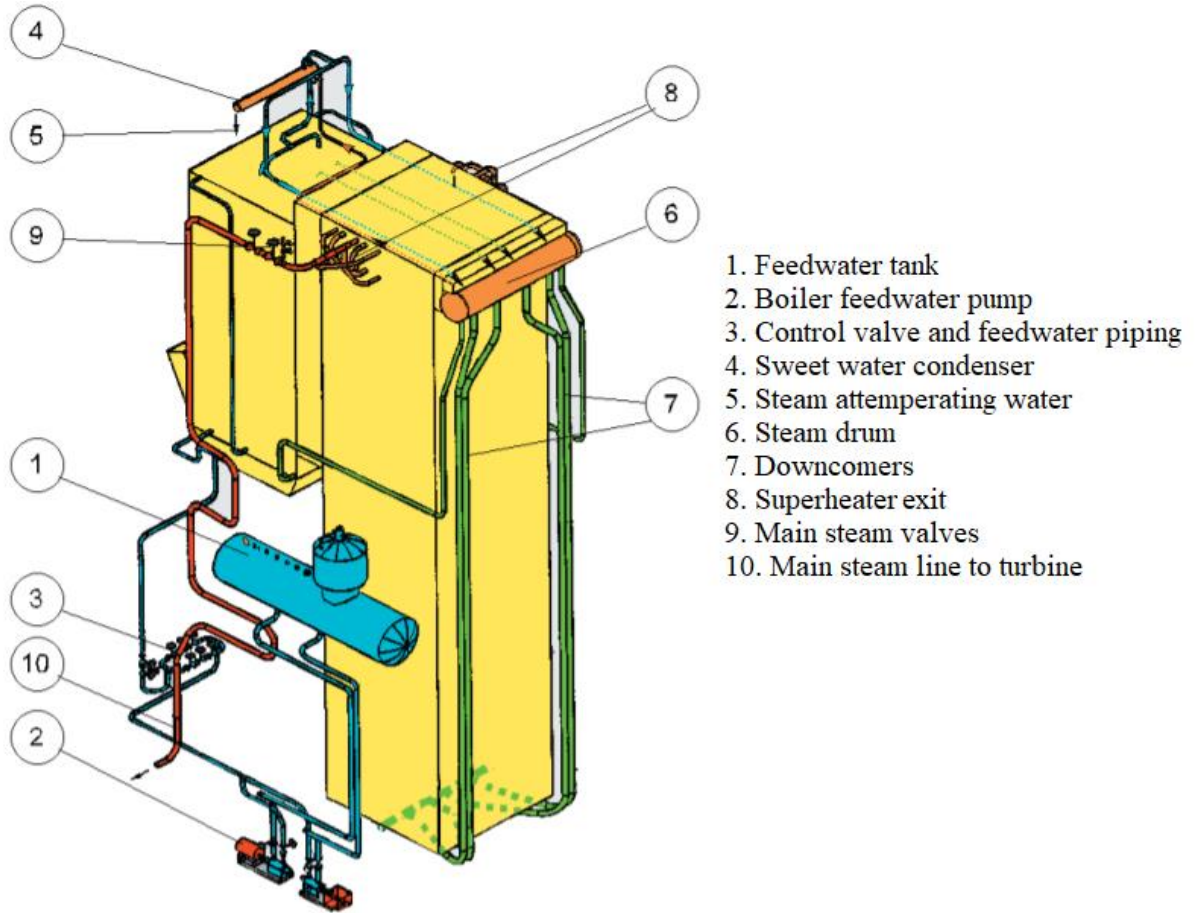


Figure 2. Water circulation system in recovery boiler (Vakkilainen 2005)

The temperature of boiler water is controlled by the internal pressure of evaporator water system. The boiler water temperature and superheated steam temperature are therefore higher in boilers with higher drum pressure. The water inside boiler tubing and steam drum is very close to boiling point, as is the steam before it enters the superheaters, where it is heated to higher temperature. Steam temperature may be controlled by spraying attemperating water to the superheated steam. This attemperating water is usually taken directly from feedwater or produced by sweet water condenser (Dolezahl) from steam, as solid impurities could form deposits in the superheaters and turbine (Vakkilainen 2005). Water boiling point as function of pressure, and typical recovery boiler main steam temperature as function of pressure are presented in Figures 3 and 4.

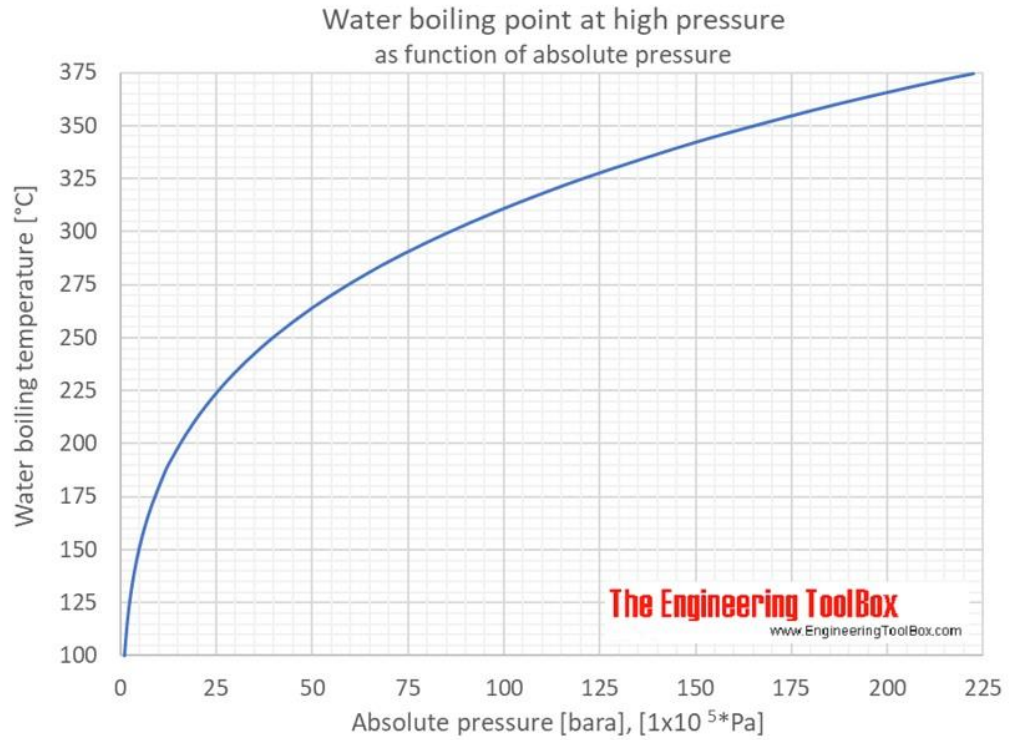


Figure 3. Water boiling point as function of absolute pressure (Engineering Toolbox 2005)

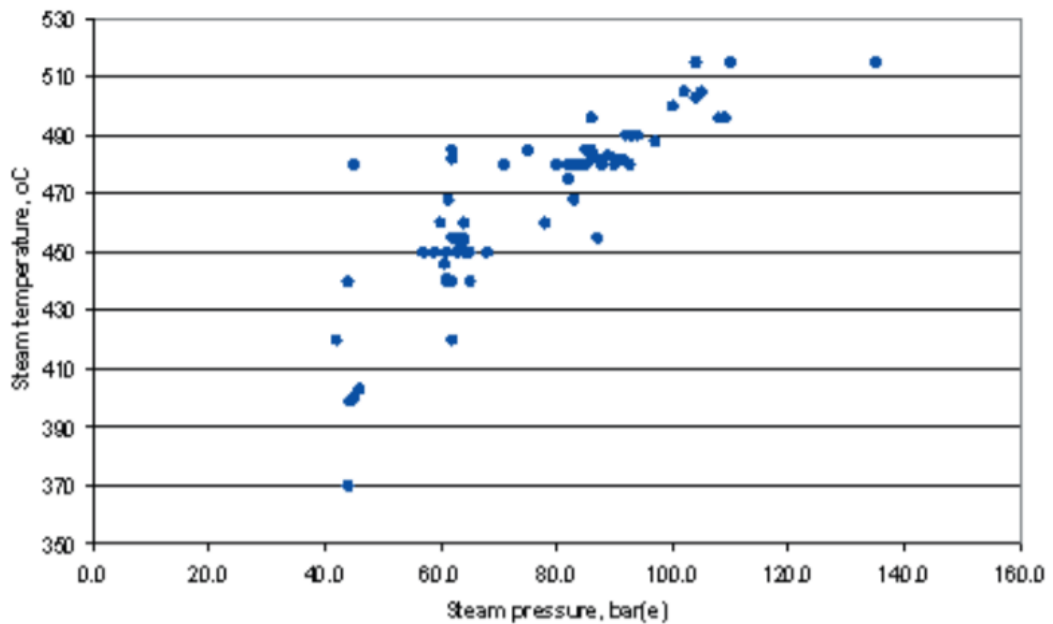


Figure 4. Recovery main steam temperature as function of pressure (Vakkilainen 2005)

The water flow from steam drum to downcomer, and back up through wall tubing is controlled by natural circulation. Natural circulation is induced by density difference caused by temperature difference of water between downcomers and wall tubing. The steam bubbles generated in evaporative surfaces are also much less dense than the water surrounding them, so they rise up inside the wall tubing (Vakkilainen 2005). The principle of natural circulation is presented in Figure 5.

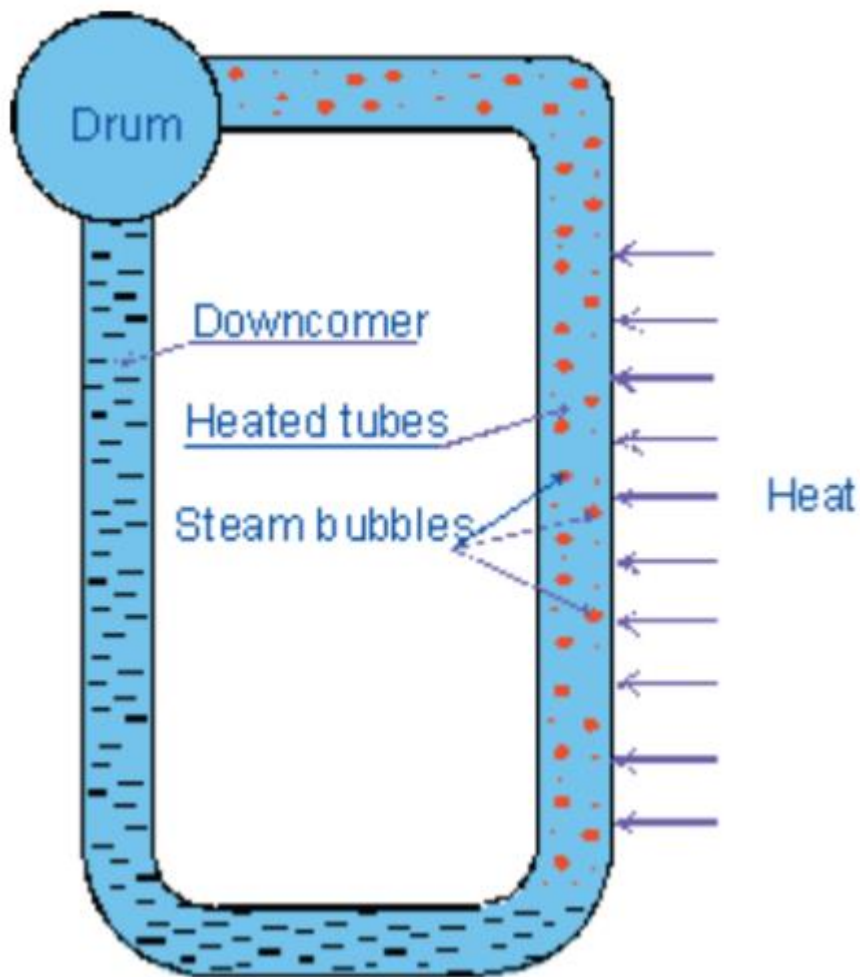


Figure 5. Principle of natural circulation (Vakkilainen 2005)

The water circulating in the steam generator is considered as a two-phase system, since part of the water exist as steam, and the rest as liquid. The balance between steam and liquid water is controlled by evaporation, which is maintained by combustion of black liquor. The volumetric distribution of liquid water and steam can be estimated to be roughly 50/50 of the total boiler volume (Karjunen, interview 2020).

The boiler water volumes in different mills are varying, based on the size of the boilers. For example, the biggest recovery boiler in Finland is located in Metsä Fibre Äänekoski mill, having a boiler water volume of 697 m³. If the estimation of having 50/50 distribution of water and steam is taken into account, liquid water inside the boiler would be roughly 350 m³

3. WATER AND STEAM QUALITY

Control of boiler water and steam quality is essential for safe and efficient process operation. Poor water quality may cause corrosion risks in whole water-steam cycle and decreased heat transfer due to waterside deposits. Therefore, several water treatment methods are applied, and relevant parameters such pH, conductivity, and impurity concentrations are closely monitored (Karjunen, 2004).

In this section the water-steam cycle impurities, water-chemistry related guidelines and chemical conditioning methods will be discussed. The subject will be focusing on all-volatile treatment (AVT) methods for all-ferrous systems, to establish how the treatment functions and what boundaries are set for boiler water quality.

3.1 Water-steam cycle impurities

Notable impurities in water-steam cycle consist of inorganic salts and minerals, organic compounds, and dissolved oxygen (O₂) and carbon dioxide (CO₂). Especially salts containing chloride (Cl⁻) and sulphate (SO₄²⁻) ions have been identified as causing corrosion in the water-steam cycle (Vuorinen, et al. 2011).

Calcium (Ca), Magnesium (Mg) and silica (SiO_2) on the other hand form hard to remove deposits on boiler tubing and turbine. Deposits on boiler tubes decrease heat transfer efficiency and cause overheating of the boiler tubes. Deposits on the turbine can decrease its capacity and efficiency (Dooley, et al. 2002).

The temperature in high pressure boilers can be close to $300\text{ }^\circ\text{C}$ and steam temperature up to $500\text{ }^\circ\text{C}$. In high temperatures, many organic compounds are likely to suffer from thermal degradation and their decomposition products may introduce organic acids to the cycle, which decreases the pH and increases corrosion risk. Likewise, dissolved oxygen and carbon dioxide also increase the corrosion risk of water-steam systems built out of carbon steel (Vuorinen, et al. 2011).

Regarding recovery boilers, most significant sources of impurities are makeup water and leaks in steam condenser lines. Up to 30% of recovery boiler feedwater consists of makeup, because a considerable amount of generated steam is used in processes around the mill. Therefore, efficient treatment of makeup water is required to keep concentrations of impurities under limit values. (Vuorinen, et al. 2011). Makeup water is usually made from fresh water sources, such as surface water from lakes and rivers. Surface water naturally contains salts, minerals, and organic matter that need to be removed before it can be used as boiler water. The makeup water treatment process usually consists of total desalination through ion exchange, and humus removal through coagulation, flocculation, and clarification (Vänskä 2010) Leaks in condenser and cooling lines may also introduce significant amounts of impurities to the cycle, as the source of cooling water is usually surface water. Other smaller sources include maintenance work, outages, and acid cleaning of the boiler waterside which can also expose the cycle to external impurities (Vuorinen, et al. 2011).

The chemical program for boiler water treatment is designed for both corrosion and scaling inhibition. It consists mainly of alkalizing & dispersing agents, oxygen scavengers and surface-active film forming products. The program should be designed considering required process conditions such as temperature and drum pressure as well as equipment materials. Proper chemical treatment can reduce the need for maintenance and acid cleaning, which itself decreases operational downtime and impurities entering the cycle (Vuorinen, et al. 2011).

The concentration of impurities in boiler water may also be controlled by blowdown of the boiler. Blowdown removes liquid water from the boiler together with the impurities in it. By increasing the blowdown flow, the concentration of impurities in boiler water decreases accordingly, as they are removed from the cycle. Typically, the boiler blowdown flow is approximately 1 % of the feedwater flow, but in boilers with less or more impurities this value may vary (Lähde, 2021)

3.2 Water chemistry guidelines

The water chemistry guidelines for water-steam cycle are designed to maintain safe and efficient boiler operation. The goal is to keep levels of impurities low and induce optimal conditions for corrosion inhibition (Dooley, et al. 2002). Guidelines are offered by multiple international associations such as Electric Power Research Institute (EPRI), VGB Powertech, International Association for the Properties of Water and Steam (IAPWS), European Committee for Standardization (CEN), and Finnish Recovery Boiler Committee (FRBC). Out of the guidelines provided by above mentioned organizations, EPRI offers the most detailed recommendations for boilers utilizing all-volatile treatment. Therefore, the guidelines provided by EPRI will be used as the main source of reference.

The guidelines contain specifications for complete water-steam cycle, considering all unit processes. The specifications are also customized for different boilers, regarding operational parameters such as temperature and pressure, equipment materials, and utilized chemical conditioning method. Four operational limits are set for each individual parameter, referred to as action levels. Action levels represent severity of a problem in the water chemistry of the cycle, such as accumulation of impurities (Dooley, et al. 2002). An explanation of the action levels as described by EPRI is shown in Table 1 below.

Table 1. Description of action levels and proposed measures (Dooley et al. 2002)

Level of action	Description
Normal	Values consistent with operational limits, negligible risk of corrosion and deposits.
Action Level 1	Potential risk for accumulation of impurities and corrosion. Values to be normalized within 1 week.
Action Level 2	Accumulation of impurities, risk of corrosion. Values to be normalized within 24 hours.
Action Level 3	Severe risk of rapid corrosion, shutdown of the unit within 4 hours recommended.

Regarding the scope of this study, guidelines for boilers using AVT, caustic treatment (CT), and phosphate treatment (PT) methods with all-ferrous materials are compared. The focus is set on relevant units of the cycle, including guidelines for feedwater, boiler water, and steam. Also, action levels 2 and 3 are left out of the topic since goal is to keep levels of impurities within limits of normal operation. Important monitoring parameters and rationale for their target values are presented in Table 2 below. Chemistry guidelines by EPRI, VGB Powertech, CEN, and FRBC for a boiler with 115 bar drum pressure are shown in Tables 3-5 below.

Table 2. Water-steam cycle chemistry monitoring parameters and rationale for their target values. (Dooley et al. 2002)

Parameter	Rationale for target values
pH	pH monitoring is essential for corrosion inhibition. Maintaining optimal pH value minimizes corrosion throughout the water-steam cycle. Optimal pH also increases magnetite film stability by minimizing its solubility in water. low pH resulting in acidic conditions increases corrosion rate of metal, but too high pH results in alkaline brittleness.
Specific conductivity	Specific conductivity is used for on-line monitoring overall level of contaminants and treatment chemicals in steam-water cycle. Unexplained changes in specific conductivity may indicate a leak or malfunction in some part of the system
Cationic conductivity	Cation conductivity offers reliable on-line monitoring for anionic impurities such as chloride. However, it does not show alkaline contaminants such as sodium hydroxide. If amines are used for feed and boiler water conditioning, their thermal degradation products also increase cationic conductivity, which might hide other contaminants.
Oxygen	High amounts of dissolved oxygen together with corrodent such as chloride and sulfate increase risk of corrosion in boiler tubing. However, very low levels (< 1 ppb) of oxygen, together with high concentrations of reducing agents increase the risk of flow-accelerated corrosion in feedwater system.
Silica	Silica forms hard to remove deposits on turbine blades, which decrease its efficiency and capacity. High concentrations of silica in boiler water increase silica carryover to steam.

Iron	Iron values indicate how well pH control and treatment chemicals are maintaining corrosion inhibition. Iron levels are in relation to iron and magnetite solubility in water, which is bound to pH.
Sodium	Excess amounts of sodium, especially sodium chloride, are cause for corrosion in turbines. Sodium levels for boiler water are set to limit amount of sodium carried over to steam. In CT and PT, sodium levels are monitored together with pH to maintain optimal alkalinity of boiler water.
Chloride	Chloride is major corrodent of water-steam cycle, excess amounts of chloride are harmful both in boiler water and steam. High concentrations of chloride in boiler water usually also increase carryover to steam.
Sulfate	Sulfate, together with chloride, is major corrodent in water-steam cycle. Sulfate may cause corrosion especially in turbine, but can be harmful also in boiler water, if its pH decreases.
Total organic carbon (TOC)	Thermal degradation products of organic contaminants may include organic acids such as acetic or formic acid, which decrease the pH and increase corrosion risk. High amounts of organics may also cause foaming in boiler drum and increase water carryover of other contaminants to steam. If amines are used for water treatment, higher TOC levels are allowed.

Table 3. Water chemistry guidelines for feedwater/attenuator spray by EPRI, VGB PowerTech, CEN, and FRBC. Applied for drum boilers utilizing all-volatile treatment of feedwater with all-ferrous systems. (Dooley et al. 2002, VGB PowerTech e.V. 2011, EN 12952-12: 2003, Vuorinen et al. 2011)

			EPRI	VGB PowerTech	CEN	FRBC
pH		N	9.2 – 9.6	> 9.2	> 9.2	9.3 – 9.6
		AL 1	< 9.2, > 9.6	9.0 – 9.2		< 9.3, > 9.6
Cationic Conductivity	$\mu\text{S}/\text{cm}$	N	≤ 0.2	< 0.2	< 0.2	≤ 0.2
		AL 1	0.2 – 0.4	0.2 – 0.5		0.3 – 1.0 ⁽¹⁾
Oxygen	$\mu\text{g}/\text{kg}$	N	1 – 10	< 100	< 100	1 – 5
		AL 1	10 – 15	100 – 250		5 – 10
Silica	$\mu\text{g}/\text{kg}$	N	≤ 10	< 20	< 20	≤ 5
		AL 1	> 10	20 – 50		10 – 20
Iron	$\mu\text{g}/\text{kg}$	N	≤ 2	< 20	< 20	≤ 5
		AL 1	> 2	20 – 30		10 - 20
Sodium	$\mu\text{g}/\text{kg}$	N	≤ 3	< 5	< 10 ⁽²⁾	≤ 5
		AL 1	3 – 6	5 - 20		10 - 20
TOC	$\mu\text{g}/\text{kg}$	N	< 200		< 200	< 100
		AL 1	> 200			200 – 600 ⁽³⁾

(1 Application of ammonia with organic amines for feedwater conditioning

(2 Sodium and potassium.

(3 Higher TOC allowed if organic amines used for feedwater conditioning

As we can see from Table 3, concentrations of impurities in feedwater are required to be low. The pH is also preferred to be around 9.2 – 9.6, which offers best corrosion inhibition and lowest iron and magnetite solubility. The concentrations of impurities, especially solids such as salts and minerals, must be low so that accumulation of impurities in boiler water is maintained low. More important reason for this is that attenuator spray water for superheated steam is taken from feedwater, which acts as a shortcut for impurities to enter steam. For this reason, solid alkalizing chemicals used for pH conditioning in CT and PT methods must be dosed into feedwater after the attenuator spray water line.

TOC values are preferred to be low, since organic compounds may cause foaming in boiler drum, which increases carryover of impurities to steam. Organic compounds, such as humic acids, and their thermal degradation products may also decrease the pH of boiler water. However, higher TOC values are allowed in plants that use amines for water conditioning since amines themselves naturally increase the TOC concentrations (Vuorinen, et al. 2011).

There is some variation between guidelines offered by different sources, for example oxygen values provided by VGB and CEN are much higher than EPRI and FRBC guidelines recommend. Reason for higher value of oxygen is not clearly stated in VGB guideline, but it is claimed that higher purity of feedwater allows higher oxygen values, which improves beneficial formation of hematite layer on metal surfaces (VGB PowerTech e.V. 2011).

Table 4. Water chemistry guidelines for boiler water by EPRI, VGB PowerTech, and FRBC. Applied for 115 bar drum boilers utilizing all-volatile, caustic, and phosphate treatment with all-ferrous systems. (Dooley et al. 2002, VGB PowerTech e.V. 2011, Vuorinen et al. 2011)

Treatment method			EPRI		VGB PowerTech		FRBC
			AVT	CT	AVT	CT	PT
pH		N	9.2 – 9.6	9.3 – 9.6	≥ 9.2	9.3 – 9.7	9.4 – 9.7
		AL 1	< 9.2, > 9.6	< 9.3, > 9.6	< 9.1	< 9.3, > 9.7	< 9.4, > 9.7
Cationic Conductivity	μS/cm	N	< 5	< 16	< 3	≤ 30	
		AL 1	5 - 12	16 – 32	3 – 6	30 – 50	
Specific Conductivity	μS/cm	N		5 – 16		5 – 12	< 15
		AL 1		< 5, > 16		< 5, > 12	15 – 30
Chloride	μg/kg	N	< 180	< 500			< 400
		AL 1	180 - 320	500 – 1100			1000 - 2000
Sulfate	μg/kg	N	< 330	< 1100			< 800
		AL 1	330 - 660	1100 - 2100			2000 - 4000
Silica	μg/kg	N	< 620	< 620	< 1400 ⁽¹⁾	< 1400 ⁽¹⁾	< 300
		AL 1	620 – 1400	620 - 1400	1400 – 2800 ⁽¹⁾	1400 – 2800 ⁽¹⁾	700 – 1400
Sodium	μg/kg	N	< 800	< 1400			< 3400
		AL 1	800 – 1700	1400 – 2300			> 9200

(1 based on 20 μg/kg silica in steam.

From Table 4 we can see that values for boiler water are allowed to be much higher than for feedwater. The reason for this is that most of dissolved solid impurities stay in the boiler water and are not carried over to steam. Some of the solids still end up in steam, so the guidelines for boiler water are designed to keep the amount of carried over impurities in acceptable values. As the boiler drum pressure increases so does the carryover of impurities, for this reason the guideline limits became stricter as drum pressure increases (Dooley et al. 2002).

The limit values are also higher for CT and PT compared to AVT. Main reason for this is that solid alkalizing agents used in CT and PT have better buffer capability against contaminants, so the boiler water conditions are more stable. In AVT sodium levels are naturally lower than the limit 800 µg/kg presented by EPRI, but this limit allows the use of sodium hydroxide for pH adjustment if the pH of boiler water suddenly drops due to contaminant leak (Dooley et al. 2002).

Table 5. Water chemistry guidelines for steam by EPRI, VGB PowerTech, and FRBC. (Dooley et al. 2002, VGB PowerTech e.V. 2011, Vuorinen et al. 2011)

			EPRI	VGB PowerTech	FRBC
Cationic Conductivity	µS/cm	N	≤ 0.2	< 0.2	≤ 0.2
		AL 1	0.2 – 0.4	0.2 – 0.5	0.3 – 1.0 ⁽¹⁾
Iron	µg/kg	N		< 20	≤ 5
		AL 1		> 20	10 – 20
Chloride	µg/kg	N	< 2		< 3
		AL 1	2 – 4		3 – 6
Sulfate	µg/kg	N	< 2		< 3
		AL 1	2 – 4		3 – 6
Silica	µg/kg	N	< 10	< 20	≤ 5
		AL 1	10 – 20	20 - 50	10 – 20
Sodium	µg/kg	N	< 2	< 5	≤ 5
		AL 1	2 - 4	5 – 10	10 – 20
TOC	µg/kg	N	< 100		< 100 ⁽²⁾
		AL 1	> 100		100 – 500 ⁽³⁾

(1 Application of ammonia with organic amines for feedwater conditioning

(2 Acetate and formiate concentration must be ≤ 15 µg/kg

(3 Higher TOC allowed if organic amines used for feedwater conditioning

Purity of steam is essential for safe and efficient operation of turbine. Impurities in steam are main concern for corrosion and formation of deposits on the turbine. Especially chloride, sulfate, and organic acids in steam may results in corrosion of turbine. Silica in steam forms hard to remove deposits that decrease the efficiency and capacity. Therefore, as we can see from Table 5, guidelines for steam are very strict compared to boiler water (Dooley et al. 2002).

3.3 pH control

pH control is the most notable chemical conditioning method for the whole water-steam cycle. Alkaline conditions allow the best protection against corrosion and minimize the solubility of magnetite film covering the boiler tubes. Optimal pH range for 115 bar drum pressure boiler systems made of carbon steel is 9.2 – 9.6, in which corrosion rate is minimal and magnetite has the lowest solubility. Lower pH values would increase the corrosion rate and dissolution of protective magnetite film. In higher pH values the solubility of magnetite starts increasing again and another problem, alkaline brittleness, arises (Dooley et al. 2002, Vuorinen et al. 2011). Solubility of magnetite as a function of pH in 300 °C is shown in Figure 6 below.

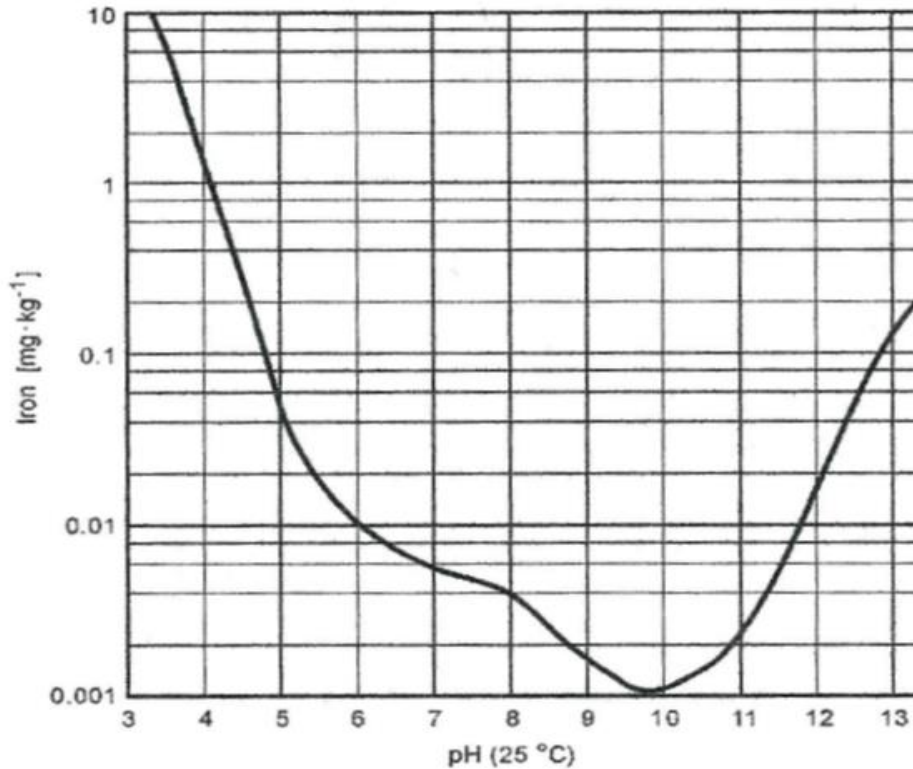


Figure 6. Solubility of magnetite in 300 °C vs pH. (Stodola J. 2003)

Volatile alkali, such as ammonia or amines, are used throughout the water-steam cycle to maintain alkaline pH. Purpose of volatile alkalizing agents is to keep pH above 9 in parts of the cycle, where solid alkalizing agents are not applicable, such as in feedwater, steam, and condensate lines. In addition to this, three main methods used for boiler water pH control are phosphate treatment, caustic treatment, and all-volatile treatment. This additional treatment is used to offer better buffer capability against impurities, since most of the contaminants accumulate in boiler water (VGB PowerTech e.V. 2011).

CT and PT methods utilize solid alkalizing agents to maintain the pH of boiler water in wanted range and offer buffer capacity against impurities that would lower the pH. In CT sodium hydroxide is used and in PT trisodium phosphate. Solid alkalizing agents must be mixed into feedwater downstream of the line where steam attemperator spray water is taken. Solid alkalizing agents can also be dosed directly into boiler drum, but in this case proper distribution and mixing must be ensured (VGB Powertech e.V. 2011).

In AVT method, volatile alkalizing agents such as ammonia and organic amines are used for adjusting the pH of whole water-steam cycle. In addition to this, small amounts of solid alkalizing agent such as sodium hydroxide can be used to increase pH of boiler water, in case of pH decrease due to contaminant leak (Dooley et al. 2002). Functionality of volatile alkalizing agents depends highly on their distribution ratio between water and steam. In boiler with high drum pressure the distribution of more volatile substances, such as ammonia, favors steam. This lowers the buffer capacity of boiler water against contaminants since majority of volatile alkali are transported to steam (VGB PowerTech e.V. 2011).

In high pressure units, better water-steam distribution ratio can be achieved by using a mixture of alkalizing agents of varying volatility, which offers better buffer capacity for boiler water against contaminants. Common alkalizing amines used in mixtures are ethanolamine (EDA), diethylethanolamine (DEAE), cyclohexylamine, (CHA) and morpholine (Morph). In addition to alkalizing agents, commercial mixtures for AVT often contain other conditioning agents such as dispersants, oxygen scavengers and film forming products (Hildén & Pohjanne 2009).

In high pressure and temperature boiler conditions, alkalizing amines and other organic conditioning agents suffer from thermal degradation. However, residence time of conditioning agents in boiler and superheaters is relatively short, so complete thermal decomposition does not have time to occur for most of the organic compounds. Other conditions such as oxygen concentration of boiler water can also alter the thermal degradation process, resulting in different decomposition products. Common thermal degradation products of amines include ammonia, acetic & formic acid, and carbon dioxide. Thermal degradation products such as organic acids and carbon dioxide can lower the pH in water-steam cycle and induce a corrosion risk especially in turbine, steam condenser lines, and steam operated combustion air preheaters. However, in low oxygen conditions organic acids are less likely to be present in degradation products (Hildén & Pohjanne 2009).

Alkalizing amines are by nature weak bases so they only partially dissociate when they are dissolved in water. Dissociation of amines is reversible reaction regulated by chemical equilibrium which depends on temperature and concentration of hydroxyl ions (OH^-) in the solution. Therefore, increasing the amine concentration in boiler water has only slight effect on

the pH. Similarly, addition of other bases, such as NaOH, decreases dissociation of amines, by increasing the OH⁻ concentration of the solution. Dissociation rate of amines also decreases with increase in temperature, making amines relatively weaker bases at high temperatures (Hildén & Pohjanne 2009).

3.4 Oxygen scavengers

Oxygen removal is important for corrosion inhibition in the whole water-steam cycle since corrosion rate of ferrous structures may increase if the oxygen concentration in the cycle is uncontrolled. Oxygen scavengers are used to mitigate any leftover oxygen that was not able to be stripped from feedwater in deaerator. Oxygen scavengers are compounds that bind oxygen to themselves by reacting with it. Common oxygen scavengers used commercially include hydrazine, carbohydrazide, methylethyl ketoxime, and diethylhydroxylamine (Lehtovuori 2007).

Some oxygen scavengers such as hydrazine act as weak bases and are partly dissociated in water. This dissociation reaction is pH sensitive and in more basic conditions most of hydrazine stays in non-ionized form. Therefore, pH affects the reaction kinetics of hydrazine's reaction with oxygen, and high pH promotes its capability to scavenge oxygen (Lehtovuori 2007). Reaction of hydrazine with oxygen is presented in equation below.



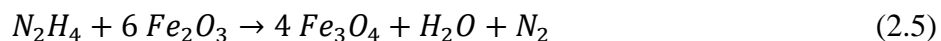
Reaction products of oxygen scavengers and oxygen consist mainly of water and nitrogen gas. Some scavengers also produce carbon dioxide and organic compounds when reacting with oxygen. Similarly to alkalizing amines, oxygen scavengers are also susceptible to thermal degradation in elevated temperatures (Lehtovuori 2007). A list of common oxygen scavengers, their reaction products with oxygen, and thermal degradation products are presented in Table 6.

Table 6. Common water-steam cycle oxygen scavengers, their reaction products with oxygen, and thermal degradation products (Lehtovuori 2007).

Oxygen scavenger	Reaction products with O ₂	Thermal degradation products
Hydrazine	H ₂ O, N ₂	NH ₃ , N ₂
Carbohydrazide	H ₂ O, N ₂ , CO ₂	NH ₃ , N ₂ , CO ₂ , H ₂
Methylethyl ketoxime	H ₂ O, methylethyl ketone, N ₂ O	N ₂ , N ₂ O, methylethyl ketone, NH ₃
Diethylhydroxylamine	H ₂ O, N ₂ , acetic acid	Diethylamine

Reaction and thermal degradation products of oxygen scavengers that contain CO₂ and organic compounds can affect the water quality in water-steam cycle. CO₂ and acetic acid can directly lower the pH and increase the risk of corrosion. Organic reaction products can also suffer from thermal degradation which can lead to formation of organic acids. However, alkalizing agents added to the boiler water should neutralize these acids and keep the pH stable. Especially solid alkalizing agents such as NaOH form less volatile salts, when reacting with organic acids. Non-volatile salts are less likely to be carried over to steam and are then able to be removed from the boiler through blowdown (Lehtovuori 2007).

In addition to this, oxygen scavengers act as reducing agents and react with metal surfaces in a passivation process. They can for example react with oxidized iron surface, reducing oxidation state of iron(III) to iron(II). This reduction forms a protective passivated magnetite film, iron(II, III) oxide, on the surface of boiler tubes (Lehtovuori 2007). Magnetite formation by reaction of hydrazine with iron(III) oxide is presented in equation below.



It should be noted that oxygen scavengers are not mandatory for boiler operation and some plants even utilize a so-called oxygenated treatment (OT) of boiler water. In OT, the oxygen concentration in boiler water is maintained in higher level, allowing a controlled oxide film

formation on the boiler tube surfaces. OT however requires more efficient control of impurities in boiler water, so that the oxide film is not subjected to corrosion, as high level of impurities together with oxygen can lead to severe corrosion rate. Overdosage of oxygen scavengers and the lack of oxygen may also lead to the boiler conditions being too reductive, leading to an increased risk of flow-accelerated corrosion. Therefore, the amount of oxygen scavengers and the oxygen levels used should be carefully controlled (Dooley et al. 2002).

3.5 Film forming amines

Film forming amines (FFA) are aliphatic organic compounds that consist of long hydrocarbon chain with one or more functional amino groups ($-\text{NH}_2$) in their structure. Simplest FFA are monoamines that have only one amino group at the end of the hydrocarbon chain. Their structure makes them amphipathic compounds, possessing both hydrophobic (hydrocarbon chain) and hydrophilic (amino groups) properties.

FFA have an affinity to bond metal surfaces due to lone electron pair of the nitrogen atom in the amino group. For monoamines, this bonding process leaves the hydrophobic hydrocarbon chain pointing outwards of the metal surface, forming a non-wettable film. FFA with more than one amino group, polyamines, are attracted to metal surfaces by multiple amino groups and form a stabler film. The hydrocarbon chains of polyamines are also arranged more horizontally across the metal surface, which improves the cohesive structure of the film (Saario et al. 2014). Film formation with mono- and polyamines on metal surfaces is presented in Figure 7.

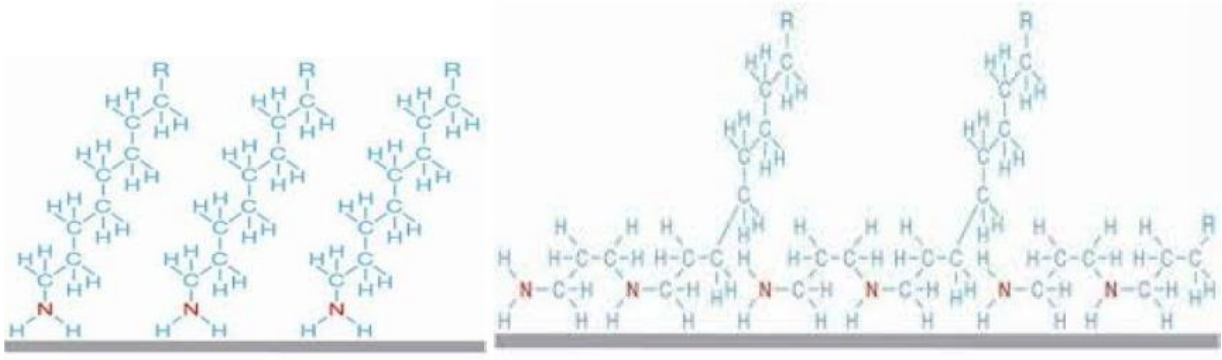
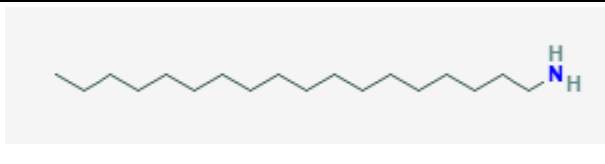
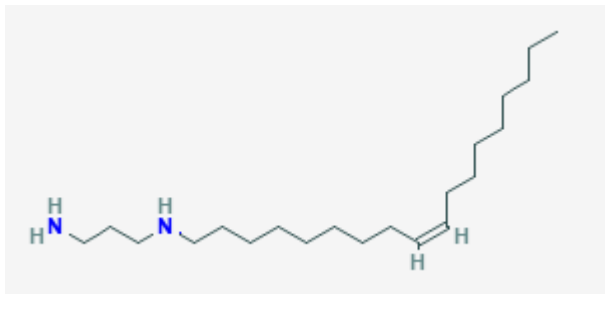
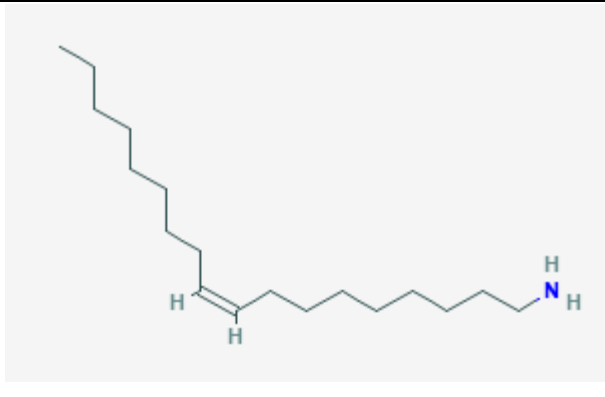
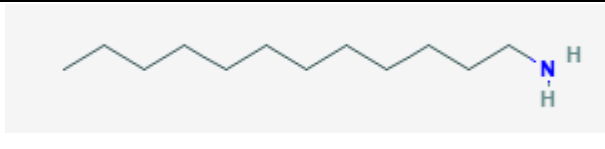


Figure 7. Film formation with mono- (left) and polyamines (right) on metal surface (Saario et al. 2014)

General chemical formula for film forming amines can be written as $R_1-[NH-(R_2)]_n-NH_2$, in which R_1 is unbranched hydrocarbon chain with 12 to 18 carbon atoms, R_2 is short hydrocarbon chain with 1 to 4 carbon atoms, and n is integer between 0 and 7. Simplest FFA commercially used is a monoamine called octadecylamine (ODA, $n = 0$, $R_1 = C_{18}H_{37}$) (Saario et al. 2014). Common FFA products and their structures are presented in Table 7 below.

Table 7. Common film forming amines and their structures (National Center for Biotechnology information 2021)

Compound	Structure
Octadecylamine (ODA)	
Oleyl propylene diamine (OLDA)	
Oleylamine (OLA)	
Dodecylamine (DDA)	

In addition to common FFA presented in Table 7, some chemical suppliers have their own products, which have non-public formulas and structures. One of such FFA product that is commercially used in Finland is marketed by Solenis under trademark Amercor 835s. Amercor 835s itself is a corrosion inhibitor chemical mixture that consist of alkalinizing amines, oxygen scavengers, and FFAs. The FFA in Amercor 835s is claimed to consist of ethoxylated N-(tallow alkyl) trimethylene diamines (Solenis 2020).

Adsorption of FFA on metal surfaces in water-steam cycle forms a protective film that acts as barrier against corrosive contaminants. Hydrophobic properties of the film make the metal surface non-wettable, which blocks dissolved corrodents, such as carbonic acid and oxygen, from interacting with the surface. Strong surface affinity of FFA enables the film to stay intact even if FFA dosage is interrupted, which offers corrosion protection even in cases when there is a problem with dosing. Studies have also concluded that FFA are capable to remove impurities deposited on the surfaces of metal. The mechanism of deposit removal is suspected to be related to their strong surface affinity (Saario et al. 2014, IAPWS TGD8-16(2019)).

FFA adsorption spontaneously occurs when metal surfaces are subjected to solution containing FFA components. In power plants and recovery boilers this can be achieved by continuous dosing of FFA to feedwater or steam header. Film formation is controlled by concentration of FFA in the solution, pH, temperature, and the surface properties of metal. In too high concentrations FFA molecules tend to form micelles in water, which may decrease their film formation activity. For ODA suggested pH range for optimal film formation is from 8.0 to 8.5, outside this range film stability decreases. For other FFA, such as tallow or soya-based products, film stability is ensured within a wider pH range (Saario et al. 2014).

Temperature affects solubility and water-steam distribution ratio of FFA. In higher temperatures their solubility increases, which improves the feasibility of application in boiler conditions. Similarly, the distribution of FFA to steam increases with increase in temperature, which has to be taken into account while planning the dosage. It is also concluded that adsorption kinetics of FFA on metal surfaces favor higher temperatures. Like other organic compounds, FFA also thermally degrade in high temperatures. However, thermal degradation happens in relatively high temperatures and residence time of FFA in boiler and superheaters is short (Saario et al. 2014).

Properties of metal surface, such as magnetite film composition also influence the film formation process. In study by Budhathotki et al. (2020) OLDA film and corrosion resistance properties were studied on fresh carbon steel samples, and samples coated with magnetite. In the study it was determined that OLDA had stronger affinity towards samples with layer of magnetite. Compared to fresh carbon steel samples, the magnetite coated samples were also

determined to be more hydrophobic after OLDA treatment, based on contact angle measurements (Budhathotki et al. 2020).

FFA are often combined with AVT method and dosed into feedwater in a mixture with alkalizing amines and oxygen scavengers. FFA can also be used together with solid alkalizing agents such as sodium hydroxide or sodium phosphates (IAPWS TGD8-16(2019)). With the use of solid alkalizing agents, such as NaOH, it should be noted that overdosing of alkali can have a greater impact on pH, compared to amines. Increase in pH above optimal range of utilized FFA, may results in unsuccessful film formation or stripping off of existing film (Saario et al. 2014). However, there are positive user experiences for utilization of FFA in boilers that have pH up to 11. (Espo J. 2021).

4 BOILER WATER LEAKS

This section covers the background information of leak severity, leak sources and leak detection methods. Severity of leaks in different boiler sections and main corrosion methods leading to tube failures will be discussed. The focus is set on water leaks regarding boiler tubes.

4.1 Leak severity in different parts of the boiler

Leak severity is highly dependent on leak size and where it is located in the boiler. Regarding recovery boilers, even small leaks in lower parts of the furnace can lead to water entering the smelt pool on the floor, which may cause a smelt-water explosion. Small leaks in upper section of the furnace or in the flue gas channel are less critical but may cause decreased energy efficiency. For safety of mill personnel and equipment, large leaks and leaks in critical parts of the boiler usually demand immediate emergency shutdown procedure (ESP) (Singh & Mahmood 2007, BLRBAC 2018). A description of leak criticality categories by BLRBAC is presented in Table 8.

Table 8. Water leak criticality in recovery boilers (BLRBAC 2018)

Leak criticality	Description
Class I	Large leaks where water is certain to reach the hearth. Fractures and ruptures of floor, wall, screen, and roof tubes.
Class II	Small leaks located where there is high likelihood water will reach the hearth. Small leaks located in floor tubes and lower furnace wall tubes, and spout leaks.
Class III	Large leaks located where water is unlikely to reach the hearth. Generating bank tube ruptures.
Class IV	Small leaks located where there is little likelihood water will reach the hearth. Small leaks in screens, generating bank tubes, wall tubes high in the furnace, external leaks in non-membrane wall units.

Leaks that have a risk of water entering the smelt pool in the furnace floor are considered the most critical. Small leaks are less critical, since a small amount water is evaporated before it can enter the furnace floor. Severity of the leak increases as the leak sizes increases, so a small leak in critical area can become more dangerous if the leak expands over time.

4.2 Leak sources

Recovery boiler is a complex unit, and its different sections suffer from different stress factors. Main causes for tube failures in different parts of the boiler are corrosion, thermal fatigue, and mechanical erosion. Corrosion failures can be further divided to categories based on location and corrosion mechanism, typical division includes gas side corrosion, furnace corrosion, and waterside corrosion (Vakkilainen 2005).

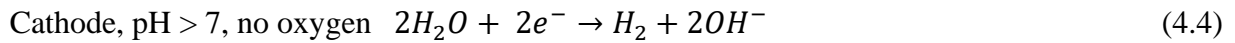
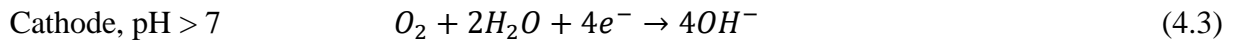
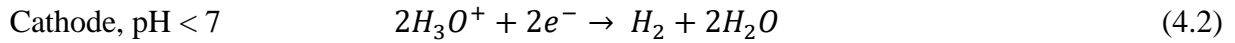
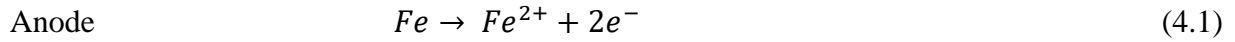
Recovery boiler has typically high carryover of inorganic material, since black liquor contains a mixture of cooking chemicals and inorganic impurities from wood. Inorganics are carried over to superheaters and flue gas channel where they form deposits on tube surfaces that decrease

heat transfer and can be corrosive. Especially alkali, sulfides, and chlorides are known to cause corrosion of superheaters and upper parts of the boiler (Vakkilainen 2005).

Furnace floor and lower furnace walls are perhaps under the most serious stress compared to other parts of the boiler. Lower furnace is where combustion takes place, so it is the area with highest temperature in the boiler. There is also the highest amount of corrosive material, such as the black liquor and smelt on the floor, that causes even more stress on the structures. Tube failures in floor and lower furnace walls are also most critical since water can directly enter the hearth. Lower furnace tubing is therefore usually made from higher grade materials, such as high alloy steel or compound structures. Typical furnace corrosion mechanisms include tube cracking, caused by thermal fatigue and chemical corrosion, and smelt corrosion, caused by chemical corrosion of metal in contact with smelt (Vakkilainen 2005).

Waterside corrosion is mainly caused by corrosive contaminants in the boiler water. As discussed in chapter 3, Water chemistry of recovery boiler must be carefully maintained to mitigate risk of corrosion. pH and corrosive impurities such as oxygen, chlorides, and sulphates are the main risk factors for direct waterside corrosion. Waterside contaminants are also linked to furnace side corrosion, as impurities can form deposits on the waterside tube surfaces. These deposits decrease the heat transfer efficiency and may cause overheating of furnace walls. Overheating causes thermal stress and can lead to cracking of tubes (Vakkilainen 2005).

General carbon steel corrosion is an electrochemical reaction series taking place on the metal surface. Two simultaneous electron transfer reactions are required for corrosion to occur, called anodic and cathodic reactions. On the anode, iron is oxidized, and electrons are released. Cathodic reaction is dependent on the properties of electrolyte, in this case the most important characteristics are pH and oxygen concentration of the boiler water. In low pH, hydronium ions are reduced, resulting in formation of hydrogen gas and water. In alkaline high pH conditions however, there are no hydronium ions present and the cathodic reaction involves reduction of dissolved oxygen and water, resulting in formation of hydroxide ions. In alkaline conditions when oxygen is not present, water molecules are reduced forming hydrogen gas and hydroxide ions (Lehtovuori 2007, LUT Moodle 2020). Typical anodic and cathodic reactions involved in corrosion of iron are presented below.



4.3 Leak detection methods

Small leaks caused by cracks in the tubing can be considered less critical than full-sized tube ruptures, but even small leaks typically expand over time. Detection of even small leaks can improve the safety of boiler operation, since actions can be taken before anything critical occurs. Several leak detection methods are utilized, and leak detection systems are commercially offered by multiple companies. Commonly used leak detection methods include water-steam mass balance monitoring, boiler water quality monitoring, and monitoring of acoustic emissions (Karjunen 2017).

Water-steam mass balance monitoring is a fairly straightforward method, if there is an unexplainable difference in the balance, it would indicate a water leak. Mass balance monitoring methods are reported to be able to detect leaks as low as 0.5 kg/s. There is some uncertainty in the monitoring since the water/steam flow meters are not absolutely accurate. Changes in boiler load also decrease the steam production of the boiler, which tends to lead to a lowered water level in the drum, as the circulating steam volume is smaller. This forces boiler automation to increase the feedwater input to increase the water level in the drum. This may cause fluctuation in the mass balance, which can indicate invalid detections of leak. Invalid leak alarms can make the system seem impractical and make it less trustworthy in the eyes of boiler operators (Karjunen 2017).

Boiler water quality monitoring is based on some traceable water quality parameter, that is used for leak indication. Typically, some chemical compound is used as a tracer, and its concentration

is monitored continuously. In boilers utilizing PT, boiler water phosphate levels and conductivity are often monitored, and this can be used as a leak indicator. A decrease in phosphate concentration or conductivity, would indicate a boiler leak. For example, Valmet Automation has a leak detection system based on combination of water-steam mass balance and phosphate monitoring. Other additional tracer chemicals can also be dosed into boiler water and used for leak detection; one such system is provided by Nalco that utilizes a fluorescent tracer chemical (Karjunen 2017).

Acoustic emissions monitoring is based on sensors that can detect noise and vibration caused by leaks and cracks in boiler tubing. Sensors are attached to the boiler structures, and they can detect specific frequencies travelling through air, fluid inside boiler tubing, or boiler structure (Kouvo, 2019).

APPLIED PART

5 TRACER CHEMICALS

Tracers are chemical substances used to monitor and identify physical, chemical, and biological processes such as flow rates or adsorption of liquids and gases. Tracer techniques are utilized in many fields including biochemistry, environmental analytics, oil and chemical industry.

This section explores general principles of tracer chemicals and different tracer types that are used commercially. Tracer dosage and monitoring is also discussed. Focus is set on potential sodium-based tracers that could be utilized in recovery boilers together with AVT method.

5.1 General principle

In principle, any chemical substance can be used as a tracer, as long as it acts inertly in its surrounding environment, and it can be accurately measured. Ideally the tracer should have high solubility in the medium it is used in, and it should not react with other substances or surface materials in the process. There also should not be other external or internal sources for said substance, as it could distort the measurement of tracer. Accuracy and affordability of tracer monitoring should also be considered while for choosing tracer substance. Lastly, tracer should not pose a risk to environmental or human health (Healy & Scanlon 2010).

Common commercially used tracers include radioactive, fluorescent, and chemical tracers. Radioactive tracers utilize radioactive isotopes, that behave similarly in chemical and biological manner as their non-radioactive counterparts. Radioactivity of these tracers can be detected in extremely low concentrations (Crespi 1971). Fluorescent tracers emit light, or other electromagnetic radiation, which can be detected by measuring fluorescence of a fluid sample, most commonly water. Fluorescent tracer technique has been applied for recovery boiler leak detection by Nalco Chemical Company. (Diambri 2000). Chemical tracer can basically be any chemical applied to monitoring target. Chemical tracers can be detected through different analytical techniques such as chromatographic methods or ion selective electrodes.

Tracer technique can either be performed as continuous dosing and monitoring, or as a pulse application, depending on monitoring target. For the application of recovery boiler waterside leak detection, continuous dosing would be most suitable. Leak detection for recovery boiler can be executed by balancing a continuous dosage of non-volatile tracer to boiler water with the boiler blowdown flow rate. The tracer concentration in boiler water can then be monitored with an on-line analyzer, and a decrease in concentration would indicate a water leak in the boiler (Diambri 2000).

5.2 Sodium based tracer chemicals

Sodium is a reactive alkali metal, that reacts with water forming sodium hydroxide. Sodium hydroxide is a non-volatile strong base that completely dissociates in water to sodium- and hydroxide-ions, forming a strongly basic solution. Sodium hydroxide reacts with acids in a neutralization reaction, forming sodium salts. An example of this is a reaction of NaOH with hydrochloric acid (HCl), resulting in sodium chloride (NaCl). Sodium hydroxide solution can also react with other substances, such as aluminum, which results in formation of sodium aluminate (NaAlO_2) Most sodium compounds are readily soluble in water and are by nature either neutral or basic.

Sodium hydroxide, and sodium salts, are ionic compounds that consist of positive sodium cations (Na^+) and negative anions. Sodium concentrations in water can be accurately analyzed with ion-selective electrodes. Commercial on-line sodium analyzers can detect concentrations as low as 0.001 parts per billion (ppb). For contrast, 0.2 ppb of sodium hydroxide would increase conductivity of water by 0.001 $\mu\text{S}/\text{cm}$, which is virtually undetectable in most cases due to background conductivity caused by other dissolved substances (Mettler-Toledo Thornton, Inc. 2014).

Regarding recovery boilers, plants that utilize PT and CT methods have already high sodium levels, which could be utilized for leak detection by sodium balance monitoring. For boilers using AVT method, moderate amount of sodium is allowed in the boiler water, but natural background sodium levels are relatively low (Vänskä 2019). Figure 8. presents boiler water sodium concentrations of a recovery boiler utilizing AVT method in Metsä Fibre Äänekoski mill measured between 2018 and 2019.

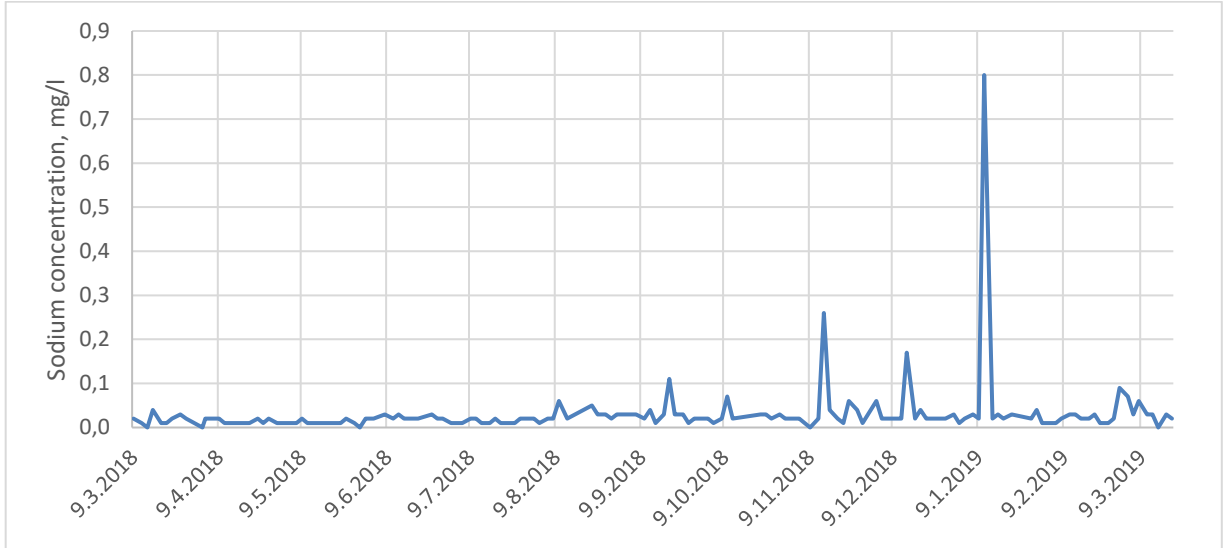


Figure 8. Boiler water sodium concentrations in a recovery boiler utilizing AVT method in Metsä Fibre Äänekoski mill between 2018 and 2019 (Vänskä 2019)

As we can see from Figure 8, sodium levels in boiler water using AVT are relatively low during normal operation. The average concentration of sodium in boiler water was 31 ppb during the measurements period, which is far less than the EPRI guideline value of <800 ppb (table 4). So, in theory there is space to increase the sodium concentration of boiler water and use sodium as a tracer. However, many sodium compounds are basic, so increase in the pH of boiler water should be considered while designing dosage.

Sodium hydroxide could be used as a potential tracer chemical since it is already established as a safe chemical for purposes of pH control in boiler water. NaOH as a tracer would introduce excess hydroxide ions to the boiler water, which would also increase its buffer capacity against acidic contaminants. Another reason to support the use of NaOH as tracer is that hydroxide ions are unlikely to form insoluble deposits with contaminants such as calcium or magnesium.

As described in AVT guideline by EPRI (Dooley, et al. 2002 p. 6-2) Solid alkalis such as trisodium phosphate or sodium hydroxide may be used together with AVT of boiler water to increase its buffering capacity, as long as concentration of solids in boiler water does not exceed recommended values. Similar proposition for use of solid alkali in high pressure boilers as pH buffers together with FFA products is presented in IAPWS guideline for the use of film forming

substances (IAPWS TGD8-16(2019), p. 26). According to representative of Solenis, manufacturer of Amercor 835s, corrosion inhibition product utilized in recovery boiler in Metsä Fibre Äänekoski mill, there should be no adverse effects to function of their FFA product with addition of NaOH to the boiler water, and the limit value for NaOH addition should be considered with pH and sodium guideline values for specific boilers (Huhtiniemi 2021).

However, no detailed studies regarding the compatibility of NaOH with FFA products, or alkalizing amines altogether were found. To ensure that the addition of NaOH does not adversely affect the stability of FFA or induce a risk of corrosion to the water-steam cycle, field studies should be conducted. If the use of NaOH is proven to be safe, the required dosage and the accuracy of detection method with NaOH as a tracer can be further experimented on.

Other sodium compounds could also be considered for tracer, but special attention should be paid to not cause corrosion or deposit risks in the boiler. For example, chlorides and sulphates are linked to increased corrosion risk, and carbonate could precipitate calcium and magnesium. Organic salts of sodium are likely to suffer from thermal degradation, which may introduce harmful degradation products such as CO₂ or organic acids to boiler water. Some studies and patents are available for the use of sodium compounds as tracer in boiler water systems, such as sodium naphthalenesulfonate (Hoots & Hunt 1987) and sodium molybdate (Chen et al. 1998). However, in case of sodium naphthalenesulfonate, it is used as a fluorescent tracer, and for sodium molybdate the traced element is molybdenum.

5.3 Sodium Tracer Monitoring and Dosage

Reliable and accurate monitoring of tracer concentration in the boiler water is the key to effective tracer technique. Monitoring should be performed with a continuous on-line analyzer, that has good sensitivity and accuracy. Sodium analyzers are pH and temperature sensitive, so they usually have a built in pH and temperature compensator, combined with both pH and sodium reference electrodes. The sodium electrode may also suffer from interference of other cations such as ammonium (NH₄⁺) (Mettler-Toledo Thornton Inc. 2014). There is always going

to be some systematic error in the accuracy of tracer analyzer, but a gradual decrease in boiler water sodium concentration should indicate a leak in the system.

Designing the optimal tracer dosage, several factors should be considered. The sensitivity of tracer analyzer should not be a problem since commercial sodium analyzers have quite wide sensitivity ranges, from 0.001 ppb up to 100 ppm. Higher dosage could improve the leak detection since as the changes in background sodium concentration would not affect the total concentration as much. Higher tracer concentration could also improve the detection time of leaks since higher concentration leads to a greater decrease in concentration in the event of leak. However, the decrease speed is always proportional to concentration, so the percentual decrease will be the same with different concentrations.

Another thing to consider is that the tracer dosage should not exceed values presented in water quality guidelines. Likewise, if basic tracer is used, such as NaOH, tracer dosage should not increase pH of boiler water over the guideline limits. Estimations for pH with different NaOH additions can be made if the original pH of boiler water containing amines is known. For reference, boiler water pH values for a recovery boiler utilizing AVT method in Metsä Fibre Äänekoski mill between 2018 and 2019 are presented in Figure 9 below.

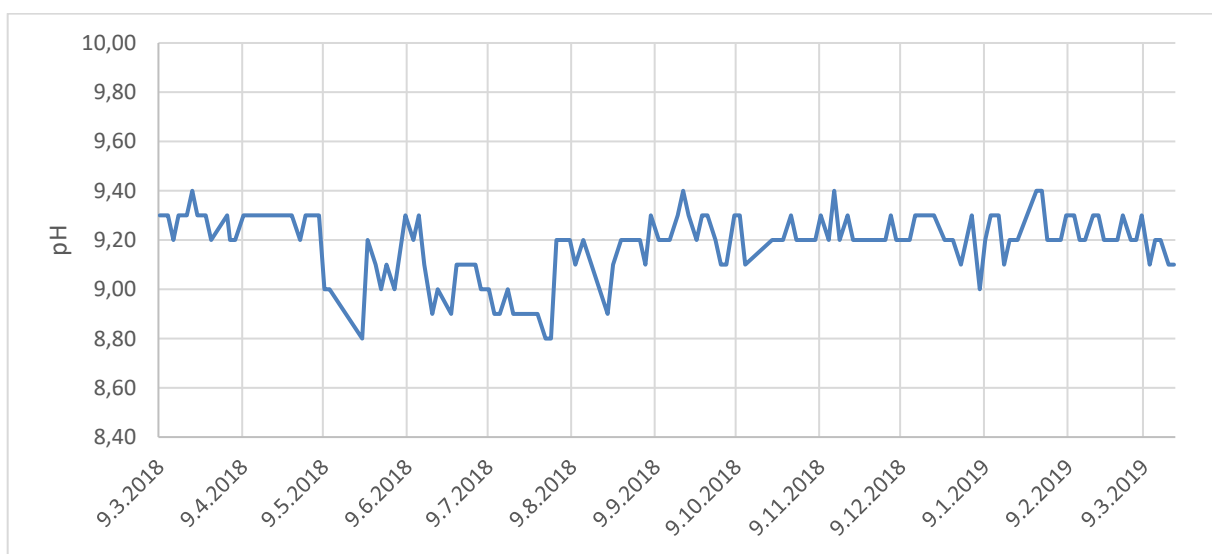


Figure 9. Boiler water pH in a recovery boiler utilizing AVT method in Metsä Fibre Äänekoski mill between 2018 and 2019 (Vänskä 2019)

As we can see from Figure 9, the boiler water pH in this specific AVT method utilizing boiler has ranged between 8.8 – 9.4, averaging at 9.2. The EPRI guideline value for pH is to stay between 9.2 – 9.6, for both AVT and CT methods. However, the VGB guidelines for CT allow upper pH limit up to 9.7. According to these guidelines and results presented in Figure 9, in this specific boiler, there is still room to increase the pH of boiler and it could even be considered recommended.

It should be noted that the amount of NaOH in moles, corresponds to same amount in sodium ions in the solution, but the analyzers usually express the sodium concentration in ppm or ppb, which corresponds to mg/l or $\mu\text{g/l}$. The concentration expressed as ppm or ppb for sodium ions and NaOH in solution however are not the same, as they have different molar masses. For future references, all figures from calculations regarding sodium or NaOH will be expressed as concentration of sodium ions.

Because NaOH is a strong base, it dissociates completely in water, so the molar concentration of hydroxide ions in the solution equals that of NaOH. Although amines are weak bases and do not dissociate completely, the amount of hydroxide ions existing in amine solution can be calculated if the pH is known. pH of a basic solution, and amount of hydroxide ions in solution with known pH can be calculated with equations 5.1 & 5.2. Estimations for pH of amine-NaOH mixtures for with different initial amine solution pH values and different sodium concentrations are presented in Figure 9.

$$pH = 14 + \log_{10}[\text{OH}^-] \quad (5.1)$$

$$[\text{OH}^-] = 10^{(pH-14)} \quad (5.2)$$

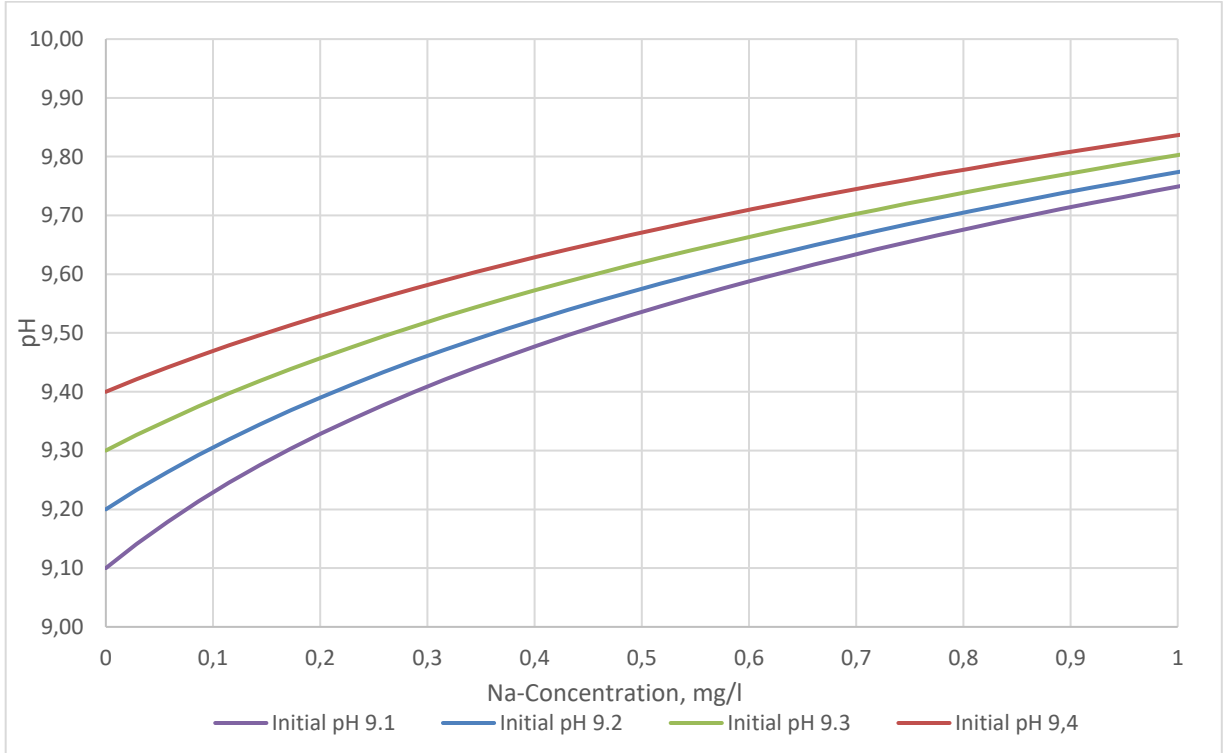


Figure 9. Estimation for pH of amine-NaOH mixture for different sodium concentrations with initial amine solution pH values between 9.1 - 9.4

As we can see from Figure 9, with these initial pH values and sodium concentration of 0,5 mg/l, the pH would be ranging between 9.53 – 9.67. Regarding the EPRI and VGB guidelines, NaOH-amines-mixtures in boiler water with sodium concentration up to 0,5 mg/l could be considered safe in long term operation. Since the pH scale behaves logarithmically, even if the sodium concentration in the boiler water happens to increase slightly above the dosage concentration due to some unexpected circumstances, the pH does not dramatically increase. For example, in this scenario, at sodium concentration of 1.0 mg/l the pH would be between 9.75 – 9.84, which is above the recommended guidelines, but not so high that it would require immediate shutdown of the boiler.

6 LEAK DETECTION WITH TRACER CHEMICALS

In this section the principles of tracer mass balance in boiler and different factors affecting the leak detection effectiveness are discussed. Scenarios with variability in factors such as boiler size, blowdown and leak flow sizes, and the tracer dosage are studied. The topic is discussed theoretically for general knowledge and as preparation for experimental work.

6.1 Boiler Mass Balance

To better understand the principles of leak detection with a tracer, it is necessary to study the mass balances regarding the boiler. During steady-state boiler operation the incoming and outgoing sodium-flows will balance over time and the sodium concentration in boiler water settles to a stable value. During a leak, the sodium output from the boiler water is increased, which disrupts the balance, and the concentration in boiler water gradually decreases to a new value. Similarly, leaks into the boiler water cycle may introduce excess sodium that can disrupt the balance by increasing the input flow. A flow chart representing a boiler water system with sodium tracer dosage is presented in Figure 10 below.

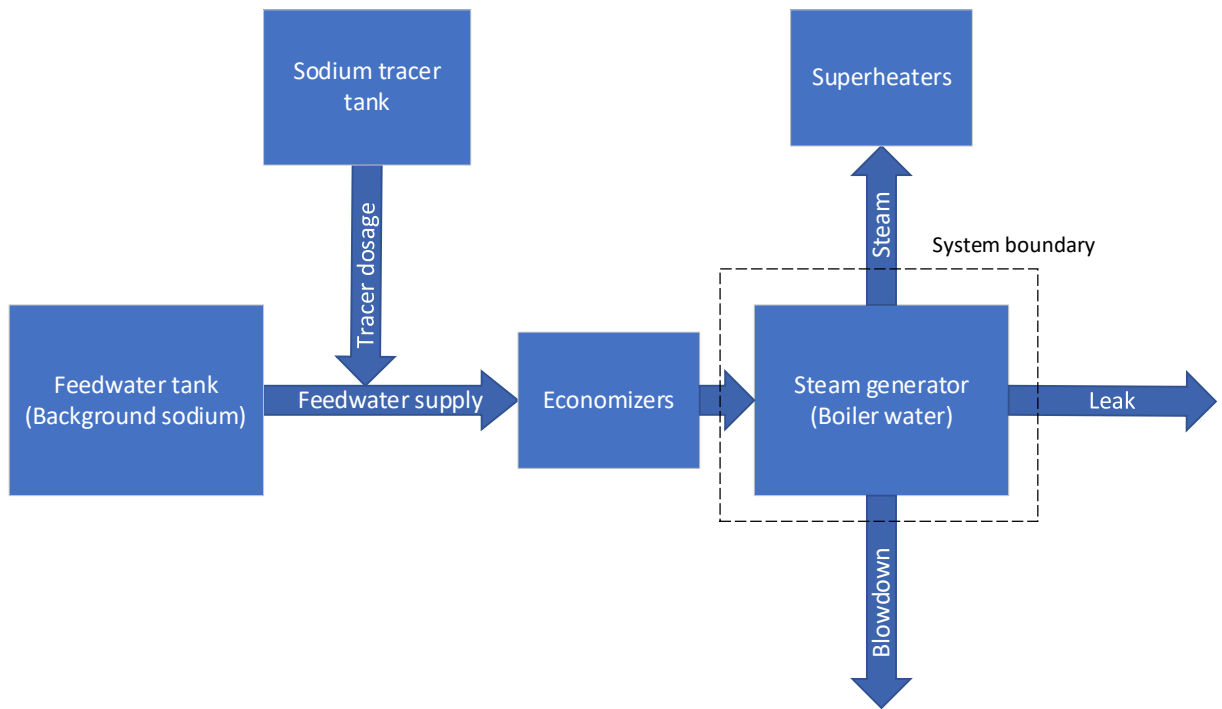


Figure 10. Flow chart of water and sodium tracer flows in boiler water system

The sodium mass balance over the system boundary presented in Figure 10. can be simply described as

$$\dot{m}_{Na,in} - \dot{m}_{Na,out} = \frac{dm_{Na}}{dt} \quad (6.1)$$

where $\dot{m}_{Na,in}$ is sodium entering the boiler water, mg/s

$\dot{m}_{Na,out}$ is sodium leaving the boiler water, mg/s

$\frac{dm_{Na}}{dt}$ is change in sodium mass in boiler water over time, mg/s

Water and steam flows in boiler systems are usually measured and expressed as mass flows. As the temperature and pressure inside the boiler are significantly higher than normal atmospheric conditions, the water density inside the boiler is also significantly lower. To simplify the expression of mass balances, the sodium concentration in each flow and part of the boiler system shall be expressed as a mass fraction of corresponding unit. Therefore, specific sodium mass flow over a system boundary can also be expressed as

$$\dot{m}_{Na,i} = \dot{m}_i * w_i \quad (6.2)$$

where \dot{m}_i is water mass flow of specific flow over system boundary, kg/s
 w_i is sodium mass fraction, mg/kg

Water is continuously evaporated and leaves the boiler as steam. Equivalent amount is replaced with feedwater that contains small amount background sodium. Additionally, sodium tracer solution is dosed into feedwater line to increase the sodium content. Sodium compounds may be considered non-volatile, so the tracer does not leave the boiler with steam, instead it is concentrated in the boiler water. A continuous blowdown of boiler is used to remove impurities from boiler water, which at the same time removes some sodium. A leak behaves similarly to blowdown, diluting the boiler water by removing sodium from it. Over time, sodium coming from feedwater supply forms a balance with blowdown and leak flows and the sodium concentration in the boiler water settles to a stable concentration. It should also be noted that a small amount of sodium enters the steam through mechanical carryover, removing a small amount of sodium from boiler water. With this in mind, Equation 6.1 can be expanded and written as follows.

$$\dot{m}_{fw} * w_{fw} + \dot{m}_D * w_D - \dot{m}_S * w_S - \dot{m}_{BD} * w_{BW} - \dot{m}_L * w_{BW} = \frac{dm_{Na}}{dt} \quad (6.3)$$

where \dot{m}_{fw} is feedwater flow, kg/s

- w_{fw} is background sodium mass fraction in feedwater, mg/kg
- \dot{m}_D is sodium tracer dosage flow, kg/s
- w_D is mass fraction of sodium in tracer dosage solution, mg/kg
- \dot{m}_s is steam flow, kg/s
- w_s is mass fraction of sodium in steam, mg/kg
- \dot{m}_{BD} is blowdown flow, kg/s
- w_{BW} is sodium mass fraction in boiler water, mg/kg
- \dot{m}_L is leak flow, kg/s

The total mass of sodium in boiler water can be described as

$$m_{Na} = w_{BW} * m_{BW} \quad (6.4)$$

where m_{Na} is total mass of sodium in boiler water, mg

m_{BW} is boiler water mass, kg

Boiler load changes affect the evaporation of water in boiler, which changes the water/steam fraction, resulting in change of water level inside the drum. Automation detects changes in drum level and adjust the feedwater flow accordingly. The water/steam fraction, controlled by boiler load, also changes the total mass of water inside the boiler. In narrow time scale, or during changes in boiler load, this may cause fluctuation in both feedwater flow, and mass of water inside the boiler. However, over larger time frame an average of feedwater flow can be utilized for calculations and if there are no significant changes in boiler load, the water mass inside boiler can be considered constant. Since the mass of boiler water inside the boiler may be

considered constant, a change in total mass of sodium equals a change in sodium mass fraction times boiler water mass. Therefore, equation 6.4 may be plugged into equation 6.3, resulting in

$$m_{BW} * \frac{dw_{BW}}{dt} = \dot{m}_{fw} * w_{fw} + \dot{m}_D * w_D - \dot{m}_s * w_s - \dot{m}_{BD} * w_{BW} - \dot{m}_L * w_{BW} \quad (6.5)$$

Equation 6.5 as it is presented is valid at every point in time, but since there is mostly likely fluctuation in both the flow and concentration measurements, the situation should be viewed over a wider time frame. This can be achieved by integrating the equation over a time period and by using average measurements of the variables. Integral of the Equation 6.5 may be presented in its general form as follows.

$$\int_0^{w_{bw,t}} (m_{BW}) dw_{BW} = \int_0^t (\dot{m}_{fw} * w_{fw} + \dot{m}_D * w_D - \dot{m}_s * w_s - \dot{m}_{BD} * w_{BW} - \dot{m}_L * w_{BW}) dt \quad (6.6)$$

Equation 6.6 may be calculated over a sufficient time span and the leak flow solved from it. Boiler water mass may be considered as constant since the water level in boiler is measured and controlled by automation and during steady-state operation the water level stays constant on average. The dosing pump is also preferably set to a constant value and the dosing solution concentration should remain constant, as it sits in a dosing tank. Other variables in the equation, except the leak flow as it is unknown, are based on continuous measurements from the mill. Solved leak flow from Equation 6.6 that is integrated over 8 hours is presented below.

$$\dot{m}_L = \frac{(\dot{m}_{fw,ave\ 8h} * w_{fw,ave\ 8h} + \dot{m}_D * w_D - \dot{m}_{s,ave\ 8h} * w_{s,ave\ 8h} - \dot{m}_{BD,ave\ 8h} * w_{BW,ave\ 8h}) * 8h - m_{BW} * \Delta w_{BW,8h}}{w_{BW,ave\ 8h} * 8h} \quad (6.7)$$

Where subscript *ave 8h* means average of the variable over 8h

6.2 Tracer Concentration Decrease During Leak

The boiler water mass balance discussed in previous chapter can also be used for calculating estimations on how the tracer concentration behaves in different leak scenarios. For this purpose, we can start by integrating Equation 6.6 over a small time step and solving the change in boiler water sodium mass fraction from it.

$$\Delta w_{BW,\Delta t} = \frac{(\dot{m}_{fw} * w_{fw} + \dot{m}_D * w_D - \dot{m}_S * w_S - \dot{m}_{BD} * w_{BW,t-\Delta t} - \dot{m}_L * w_{BW,t-\Delta t}) * \Delta t}{m_{BW}} \quad (6.8)$$

where $w_{BW,t-\Delta t}$ is boiler water sodium mass fraction at previous time step, mg/kg

Δt time step, s

For simplification of estimations with equation 6.8, feedwater, tracer dosing, and steam flow and their corresponding mass fractions may be considered as constants. At time $t = 0$ the system may be considered to be in a steady state without a leak and the sodium mass balance can be expressed as

$$\dot{m}_{fw} * w_{fw} + \dot{m}_D * w_D - \dot{m}_S * w_S = \dot{m}_{BD} * w_{BW,t=0} \quad (6.9)$$

where $w_{BW,t=0}$ is initial sodium mass fraction in the boiler water, mg/kg

which can be replaced into equation 6.8 resulting in

$$\Delta w_{BW,\Delta t} = \frac{(\dot{m}_{BD} * w_{BW,t=0} - \dot{m}_{BD} * w_{BW,t-\Delta t} - \dot{m}_L * w_{BW,t-\Delta t}) * \Delta t}{m_{BW}} \quad (6.10)$$

For Equation 6.10 blowdown flow, sodium concentration at time $t = 0$, leak flow, and boiler water mass may be considered as constants, that can be chosen to represent different leak scenarios. Term $w_{BW,t-\Delta t}$ for successive times steps is obtained as the equation is calculated. At $t = \Delta t$, $w_{BW,t-\Delta t}$ equals $w_{BW,t=0}$. The change in sodium mass fraction in boiler water may also be expressed as

$$\Delta w_{BW,\Delta t} = w_{BW,t} - w_{BW,t-\Delta t} \quad (6.11)$$

Which can be replaced to Equation 6.10 resulting in

$$w_{BW,t} = w_{BW,t-\Delta t} + \frac{(\dot{m}_{BD} * w_{BW,t=0} - \dot{m}_{BD} * w_{BW,t-\Delta t} - \dot{m}_L * w_{BW,t-\Delta t}) * \Delta t}{m_{BW}} \quad (6.12)$$

Estimations with equation 6.12 should be done over small time steps for better accuracy. Estimations for tracer concentration decrease over time for different initial tracer concentrations, leak sizes, boiler water masses, and blowdown flows are presented in Figures 11-14.

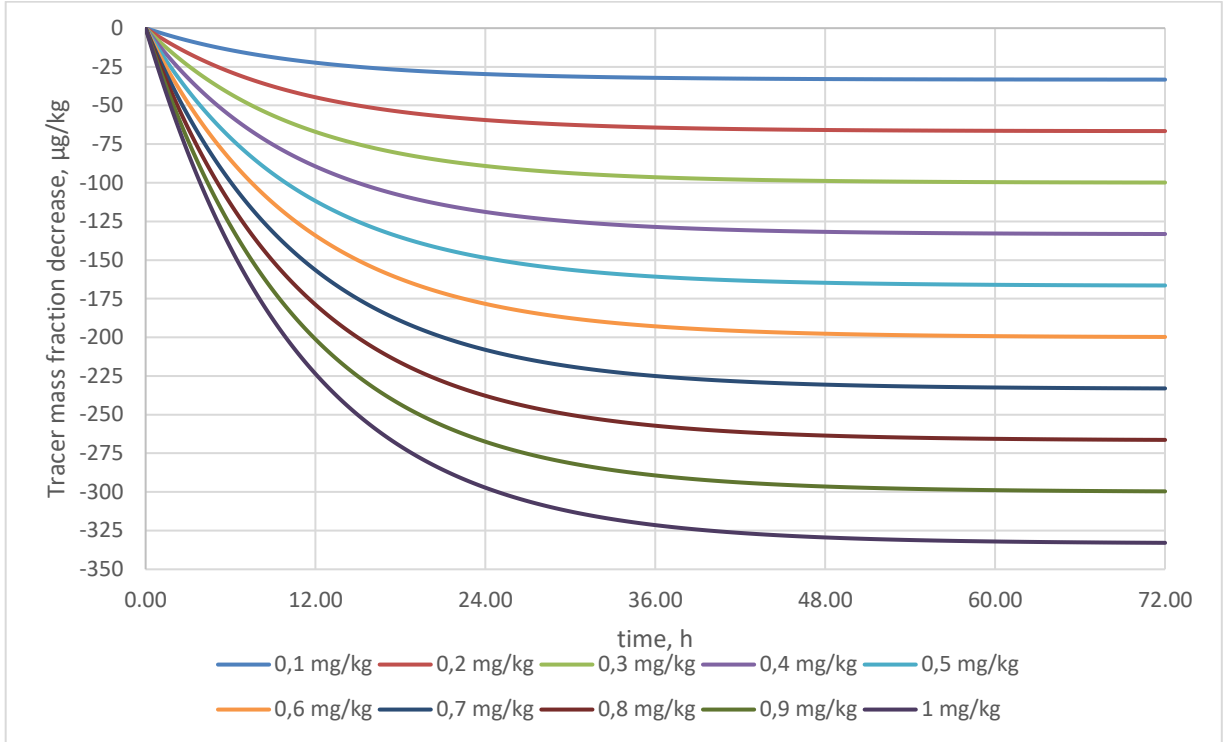


Figure 11. Estimation of tracer mass fraction decrease over time for different initial mass fractions in boiler with boiler water mass of 350 tons, blowdown flow of 6 kg/s, and leak flow of 3 kg/s

As we can see from Figure 11, tracer mass fraction decrease over time is proportional to initial mass fraction, but the percentual decrease is identical. A 10% decrease for this case is achieved in approximately 4 hours with all initial mass fractions. However, this estimation does not consider the fact that leaks tend to expand over time, which would lead to gradual increase of the leak flow.

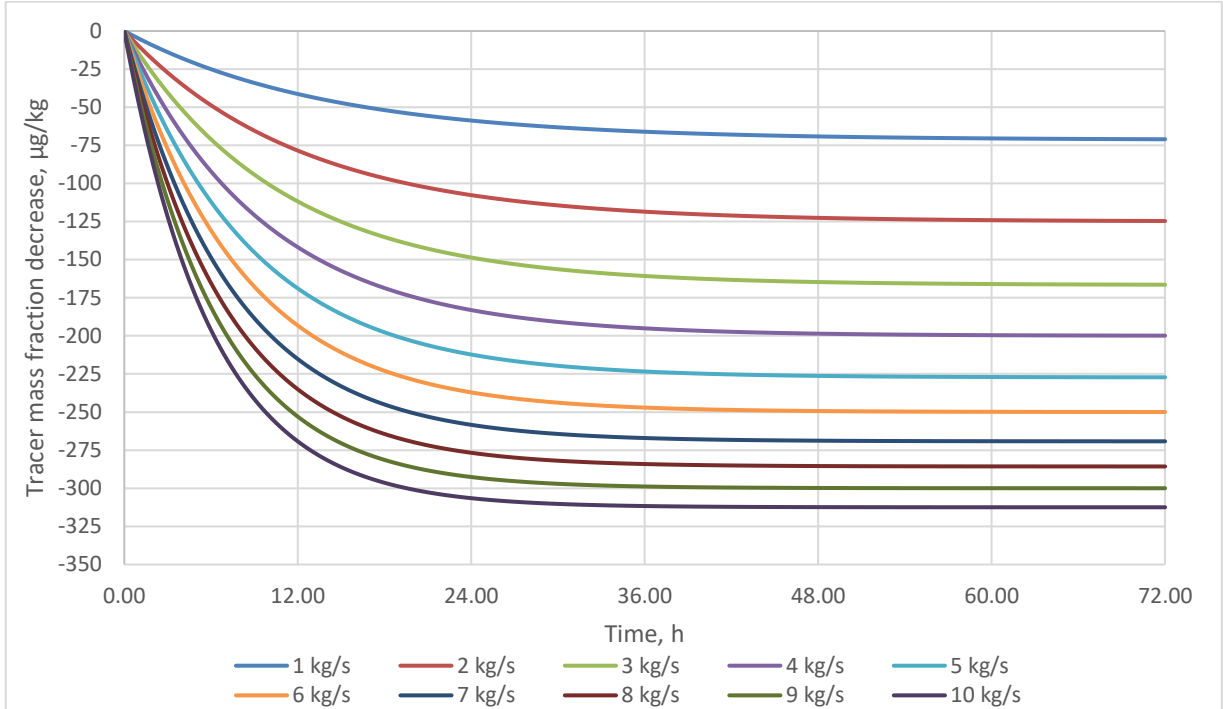


Figure 12. Estimation of tracer mass fraction decrease over time for different leak sizes in boiler with boiler water mass of 350 tons, initial tracer concentration of 0.5 mg/kg, and blowdown flow volume of 6 kg/s

Figure 12 presents how leak size affects the tracer mass fraction decrease. As expected, bigger leaks cause a faster decrease in mass fraction, so they can be detected in less time. Smaller leaks require more time to be detected but they are also usually less critical. Bigger leaks also lead to greater mass fraction decrease, which makes them easier to detect. In this case the mass fraction decrease for all leak sizes starts to flatten out after approximately 60 hours, but bigger leaks lead to overall greater decrease.

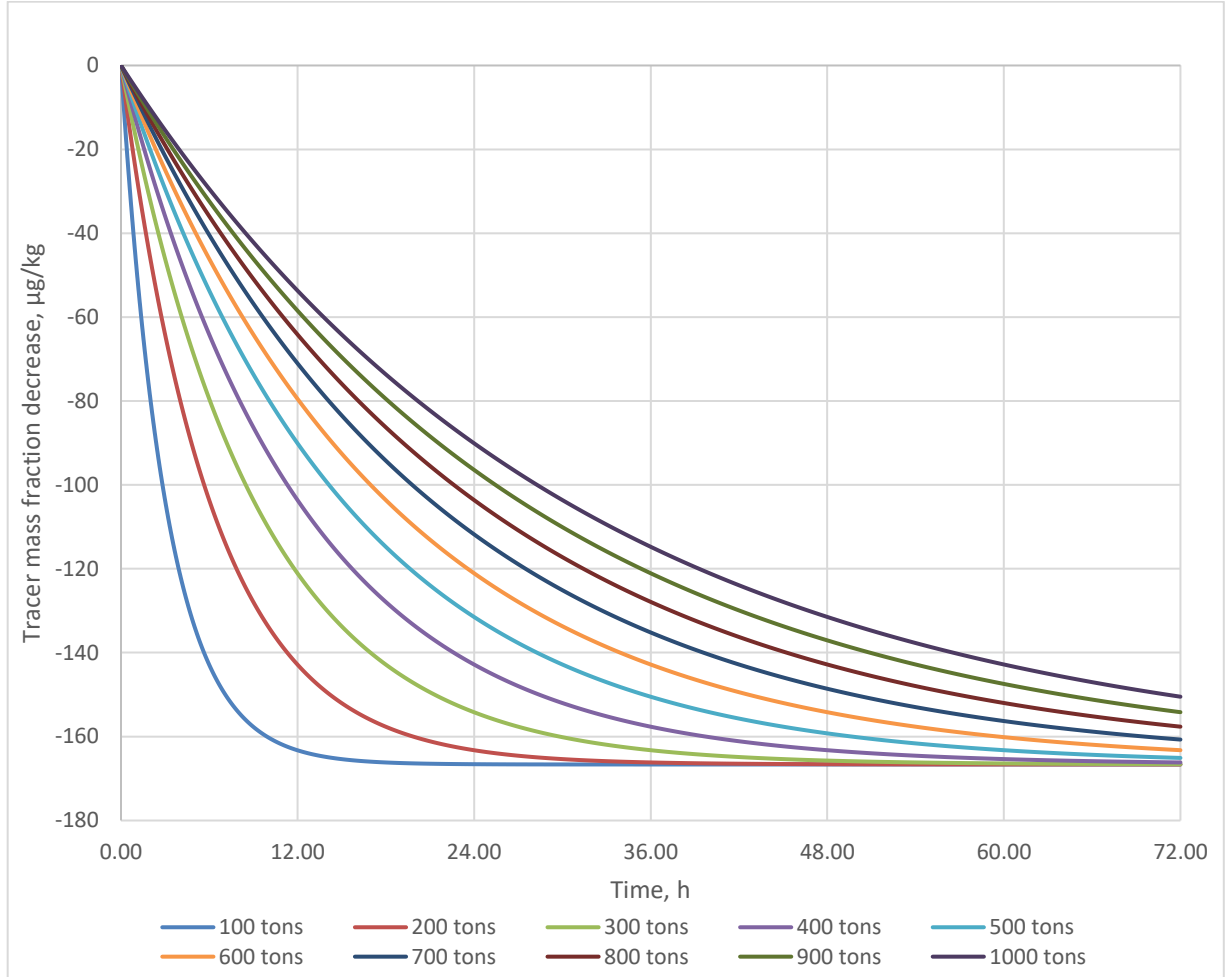


Figure 13. Estimation of tracer mass fraction decrease over time for different boiler water volumes in boiler with, initial tracer concentration of 0.5 mg/kg, blowdown flow volume of 6 kg/s, and a leak flow volume of 3 kg/s

As we can see from Figure 13, the tracer mass fraction decrease is faster for boilers with smaller boiler water masses. In this estimation the mass fraction decrease for all different boiler water masses flattens out at a decrease of approximately -166 $\mu\text{g}/\text{kg}$, but boilers with greater boiler water mass take far more time. This indicates that tracer technique for boiler leak detection is more effective for smaller boiler sizes.

Small deviations in the total boiler water mass affect the sodium mass fraction decrease only slightly, but as the difference in either calculations or actual boiler water mass is estimated badly, it could affect the leak detection accuracy significantly.

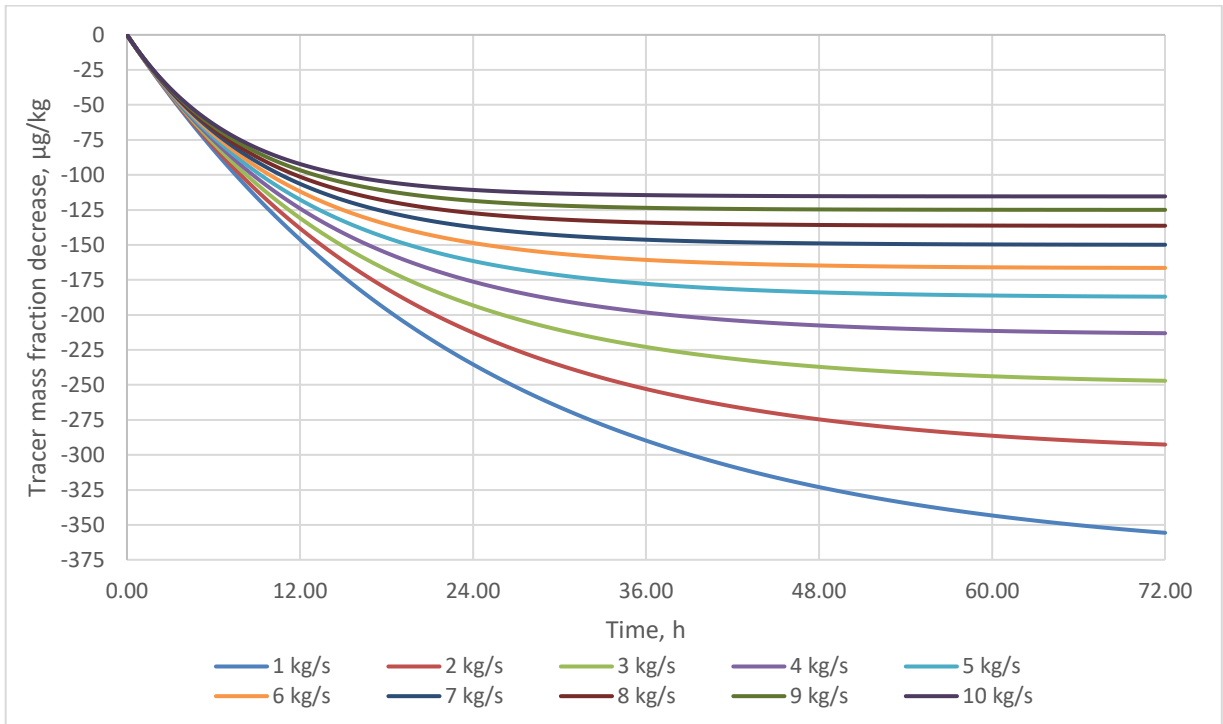


Figure 14. Estimation of tracer mass fraction decrease over time for different blowdown flows in boiler with, boiler water volume of 350 tons, initial tracer concentration of 0.5 mg/kg, and a leak flow volume of 3 kg/s

As we can see from Figure 14, the initial mass fraction decrease speed is not affected by blowdown flow volume. However, the difference in mass fraction decrease between different blowdown flows starts to gradually increase over time, and smaller blowdown flows leading to greater mass fraction decrease. This is due to fact that tracer dosage must be tied to blowdown flow and to keep the tracer mass fraction constant during normal operation, a greater tracer dosage is required with larger blowdown flows.

Overall it can be said that the initial tracer mass fraction in boiler water should not affect the accuracy of leak detection, as long as it is substantially higher than the background sodium coming from feedwater. The most relevant limiting factor for how fast a leak can be detected is the boiler water mass, as higher amounts of boiler water mass lead to slower concentration decrease. The boiler blowdown rate also affects the final value to which tracer mass fraction

will decrease during a leak, so with smaller blowdown flows smaller leaks can be detected more accurately. bigger leak sizes are always easier to detect, but they are also more critical, as a bigger leak has higher risk of water entering the boiler floor. Tracer based leak detection would be most effective in boilers with small total boiler water masses and small boiler blowdown rates.

6.3 Tracer Dosage

As discussed in chapter 6.1, during steady state operation the incoming and outgoing sodium flows are balanced and the sodium mass fraction in boiler water settles to a stable value. During normal operation we can also state that there is no leak in the boiler system so the balanced is controlled by tracer dosage, feedwater flow together with sodium mass fraction in it, blowdown flow, and the small amount of sodium entering the steam through mechanical carryover. Therefore, we can take the Equation 6.3 and solve correct dosage from it, assuming that terms $\frac{dm_{Na}}{dt}$ and \dot{m}_L both equal zero, resulting in following equation.

$$\dot{m}_D * w_D = \dot{m}_{BD} * w_{BW} + \dot{m}_s * w_s - \dot{m}_{fw} * w_{fw} \quad (6.13)$$

Solving the correct dosage from Equation 6.13 requires additional information to be accurately calculated. Only variable that can be chosen freely is the sodium mass fraction in boiler, as the blowdown, steam and feedwater flows, and their corresponding mass fractions are all boiler specific. The dosage flow may also be limited by the capacity of dosing pumps available at the mill. But for an example some values may be gathered from existing information and the rest variables filled with educated guesses.

For this example, an educated guess for feedwater flow of 300 kg/s and blowdown flow of 6 kg/s may be used. Steam flow is the difference in these values, being 294 kg/s. It may also be assumed that the water separation from steam in boiler drum works near perfectly, resulting in

minimal mechanical carryover, and only 0.1% of sodium in boiler water entering steam. In chapter 5.2, background sodium concentrations in a recovery boiler utilizing AVT method at Metsä Fibre Äänekoski mill was presented in Figure 8. The average background sodium in boiler water during the reference period was 31 µg/kg. Since during this time there was no dosing of excess sodium into the boiler, the sodium mass fraction in feedwater may be solved from Equation 6.13 and calculated with above information followingly.

$$w_{fw} = \frac{6 \frac{kg}{s} * 31 \frac{\mu g}{kg} + 294 \frac{kg}{s} * 0.1\% * 31 \frac{\mu g}{kg}}{300 \frac{kg}{s}} = 0.65 \frac{\mu g}{kg}$$

A typical chemical dosing pump capacity in this case could be ranging between 1 – 12 L/h. If the tracer dosing tank volume is for example a typical 1 m³, the dosage solution could be made by adding an accurately measured volume of concentrated NaOH solution with known concentration and diluting it with pure water to the desired concentration. For this example, 10 liters of 50 m-% NaOH solution is diluted to the final volume of 1 m³, 1000 liters. The concentrated NaOH solution has substantially higher density than pure water, which should be considered for calculations, the density of 50 m-% NaOH solution in 25 °C is 1.515 kg/L (SIGALD-415413). The density of diluted final dosing solution may be considered as equal to that of pure water. The final concentration as a mass fraction inside the dosing tank after the dilution may be calculated following equation.

$$w_D = \frac{V_{NaOH,50\%} * \rho_{NaOH,50\%} * 50\% * \frac{M_{Na}}{M_{NaOH}}}{V_D * \rho_{H_2O}} \quad (6.14)$$

With above information and Equation 6.14, the mass fraction of dosing solution would be following.

$$w_D = \frac{10 \text{ L} * 1,515 \frac{\text{kg}}{\text{L}} * 50\% * \frac{23 \frac{\text{g}}{\text{mol}}}{40 \frac{\text{g}}{\text{mol}}}}{1000 \text{ L} * 1 \frac{\text{kg}}{\text{L}}} = 4.36 * 10^6 \frac{\mu\text{g Na}}{\text{kg}}$$

Now the required sodium tracer dosage flow \dot{m}_D , to maintain a stable concentration of 500 $\mu\text{g}/\text{kg}$ in boiler water may be solved and calculated from Equation 6.13.

$$\dot{m}_D = \frac{6 \frac{\text{kg}}{\text{s}} * 500 \frac{\mu\text{g}}{\text{kg}} + 294 \frac{\text{kg}}{\text{s}} * 0,1\% * 500 \frac{\mu\text{g}}{\text{kg}} - 300 \frac{\text{kg}}{\text{s}} * 0.65 \frac{\mu\text{g}}{\text{kg}}}{4.36 * 10^6 \frac{\mu\text{g Na}}{\text{kg}}} = 6.77 * 10^{-4} \frac{\text{L}}{\text{s}} = 2,44 \frac{\text{L}}{\text{h}}$$

7 FIELD TRIALS WITH SODIUM TRACER

Field trials were conducted at Metsä Fibre Äänekoski mill with NaOH as the tracer chemical. The recovery boiler in Äänekoski mill is a high-pressure steam boiler with a drum pressure of 115 bars and total boiler water volume of 697 m³. However, it should be noted that during operation, there is a two-phase balance between steam and liquid water inside the boiler, so the total volume reserved for boiler water does not represent the actual amount of liquid water. The feedwater for the boiler is treated with a corrosion inhibiting product Amercor 835s, consisting of mixture of alkalizing and film forming amines, and oxygen scavengers. No solid alkalization of the boiler water is utilized in normal operation and the boiler water treatment is considered

all-volatile. The nominal feedwater flow, steam production, and blowdown flow of the boiler are 300 kg/s, 294 kg/s, and 6 kg/s respectively.

The experiments consisted of reference periods with and without NaOH addition to boiler water, during which the boiler water and steam quality was monitored through several factors. The purpose of these reference periods was to ensure that NaOH does not adversely affect the quality of boiler water or increase the risk of corrosion to the boiler or the steam line. A major interest of the field trials is to ensure that the NaOH addition does not weaken the film formation capability of FFA products utilized in the treatment of boiler water.

Additionally, boiler water leaks were simulated by adjusting the boiler blowdown rate together with steady dosage of NaOH, during which the decrease of sodium concentration in boiler water was monitored. Different leak sizes were simulated together with different sodium dosages to find out how small leaks are able to be detected accurately, and how the sodium dosage affects the detection accuracy.

7.1 Test Arrangements

The field trials conducted in Metsä Fibre Äänekoski mill were carried out over a four-week period, which was divided into four week-long sections. The first three weeks were used to monitor the boiler water and steam quality and the fourth week to perform boiler water leak simulations. During the first week there was no dosage of NaOH into the boiler water, and on the second and third week a continuous dosage of NaOH was administered so that the sodium mass fraction in boiler water was 0.5 mgNa/kg and 1.0 mgNa/kg respectively.

During the leak simulations the dosage of sodium was varied between 0.5 and 1.0 mgNa/kg in boiler water, to test how different dosages affect the leak detection accuracy. The simulations were arranged by increasing the blowdown flow of the boiler for 8 hours at a time. During the tests, the sodium concentration and boiler water conductivity decrease were measured, and leak size determined from the results. After each simulation, the sodium concentration in boiler water

was increased back to desired level and continuous dosage resumed. In total 4 leak simulations were conducted during the trial period.

A NaOH dosing solution was prepared in a 1 m³ dosing tank by diluting 20 liters of 50 m-% NaOH solution with demineralized water. The sodium mass fraction of the dosing solution was measured to be 9.3 gNa/kg. However, after the dosing pump was tested it turned out that the minimal pump capacity was 2.25 L/h. The blowdown flow rate of the boiler was set to 6 kg/s and continuing with this concentration would lead to a minimum sodium concentration in boiler water to be 0.95 mgNa/kg. Therefore, it was decided that the dosing solution should be diluted to a lower concentration. Approximately half of the dosing solution was removed from the dosing tank and the remaining solution diluted with demineralized water, resulting in final concentration of 4.8 gNa/kg. NaOH was fed into the water-steam cycle through an existing dosing line and entered the cycle at the feedwater line before the economizers. The dosing line connected to the feedwater line after the point where attemperator spray water is taken, so that no NaOH could enter the steam through attemperator spraying.

7.2 Monitoring parameters and analytical methods

During the 3-week monitoring period, several factors representing the boiler water and steam quality were measured, such as pH, conductivity, sodium, and suspended iron concentrations. A full list of monitoring parameters, their respective sample lines, analytical instruments and methods are presented in Table 9 below. The reasoning for selected monitoring parameters is discussed below.

Table 9. Water-steam cycle monitoring parameters, their respective sample lines, analytical instruments and methods during the sodium tracer field trials in Metsä Fibre Äänekoski mill

Monitoring parameter	Sample lines	Analytical instrument	Analytical method
Sodium concentration	Boiler water, Feedwater, Saturated steam	Swan SOLO sodium	Ion-Selective Potentiometry
pH	Boiler water	Mill online pH analyzer	Potentiometry
Conductivity	Boiler Water	Mill online conductivity analyzer, Swan FAM Powercon +	Conductometry
Redox potential	Boiler Water	Swan FAM pH/Redox	Potentiometry
Dissolved Oxygen concentration	Boiler Water	Mettler Toledo Thornton M300	Amperometry
Suspended Iron concentration	Boiler Water	Millipore MF TM 0.45µm membrane filters, Kobold DPL-1P05G4C34P flowmeter	Membrane Filtration
Dissolved Hydrogen concentration	Feedwater, Saturated steam	Orbisphere Laboratories Model 3600 Hydrogen analyzer	Amperometry

Sodium concentration in feedwater and boiler was monitored to establish the sodium background concentration in the cycle, and to ensure that the wanted dosage is administered. Sodium concentration in steam was also monitored closely to make sure that sodium does not enter the steam through carryover, as even small concentrations of sodium in steam may cause corrosion and scaling to the turbine.

The pH and conductivity of boiler water are measured continuously in the mill and may be considered as standard parameters to represent the quality of boiler water. pH was monitored to identify if NaOH addition affects it as was expected in chapter 5.3, and to ensure that NaOH

addition does not increase the pH over the boiler water guideline limits. Conductivity was also monitored to find out how much NaOH increases conductivity, so that normative operational limits for different NaOH dosages could be determined.

Redox potential, also known as oxidation/reduction potential, is described as a tendency of chemical species to gain or lose electrons. In this case the redox potential of boiler water was measured to determine if the conditions in boiler waterside are either reductive or oxidative. A solution with more positive redox potential can be considered as more oxidative, and one with negative redox potential as reductive. In the case of boiler water, the redox potential is preferred to be negative, since the passivation of magnetite film on the boiler tubing is mainly controlled by a reduction reaction of iron(III)oxide. Typical redox potential value for boiler water in normal operation is between -300 and -200 mV, based on previous measurements on different boilers (Lähde, 2021). The purpose for redox potential monitoring was to ensure that the conditions in boiler are normal, and that the addition of NaOH does not offset the value.

Dissolved oxygen concentration in boiler water was measured to identify if the deaeration of feedwater works properly, since in this case no oxygen should be in boiler water. Presence of oxygen could affect the quality of boiler water by inducing oxidation of dissolved organics into organic acids, or magnetite, causing a risk of corrosion. Therefore, dissolved oxygen was measured to ensure that the boiler conditions are normal regarding oxygen during the trial period.

Both suspended iron and dissolved hydrogen concentrations may be used to determine if acute corrosion is happening in the boiler. High concentration of suspended iron could mean that the magnetite film on the boiler tubing is released into the cycle, which could indicate that the amine film formed by FFA products has also become unstable. If no suspended iron is detected in the boiler, and the pH conditions are normal, it can be assumed that the magnetite film is passivated properly and stays intact. High hydrogen concentration would also imply that there is acute corrosion happening inside the boiler, since hydrogen is released in the corrosion reactions, see chapter 4.2. Dissolved hydrogen was measured from both feedwater and saturated steam, and the difference between these values would indicate how much corrosion is occurring inside the

boiler. If no corrosion is happening, the difference between feedwater and saturated steam should be negligible.

7.3 Test results – Boiler water quality

This section presents the test results from trial period in Metsä Fibre Äänekoski mill, regarding the first three weeks that were dedicated to boiler water quality monitoring. Each monitoring parameter and their results are discussed individually, and the parameters linked to each other are cross-referenced as deemed necessary. The results for leak simulation experiments are presented and further discussed afterwards in their own chapter.

7.3.1 Sodium concentration

At the start of the trial period, sodium concentration was measured from both feedwater and boiler water to establish the amount of background sodium in the cycle.

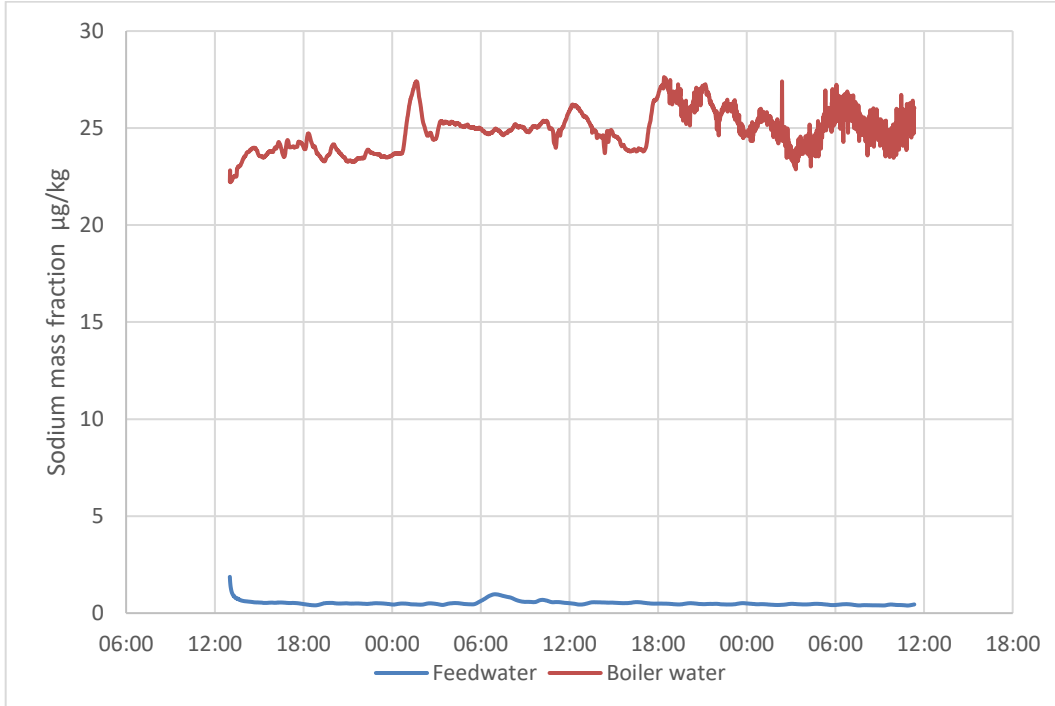


Figure 15. Sodium mass fraction in recovery boiler feedwater and boiler water without additional sodium dosage, sodium tracer trial period in Metsä Fibre Äänekoski

As we can see from Figure 15, the amount of background sodium in feedwater is fairly low, the average mass fraction being only 0.5 µg/kg, resulting in boiler water mass fraction of 25 µg/kg on average. This suggests that the make-up water demineralization works efficiently and is capable to remove most of sodium impurities and that there are no sodium leaks to the cycle. Such low background sodium concentration benefits this study, as it would allow more accurate arrangement of sodium tracer dosing even with lower NaOH concentrations.

There is some fluctuation in the amount of sodium in boiler water, for which the reason is unsure. Possible cause for the fluctuation could be the dynamic balance between steam and liquid water inside the boiler water, that also fluctuates somewhat.

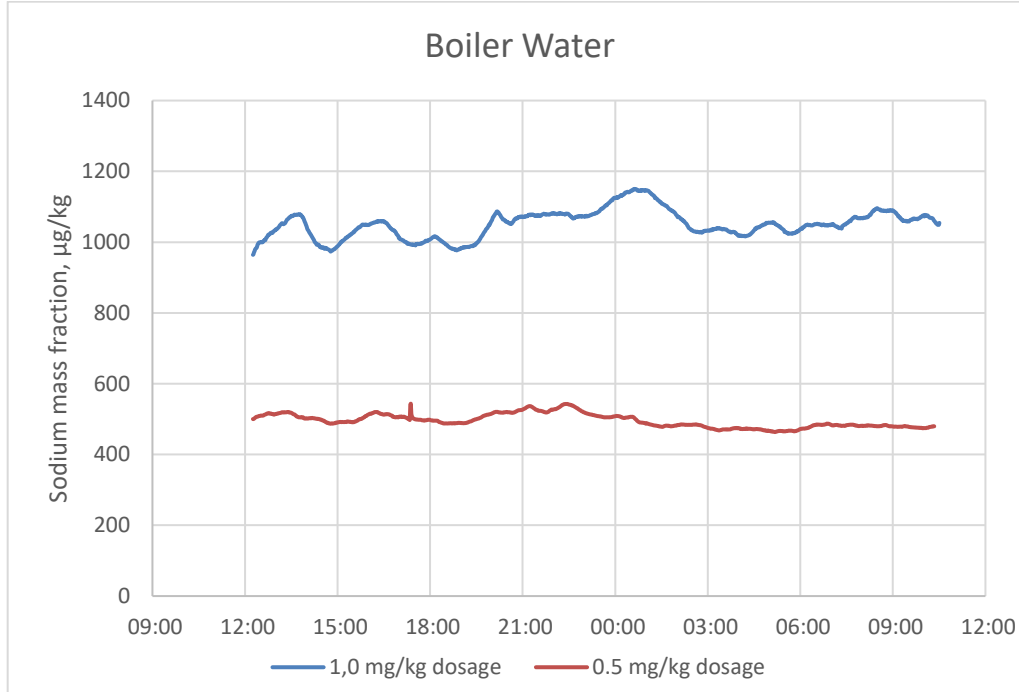


Figure 16. Sodium mass fraction in boiler water with NaOH dosage of 0.5 and 1.0 mgNa/kg respectively, sodium tracer trial period in Metsä Fibre Äänekoski

The amount of sodium in boiler water was also measured during the dosage of NaOH. As we can see from Figure 16, there is similar fluctuation to the sodium mass fraction in boiler water as was observed with the background sodium. However, on average the sodium mass fraction in boiler was stable with the NaOH dosage.

The fluctuation of sodium mass fraction was measured to be highest during the background measurement period, with a %-difference of approximately $\pm 12\%$ from the average, during the biggest spikes. With both 0.5 and 1.0 mgNa/kg NaOH dosages, the highest fluctuation from average was around $\pm 8\%$. The average, minimum, and maximum measured sodium mass fractions, together with their respective differences from the average during each measurement period are presented in Table 10 below.

Table 10. Sodium mass fraction in boiler water with different NaOH dosages, sodium tracer trial period in Metsä Fibre Äänekoski

Background	$\mu\text{gNa/kg}$	%-difference of average
Min	22,2	-11,8%
Max	27,6	+12,6%
Average	24,8	
0.5 mgNa/kg dosage	$\mu\text{gNa/kg}$	%-difference of average
Min	463,4	-6,4%
Max	543,7	+9,7%
Average	495,4	
1.0 mgNa/kg dosage	$\mu\text{gNa/kg}$	%-difference of average
Min	973,3	-7,4%
Max	1150,5	+9,%
Average	1051,5	

Sodium was also measured from the saturated steam, to ensure that increased sodium concentration in boiler water does not lead to sodium carryover. Fortunately, the sodium levels in saturated steam were low throughout the whole trial period, indicating that the water separation from steam inside the drum works effectively. Sodium mass fraction measurement results in saturated steam for different sodium dosages is presented in Figure 17 below.

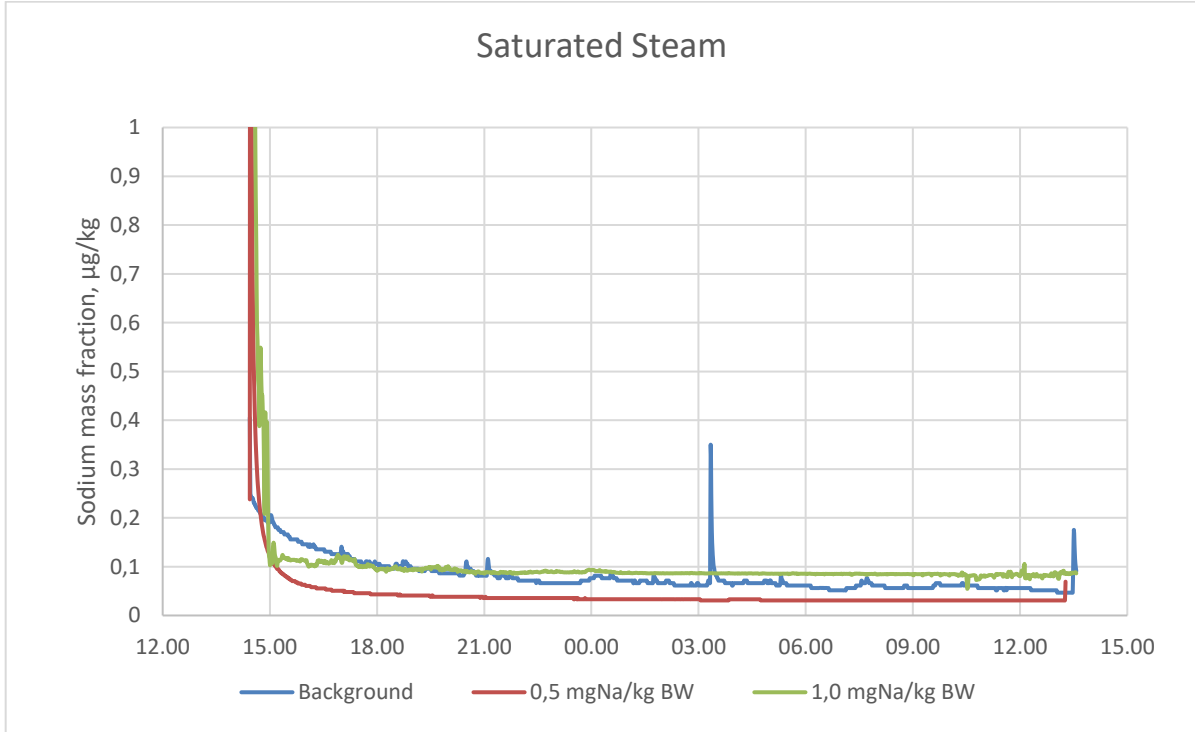


Figure 17. Sodium mass fraction in saturated steam with different NaOH dosages to boiler water, sodium tracer trial period in Metsä Fibre Äänekoski

As we can see from Figure 17, the sodium mass fraction in saturated steam was very low throughout the whole trial period, reaching a maximum value of only 0.1 $\mu\text{g}/\text{kg}$. Compared to the guideline values this result is excellent, as the guideline limit for sodium in steam is 5 $\mu\text{g}/\text{kg}$. As the sodium mass fraction in steam is so low, it can be established that no sodium is transferred to steam through carryover, so for the leak calculations presented in chapter 6, the steam flow and steam sodium mass fraction may be neglected.

7.3.2 pH and conductivity

The pH of boiler water is one of the main parameters used to monitor the boiler water quality, as it is recommended to maintain a pH between 9.2 and 9.7 for optimal corrosion protection. pH is monitored continuously at the mill with an online analyzer, so no additional

measurements were taken during the period. pH was monitored carefully throughout the whole as trial period, as it was certain that the planned NaOH addition would cause and increase.

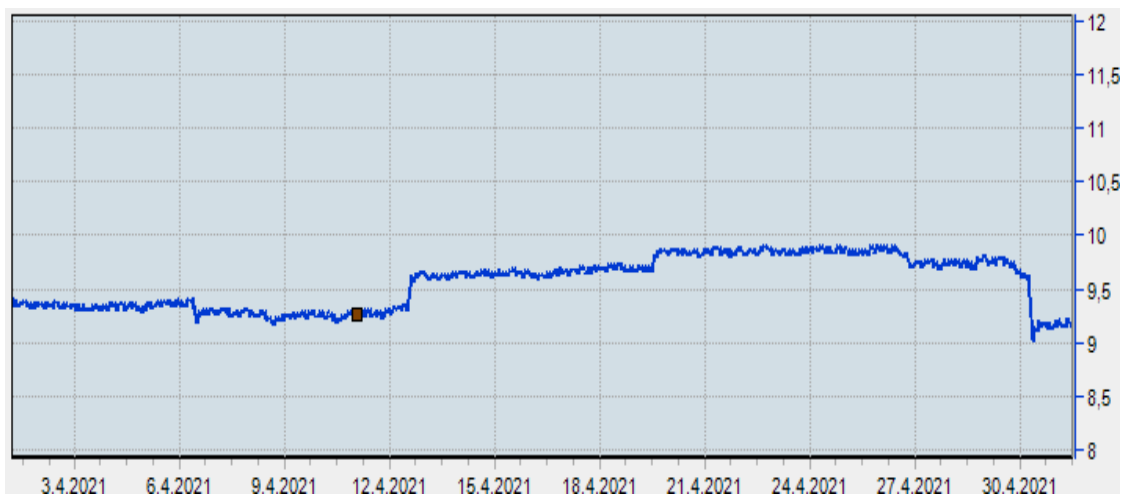


Figure 18. pH of boiler water during the sodium tracer trial period in Metsä Fibre Äänekoski mill

As shown in Figure 18, pH was around 9.35 at the start of the trial period, solely with the amine mixture used for boiler water treatment. On 12.4. a continuous NaOH dosage of 0.5 mgNa/kg in boiler water began, and the pH increased to 9.65. On 19.4. the NaOH dosage was increased to 1.0 mgNa/kg and the pH of boiler water increased to 9.8 accordingly. pH of 9.8 is slightly above the boiler water guideline recommendation upper values, but the dosage was continued as it was assessed safe for the relatively short period required for the tests.

After the NaOH dosage was suspended on the 29.4. the pH only decreased to around 9.65, even after the sodium levels in boiler water had decreased to approximately 0.1 mgNa/kg. This amount of NaOH should not lead to such high pH values, so on the 30.4. it was decided to clean and recalibrate the online pH analyzer, after which pH reached a value of 9.3. According to the mill personnel, the analyzer was calibrated before the trial period, and is usually recalibrated once a month. This leads to a conclusion that the calibration of pH analyzer could have been slightly off during the test period, and the actual pH might have been slightly lower than measured towards the end of the period.

Overall, the measured pH values of boiler water with different NaOH dosages followed the calculations presented in chapter 5.3, and a NaOH dosage of 0.5 mgNa/kg can be maintained safely without exceeding the guideline pH values.



Figure 19. Specific conductivity, mS/m, of boiler water during the sodium tracer trial period in Metsä Fibre Äänekoski, measured with mill online analyzer

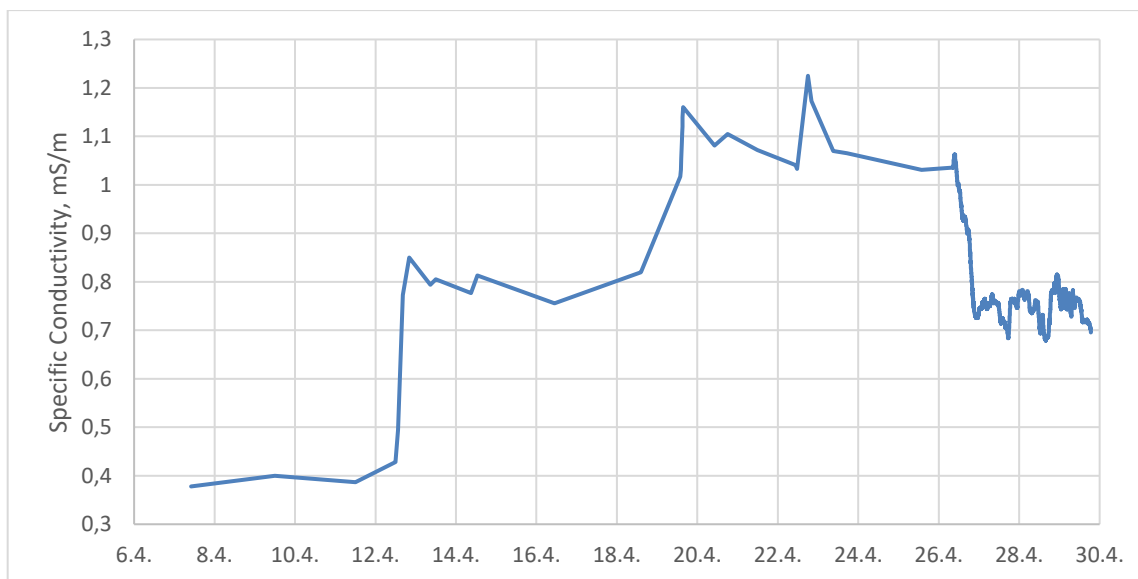


Figure 20. Specific conductivity of boiler water during the sodium tracer trial period in Metsä Fibre Äänekoski, measured with Swan FAM Powercon +

The specific conductivity of boiler water is also measured continuously in the mill as a way to roughly determine the amount of impurities in the boiler water. Conductivity with different NaOH dosages was monitored to establish baseline values that can be considered normal with different tracer dosages. The measurements were done with mill online analyzers and additionally with Swan FAM Powercon + conductivity analyzer.

There are no strict guideline values for specific conductivity of AVT boilers, but for ones utilizing CT, the guideline value is between 5 – 16 $\mu\text{S}/\text{cm}$. As we can see from Figure 19, the specific conductivity of boiler water measured with mill online analyzer was around 3.75 $\mu\text{S}/\text{cm}$ at the start of the trial period, without NaOH addition. As the NaOH dosage was administered to 0.5 and 1.0 mgNa/kg, the specific conductivity increased to 6.25, and 7.5 $\mu\text{S}/\text{cm}$ on average, respectively.

The measurements done with Swan FAM Powercon +, presented in Figure 20, demonstrated slightly higher results, compared to mill online analyzer. The average conductivity without NaOH dosage was around 4.0 $\mu\text{S}/\text{cm}$, and with the above-mentioned NaOH dosages the conductivity increased to 8.0 and 10.5 $\mu\text{S}/\text{cm}$.

The increase of specific conductivity was not linear regarding the increase of sodium concentration in boiler water. In such low concentrations the increase should be linear if the temperature of sample is fixed, as it was during the test period. After NaOH dosage was suspended, the specific conductivity with mill online analyzer decreased to 4.25 $\mu\text{S}/\text{cm}$, a bit higher than it was before the test period. This could indicate that there were also some other impurities in the water during the test period, which could be the cause for the nonlinear increase of conductivity.

7.3.3 Redox potential and dissolved oxygen

Redox potential of boiler water was measured to determine if the boiler conditions were reductive during the trial period, to establish that the conditions are optimal for corrosion

protection and magnetite film stability. Typical value for the redox potential of such recovery boiler's water is between -200 and -300 mV.

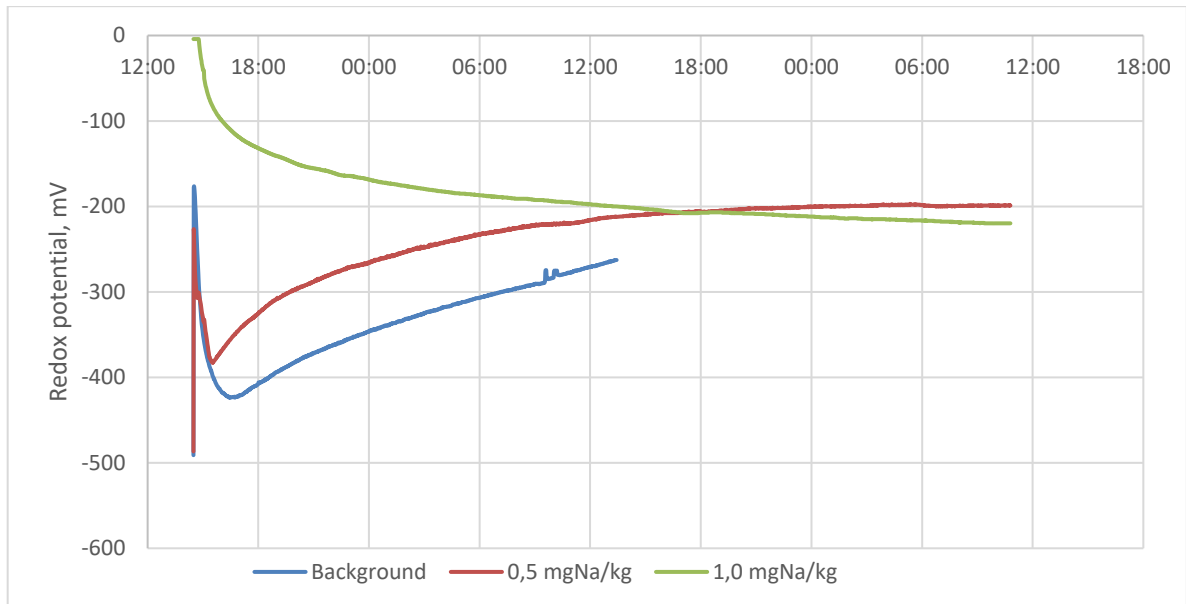


Figure 21. Redox potential of boiler water with different NaOH dosages, sodium tracer trial period in Metsä Fibre Äänekoski

As we can see from Figure 21, the redox potential of boiler water was ranging from around -200 to -250 mV. This indicates that the conditions in the waterside of the boiler are reductive, which encourages the formation and stability of magnetite film, ensuring good corrosion protection.

The dissolved oxygen concentration of boiler water was also measured, to determine if the boiler conditions are normal, and that the deaeration of feedwater works normally. Throughout the whole trial period, the dissolved oxygen in boiler water was low, averaging at 0.3 µg/kg. The measurement results for dissolved oxygen are presented in Figure 22 below.

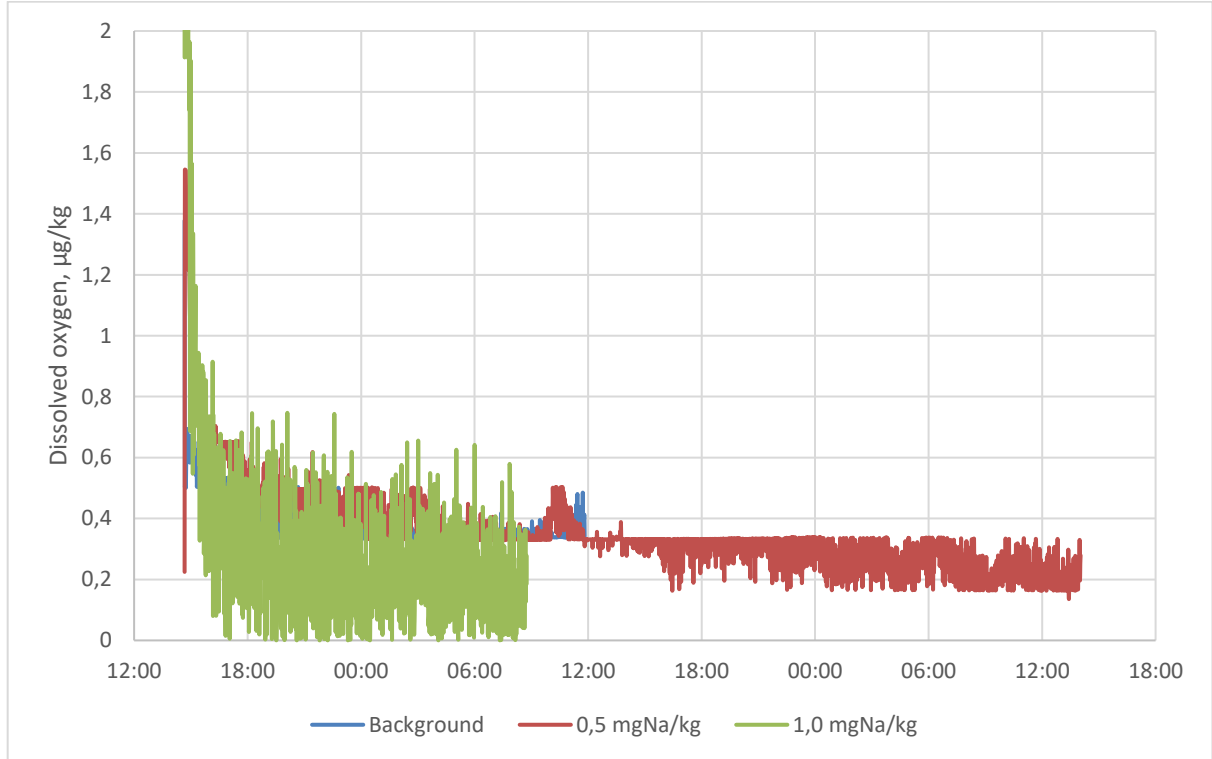


Figure 22. Dissolved oxygen concentration in boiler water with different NaOH dosages, sodium tracer trial period in Metsä Fibre Äänekoski

7.3.4 Suspended iron and hydrogen concentration

The suspended iron and hydrogen concentration were measured to establish if corrosion is happening inside the boiler. High amounts of suspended iron would indicate that the magnetite film stability is compromised, and is peeling off, which would lead to material loss on the tube surfaces. Hydrogen is produced in both corrosion process of iron and in magnetite film formation, which would again indicate that there is a risk of corrosion and material loss. There are no guideline limits for either, but optimally the suspended iron concentration should be below 5 µg/kg, and the difference in hydrogen concentration between feedwater and saturated steam should be close to zero (Lähde, 2021).

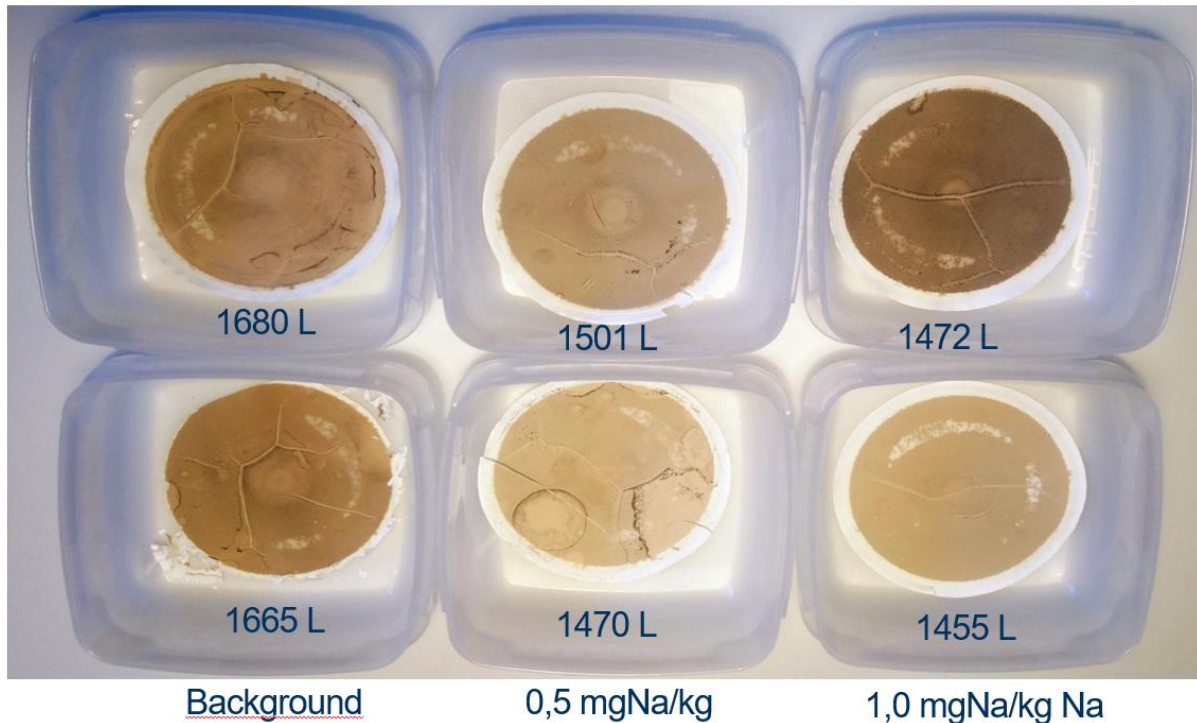


Figure 23. Residue from membrane filtration of boiler water with different NaOH dosages during the sodium tracer trial period in Metsä Fibre Äänekoski. The amount of boiler water, in liters, passed through the membranes presented respectively. Membrane pore size $0.45\mu\text{m}$

Figure 23 presents the membrane filters after the suspended iron filtrations during the trial period. The color of the residue on the filters has a tint of brown with areas containing higher amounts of black particles. The brown color is unusual for suspended iron filtrations, and points towards a part of the residue being organic, which could originate from either make-up water, or the Amercor 835s water treatment product. The black particles are typical for iron filtration, pointing towards the iron being in form of magnetite (Lähde, 2021).

Regardless, if the total mass of the residue on the filters is considered as iron, the average mass fraction of suspended iron in boiler water would be below the optimal $5\ \mu\text{g}/\text{kg}$ throughout the whole trial period, which may be considered as extremely good result. The average suspended iron concentration with different NaOH dosages during the trial period is presented in Table 11 below.

Table 11. Average suspended iron concentration in boiler water with different NaOH dosages during the sodium tracer trial period in Metsä Fibre Äänekoski

Measurement period	Average suspended iron concentration in boiler water, $\mu\text{g}/\text{kg}$
Background	1.8
0.5 mgNa/kg in BW	3.7
1.0 mgNa/kg in BW	2.4

Dissolved hydrogen concentration was measured from both feedwater and saturated steam. The difference between these samples indicates how much hydrogen is generated on the waterside of the boiler, which is proportional to the rate of corrosion on the boiler tube surfaces. The ideal situation would be that the difference in feedwater and steam samples is close to zero, indicating that no corrosion is happening. The results for dissolved hydrogen measurements with different NaOH dosages are presented in Figures 24-26.

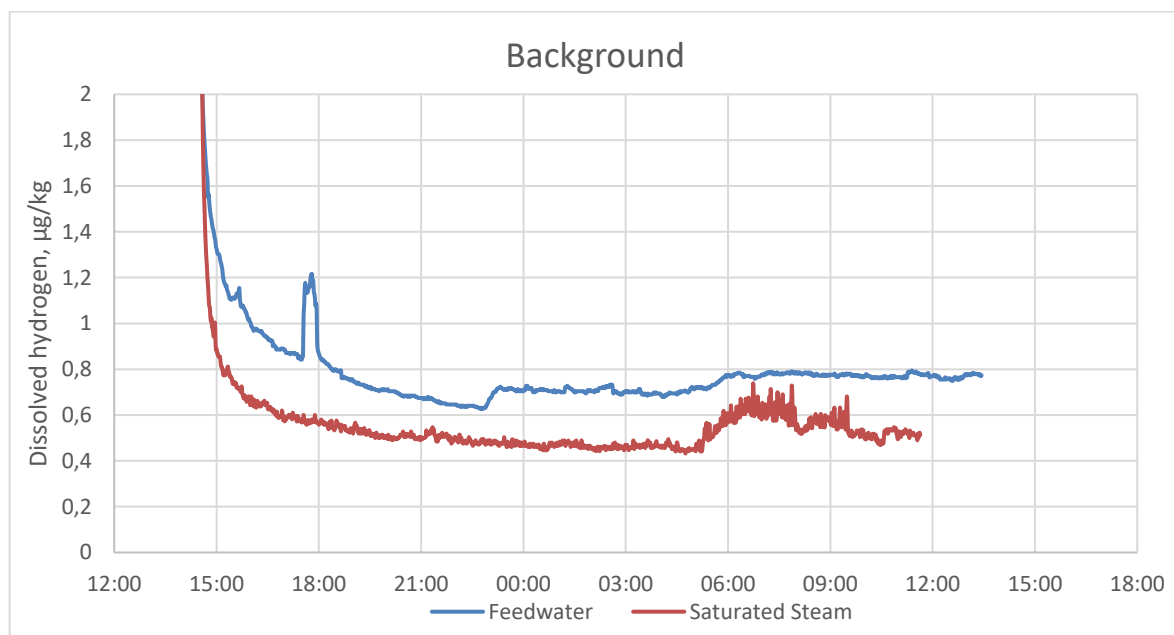


Figure 24. Dissolved hydrogen concentration in feedwater and saturated steam without additional NaOH dosage to boiler water, sodium tracer trial period in Metsä Fibre Äänekoski

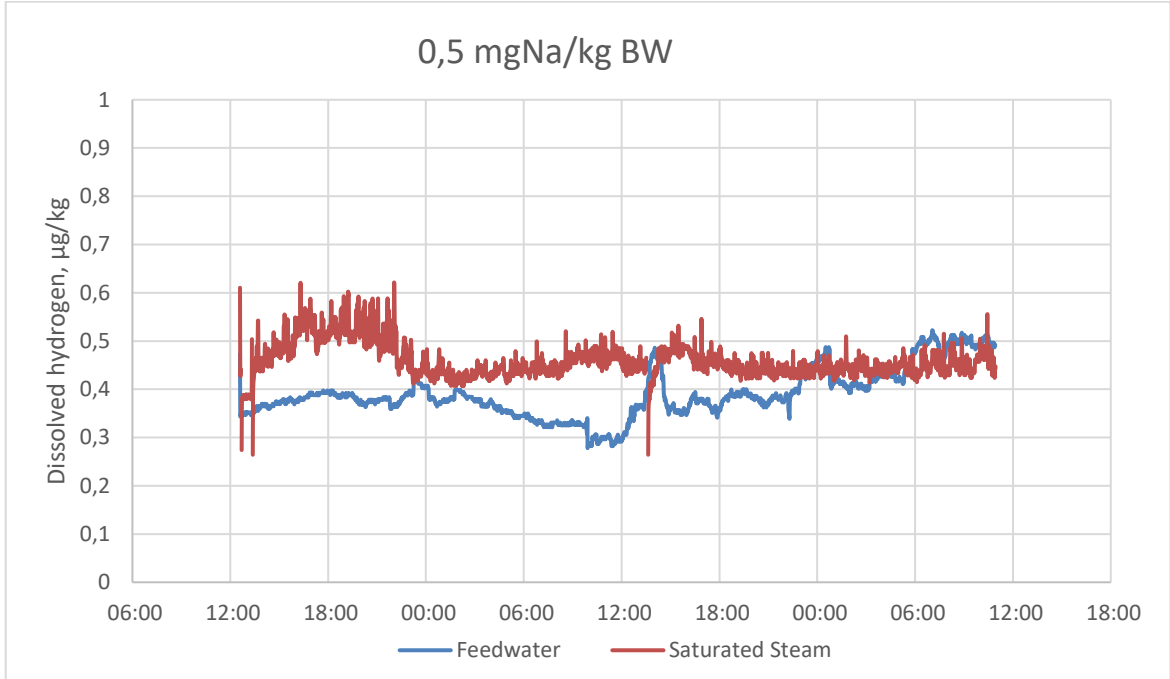


Figure 25. Dissolved hydrogen concentration in feedwater and saturated steam with NaOH dosage of 0.5 mgNa/kg in boiler water, sodium tracer trial period in Metsä Fibre Äänekoski

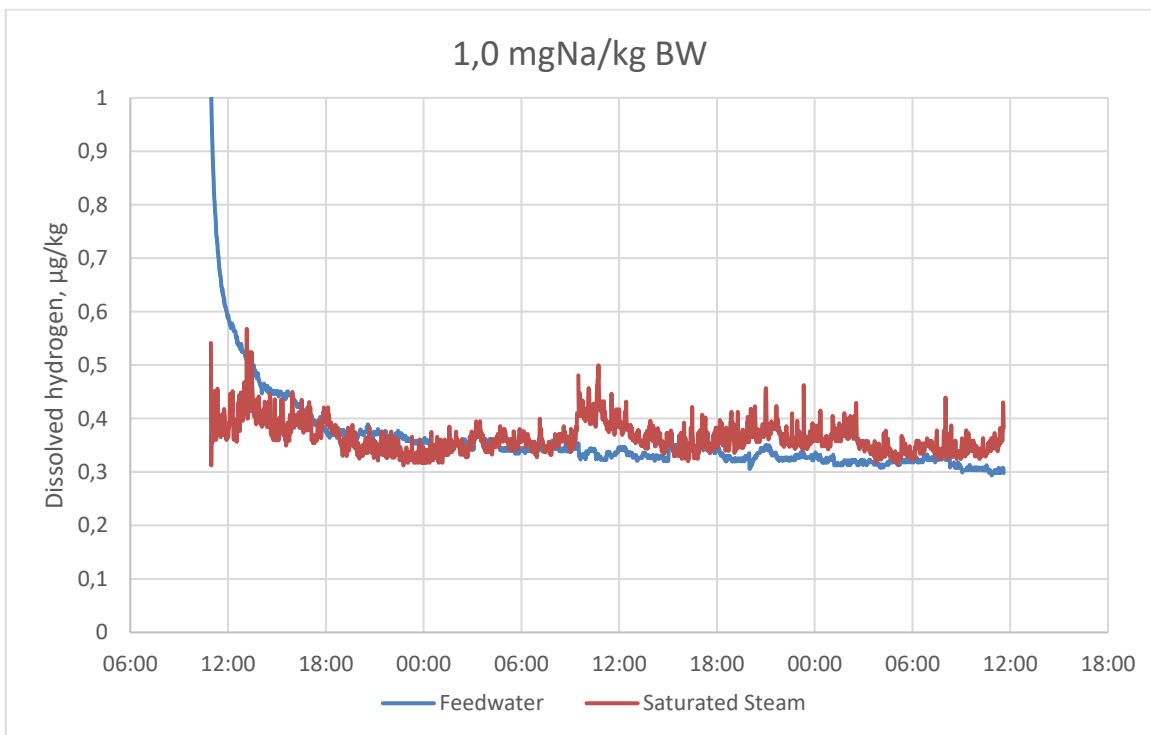


Figure 26. Dissolved hydrogen concentration in feedwater and saturated steam with NaOH dosage of 1.0 mgNa/kg in boiler water, sodium tracer trial period in Metsä Fibre Äänekoski

As shown in Figures 24-26 the dissolved hydrogen concentrations in feedwater and steam were relatively low throughout the whole test period, with different NaOH dosages. The difference between feedwater and steam was also low over the test period, indicating that the corrosion rate on the boiler waterside is low.

On the background measurement period the hydrogen concentration was even measured to be higher in feedwater than saturated steam. This is most likely just daily fluctuation of the hydrogen level, since only one analyzer was utilized, and different sample lines were monitored on separate days.

8 LEAK SIMULATION EXPERIMENTS

Leak simulation experiments were conducted as part of the sodium tracer trial period in Metsä Fibre Äänekoski mill. The simulations were executed by administering a continuous dosage of NaOH into the boiler water after which the boiler blowdown flow rate was increased. The increased blowdown caused the sodium mass fraction in boiler water to decrease, which was monitored with a sodium analyzer together with the specific conductivity of boiler water. After each simulation, the sodium mass fraction of boiler water was brought back to desired value and the continuous dosage stabilized.

In total four leak simulations were carried out, each lasting 8 hours at a time. The specific operational conditions for each simulation are presented in Table 12 below. Term \dot{m}_L in this context is used for the blowdown flow increase, as it simulates the leak in these experiments.

Table 12. Recovery boiler operational conditions regarding boiler water and tracer feed during the leak simulation experiments in Metsä Fibre Äänekoski mill

Simulation №	$\dot{m}_{fw,ave}$, kg/s	w_{fw} , µgNa/kg	\dot{m}_D , kg/h	w_D , mgNa/kg	$\dot{m}_{BD,ave}$, kg/s	\dot{m}_L , kg/s
1	287	0.5	4.4	4800	6.0	3.2
2	258	0.5	3.1	3400	6.5	2.6
3	261	0.5	3.1	3400	6.3	2.9
4	280	0.5	3.1	3400	6.0	1.9

8.1 Boiler water mass

The real total mass of boiler water is hard to define directly from the total boiler water volume, as it is dependent on both the two-phase water-steam balance and the pressure inside the boiler. The boiler in Metsä Fibre Äänekoski mill has a total volume of 697 m³ with a drum pressure of 115 bars. The water inside boiler is at its boiling point, in this pressure being 321 °C. The density of water at this temperature 0.667 tonnes/m³ (Engineering Toolbox, 2005)

From these values, if it is roughly assumed that half of the volumetric capacity of boiler is liquid water and half steam, then the total mass of boiler water would 232 tonnes. However, this estimation is only indicative, so it was decided to calculate a more accurate value for boiler water mass from the leak simulation experiment results. This may be done by solving the boiler water mass from Equation 6.6 and integrating the formula over 8 hours similarly to as presented in chapter 6. As mentioned in chapter 7.3.1, sodium mass fraction in steam was very low. Therefore, the amount of sodium exiting the boiler through steam may be neglected from the equation, as it does not have a meaningful effect in sodium mass balance.

$$m_{BW} = \frac{(\dot{m}_{fw,ave\ 8h} * w_{fw,ave\ 8h} + \dot{m}_D * w_D - (\dot{m}_{BD,ave\ 8h} + \dot{m}_L) * w_{BW,ave\ 8h}) * 8h}{\Delta w_{BW,8h}} \quad (8.1)$$

Additionally, it was decided to construct a non-linear regression model for the measured data with Equation 6.12 and find the best fit by minimizing the sum of squared residuals SS_{res} between them. Term SS_{res} is described as

$$SS_{res} = \sum_0^{8h} (w_{BWmeasured,t} - w_{BWcalculated,t})^2 \quad (8.2)$$

Where $w_{BWmeasured,t}$ is measured sodium mass fraction in boiler water at time t

$w_{BWcalculated,t}$ is calculated sodium mass fraction in boiler water at time t

The measured sodium mass fractions and specific conductivities in boiler water during the leak simulations together with the calculated regression model for them are presented in Figures 27-30 below.

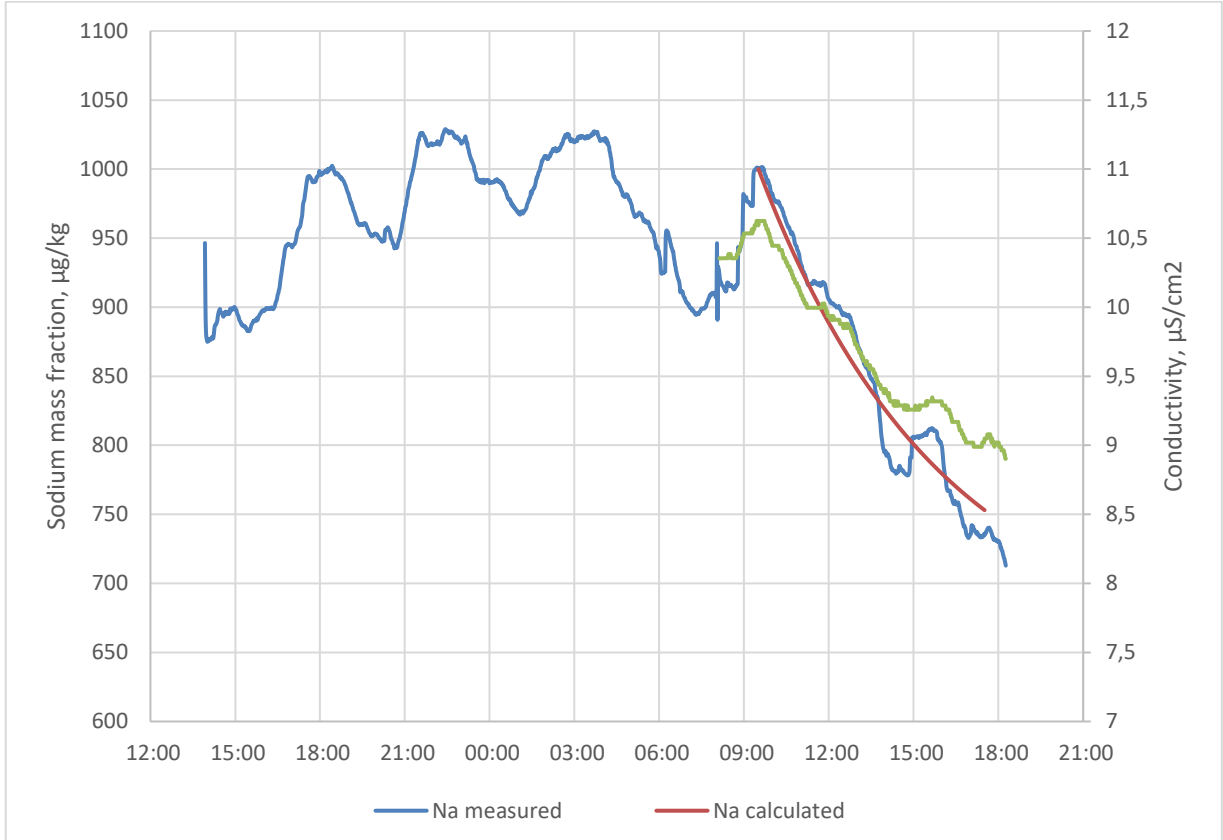


Figure 27. Sodium mass fraction and specific conductivity of boiler water measured during leak simulation experiment, together with the calculated regression model for sodium decrease. Leak simulation № 1, 26.4.2021, duration 9:30-17:30, sodium tracer trial period Metsä Fibre Äänekoski mill

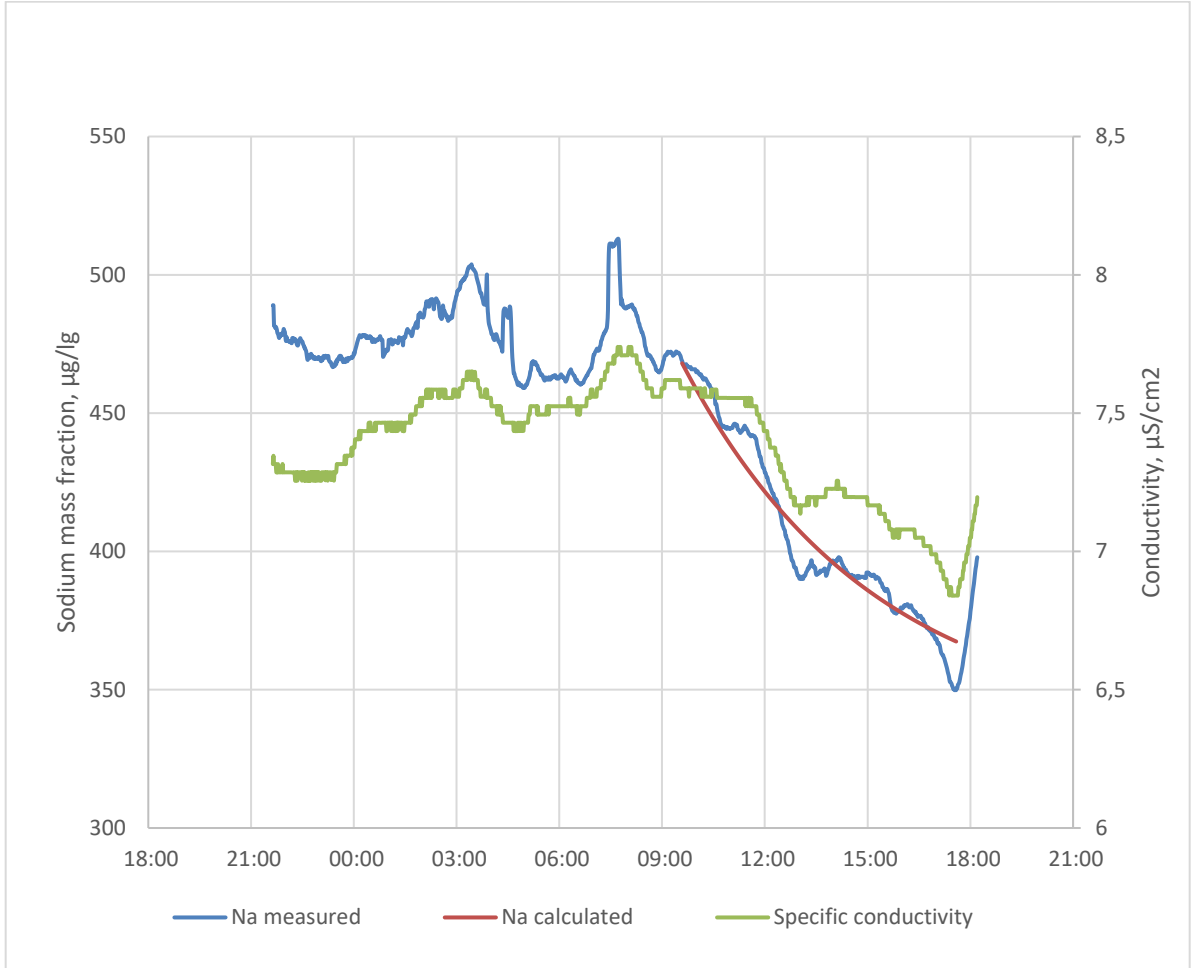


Figure 28. Sodium mass fraction and specific conductivity of boiler water measured during leak simulation experiment, together with the calculated regression model for sodium decrease. Leak simulation № 2, 27.4.2021, duration 9:35-17:35, sodium tracer trial period Metsä Fibre Äänekoski mill

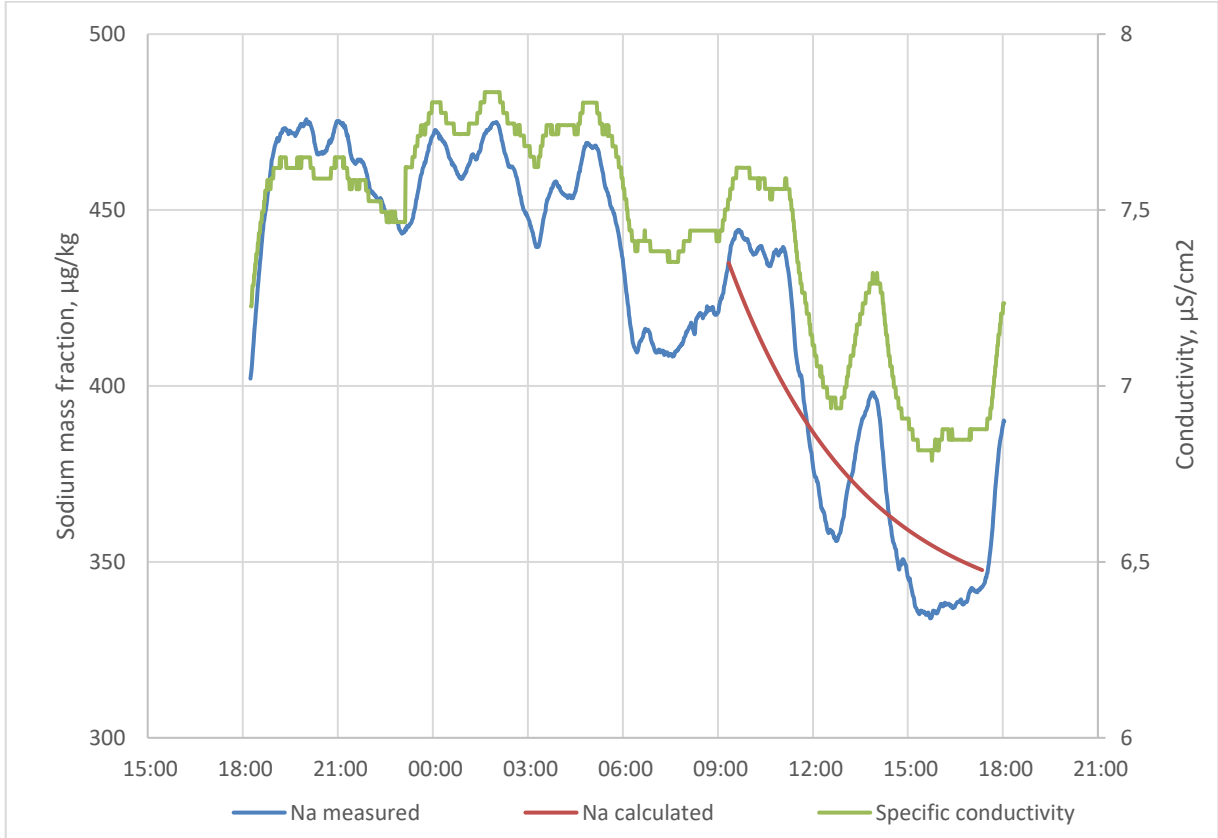


Figure 29. Sodium mass fraction and specific conductivity of boiler water measured during leak simulation experiment, together with the calculated regression model for sodium decrease. Leak simulation № 3, 28.4.2021, duration 9:20-17:20, sodium tracer trial period Metsä Fibre Äänekoski mill

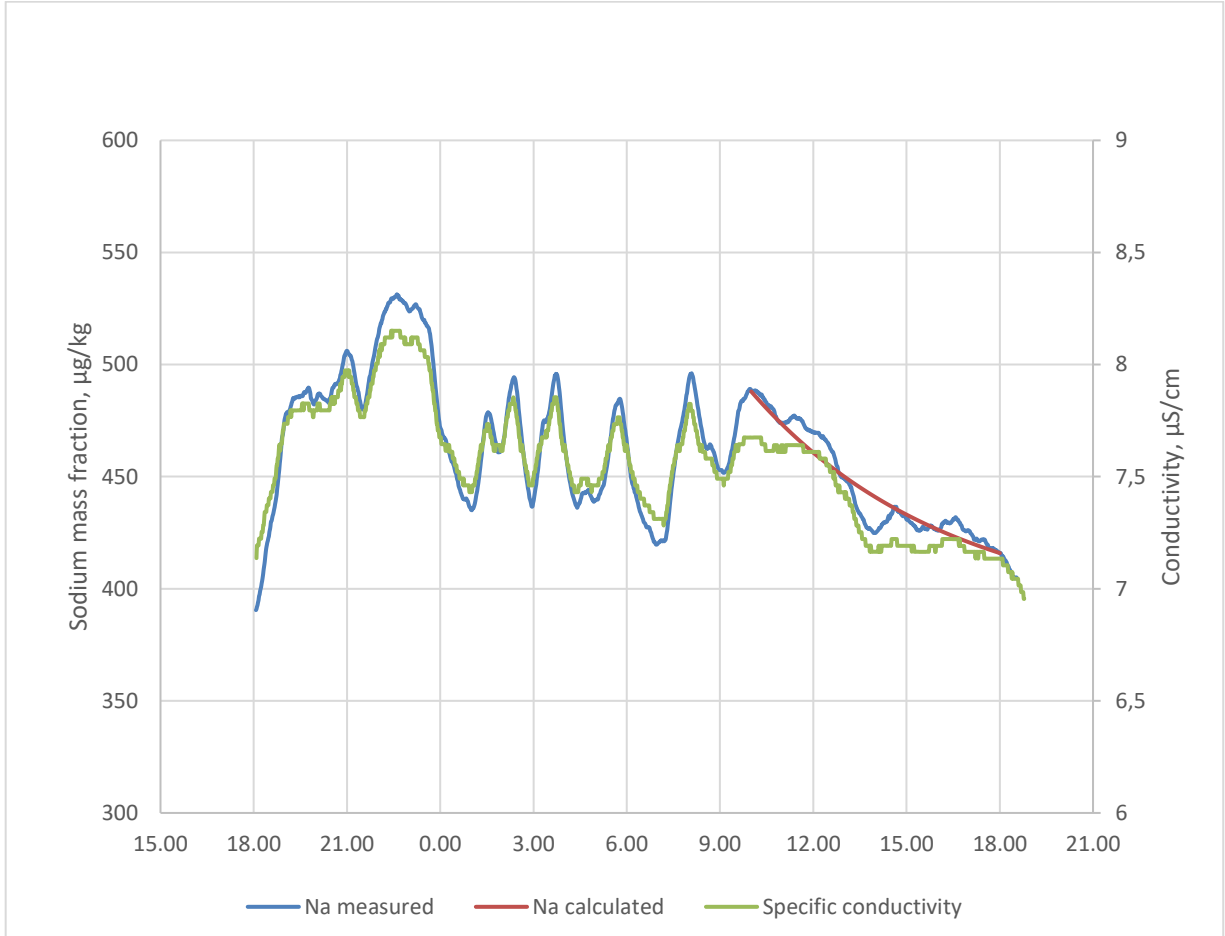


Figure 30. Sodium mass fraction and specific conductivity of boiler water measured during leak simulation experiment, together with the calculated regression model for sodium decrease. Leak simulation № 4, 29.4.2021, duration 10:00-18:00, sodium tracer trial period Metsä Fibre Äänekoski mill

Figures 27-30 present the measurement results from the leak simulation experiments conducted as part of the sodium tracer trial period. The figures present both measured sodium mass fraction and the specific conductivity of boiler water during the experiments. Additionally, “Na calculated” represents the regression model of sodium decrease during leak, calculated with Equation 6.12, fitted to the experimental data.

All four of the experiments demonstrated that a visible decrease in sodium mass fraction, and specific conductivity, are present during a leak in the boiler. However, similar fluctuation was observed in both sodium and conductivity measurements, as was during the boiler water quality monitoring period results presented in Chapter 7.3. The fluctuation may make it slightly harder

to distinguish the period at which leak was simulated, since the reference period for each simulation was quite narrow.

Out of the sodium mass fraction measurements, the total boiler water mass inside the boiler was calculated with Equation 8.1 and by finding the best fit for regression model of the data. Small deviation was detected in both arrangements, but the average boiler water mass from four leak experiments for Equation 8.1 and regression model were 218 and 179 tonnes, respectively. The complete results for calculated total boiler masses with equation 8.1 and estimations with the regression model are presented in Table 13 below.

Compared to the theoretical boiler water mass of 232 tonnes, presented in the beginning of this chapter, both estimations are of similar magnitude, and it could be roughly estimated that the total boiler water mass is around 200 tonnes. Small deviation, as in 25-50 tonnes, in this estimation does not affect the leak calculations significantly, as discussed in Chapter 6.2. However, if the estimation is off by a far larger amount, 100-200 tonnes, it would make the leak detection calculations far less accurate. Therefore, it would seem accurate enough from leak detection point of view to use 200 tonnes as a basis for leak calculations for this boiler.

Table 13, Total boiler water masses calculated with equation 8.1 and estimated with a regression model from the leak simulation experiment measurement data

No	$m_{\text{BW,Eq.8.1}}$, tonnes	SS_{res}	$m_{\text{BW,reg}}$, tonnes
1	237	170875	213
2	191	29256	183
3	193	173950	140
4	252	21773	178
Average	218	98963	179

8.2 Leak trends

As discussed in previous chapters, a momentary value for leak may be calculated from set of measured data over a desired time period. However, a more efficient way of presenting the data, in terms of leak, is to continuously calculate a new value for the leak from continuous measurements and present the values as a moving trend. This allows the situation to be assessed more closely, as the current leak value may be compared to previous movements of the trend.

Leak trends were calculated for the leak simulation experiment measurement results with Equation 6.7. The calculations for momentary leak in each time step of the trend were done over an 8-hour period, using the measured sodium mass fraction from boiler water, and the values presented in Table 12. For boiler water mass 200 tonnes was used, as discussed in Chapter 8.1. The leak trends and their corresponding sodium mass fraction measurements are presented in Figures 31-34 below.

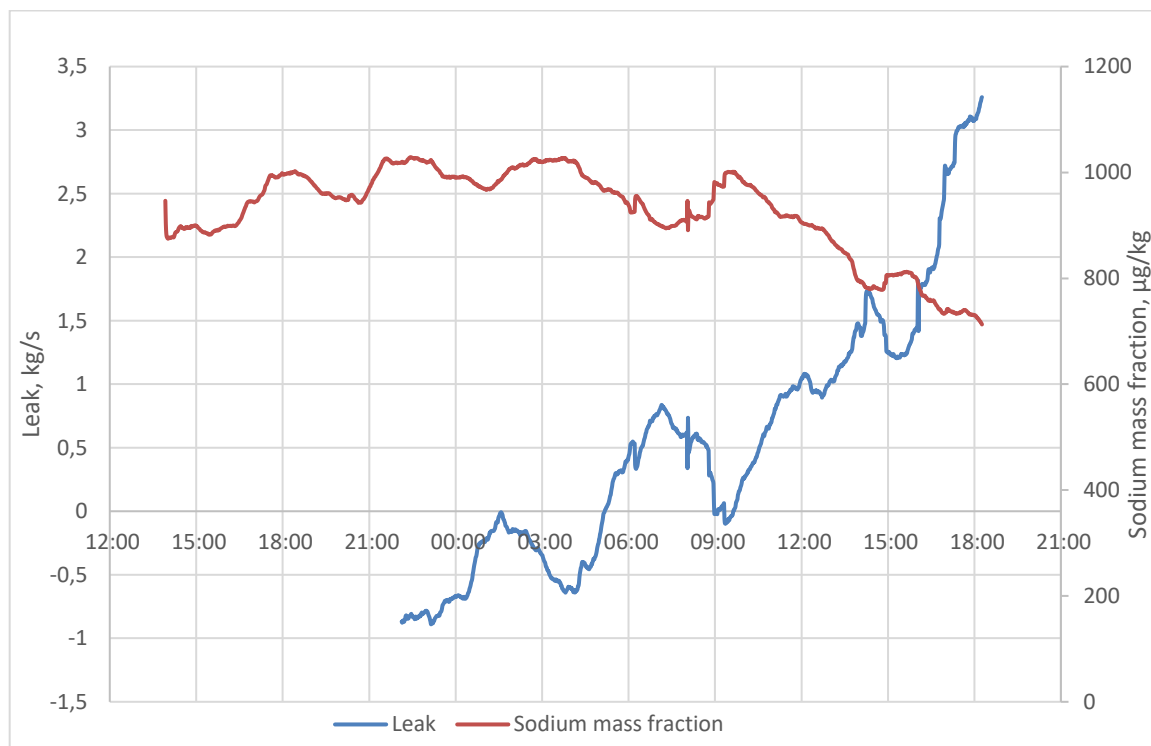


Figure 31. Leak trend and measured sodium mass fraction for simulation № 1. Simulated leak implemented over a period of 9:30-17:30.

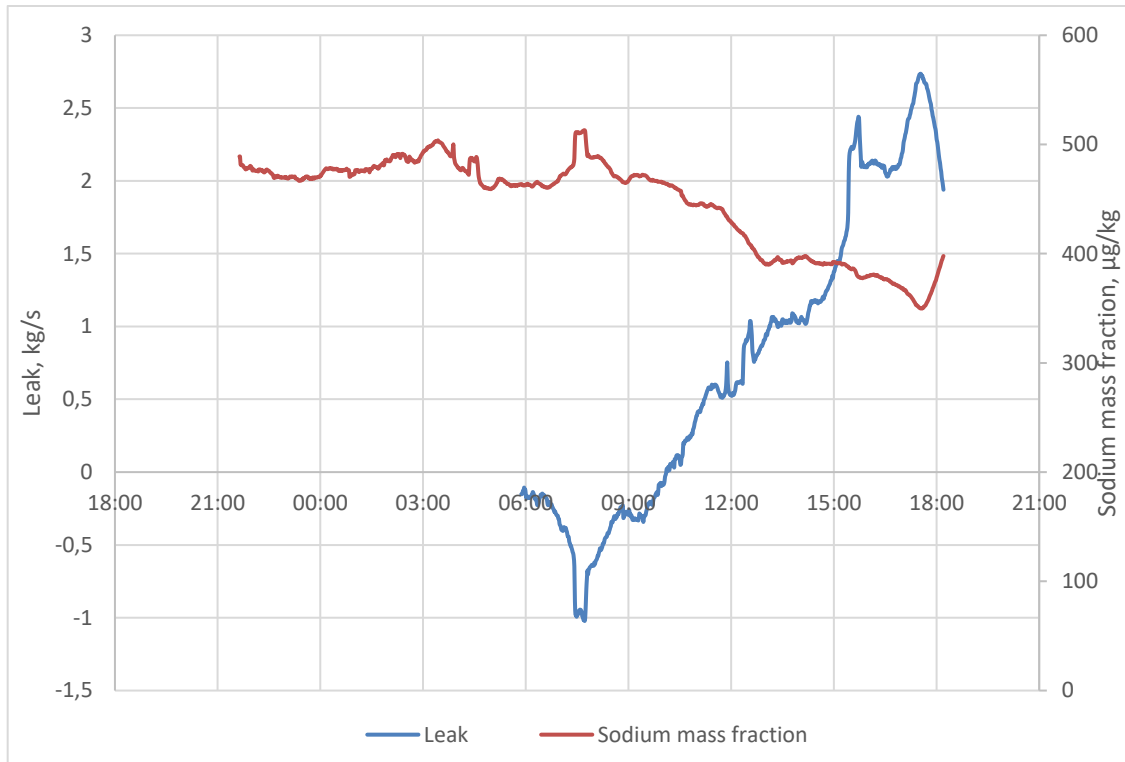


Figure 32. Leak trend and measured sodium mass fraction for simulation № 2. Simulated leak implemented over a period of 9:35-17:35.

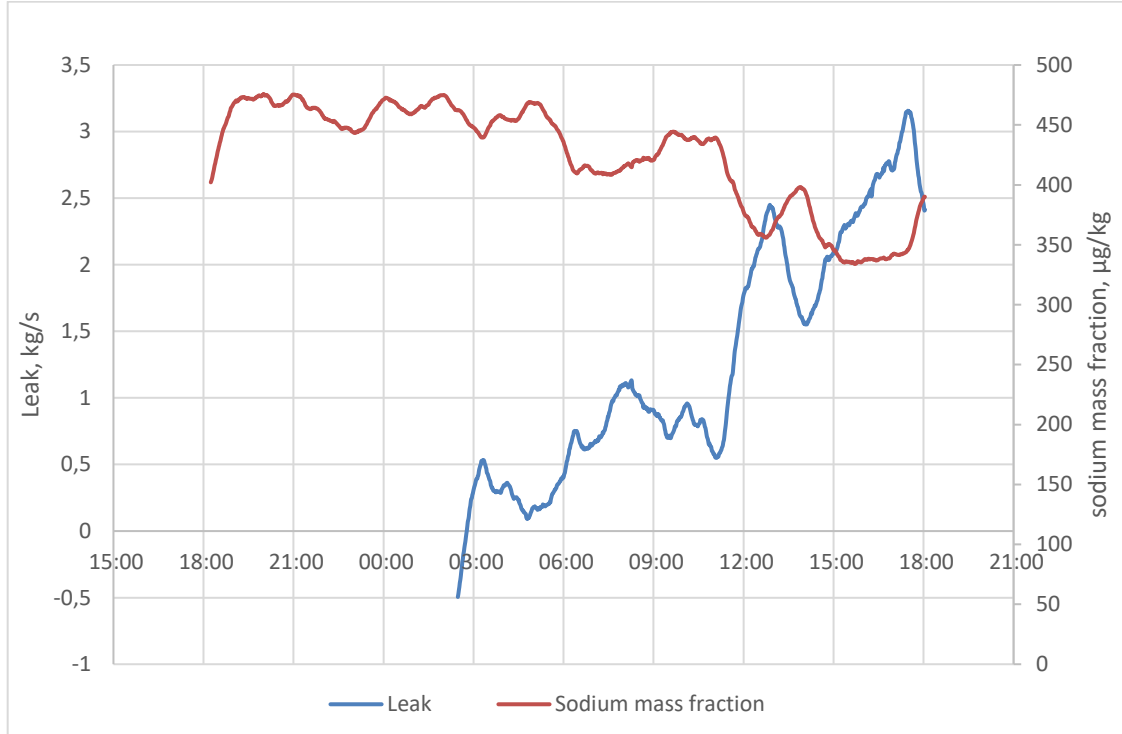


Figure 33. Leak trend and measured sodium mass fraction for simulation № 3. Simulated leak implemented over a period of 9:20-17:20.

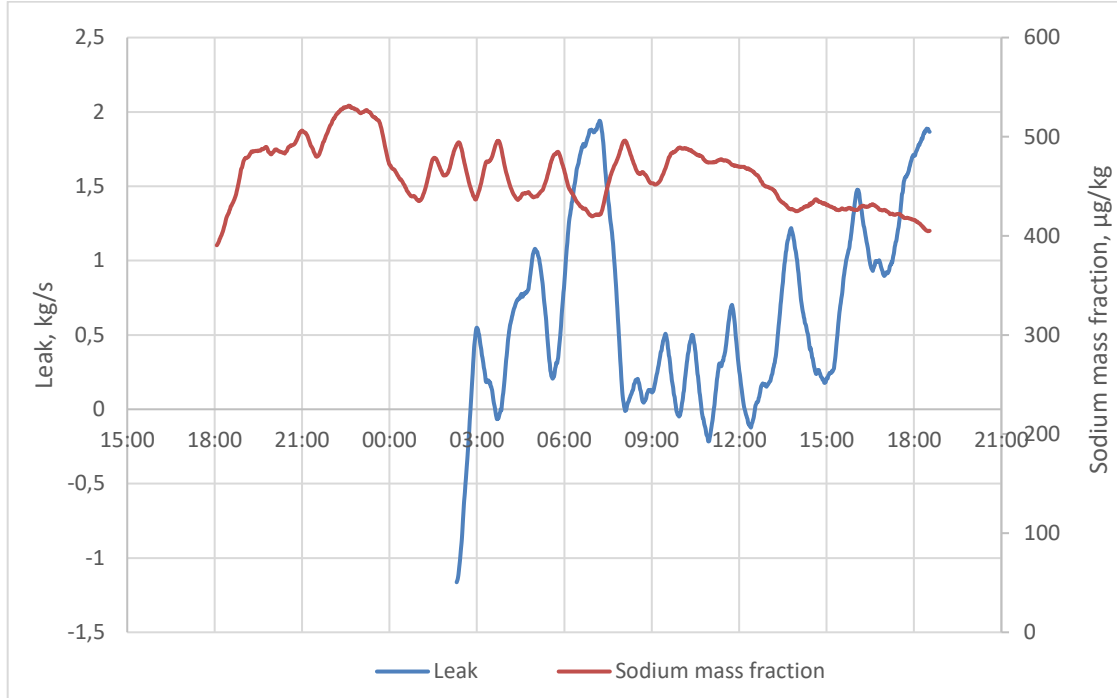


Figure 34. Leak trend and measured sodium mass fraction for simulation № 4. Simulated leak implemented over a period of 10:00-18:00.

The leak trends for simulations 1-3 presented in Figures 31-33 show a similar progress over the time period the calculations were done. All three of them show a gradual increase in leak value as the sodium mass fraction in boiler water decreases. All of them have minor fluctuation in the sodium mass fraction, which is also visible in the corresponding leak trend. To correctly interpret the figures, it should be noted that the leak trend at each time step is calculated from the sodium measurements over the previous 8 hours.

In Figure 34 however, a more severe fluctuation occurred in the sodium mass fraction measurement, which affects the leak trend accordingly. The fluctuation caused large spikes in the leak trend for simulation № 4, which might lead into inaccurate conclusions. This type of fluctuation might be a problem for leak detection accuracy, if the data is observed without any form of filtration, as it might cause false alarms if the trend reports a severe leak incorrectly. Luckily, the leak spikes in this case are quite sharp and short-term, which implies that they are caused by fluctuation in the sodium measurement.

The leak detection systems in mills are usually automated and report a leak alarm if a programmed threshold is surpassed. The type of fluctuation observed in simulation № 4 could be filtered out by implementing thresholds that either require the leak trend to exceed a certain value, or for the leak trend to remain exceeding another lower value for set amount of time, before a leak alarm is executed. In case of simulation № 4, the spikes during fluctuation did not exceed a leak value of 2 kg/s and lasted only a maximum of 2 hours.

As discussed in Chapter 4, smaller leaks are not considered as critical and can be dealt with more time. Larger leaks however require immediate actions as they are detected, so a threshold at which the leak detection system alerts should be programmed. Based on this and the experience from these experiments, an increase in the leak trend to 3 kg/s could be used as a threshold limit for leak detection system. To deal with the smaller fluctuation, another threshold could be implemented that if the leak trend exceeds a value of 1 kg/s for over 8 hours, an alarm is sounded.

Another way to deal with the fluctuation of the sodium measurement would be to analyze the data through a moving average. Unfortunately, this type of filtering would require the sodium mass fraction in boiler water to be measured for a longer time period, to be able to establish an accurate moving average. The leak simulations were also done over an unfortunately short time period, as the progression of leak trend could not be observed over more than 8 hours after the simulated leak was implemented. Despite this, the measurements were able to detect a visible decrease in the sodium mass fraction, and an increase in leak value could be observed.

9 CONCLUSIONS

This study was conducted to advance the operational safety of steam boilers, through improved boiler water leak detection. The focus was set on developing a leak detection method that could detect small leaks in critical parts of the boiler, for boilers utilizing all-volatile treatment of boiler water. The chosen leak detection method was mass balance monitoring of sodium hydroxide (NaOH) dosed into boiler water as a tracer chemical.

For the experimental part of the study, NaOH was tested as a tracer chemical in AVT recovery boiler through a trial period conducted in Metsä Fibre Äänekoski mill. The trial period consisted of boiler water quality monitoring period, during which the safety of NaOH as a tracer chemical was addressed, and a leak simulation experiment period, during which the accuracy of tracer method was tested.

NaOH was found to be safe as a tracer chemical, as it did not increase the corrosion rate of the boiler tubing implying it did not adversely affect the stability of amine and magnetite films on the boiler tube surfaces. A suitable concentration for NaOH addition was found to be up to 0.5 mgNa/kg in boiler water, as in this concentration all the boiler water quality parameters, including pH, stayed inside the boiler water guidelines.

The lowest leak size that was tested during the trial period was 1.9 kg/s, and it was able to be detected in 8 hours using the tracer method. There was some fluctuation in the sodium concentration measurement, which may require filtering of the data for it to be analyzed accurately. Fortunately spikes in the data caused by fluctuation were quite narrow, implying that filtering of the data would be manageable.

Overall, the leak detection capability of sodium as tracer element, and the safety of NaOH was proven to be plausible. With the use of this method, leaks can be detected and located in the most critical parts of the boiler, the steam generator. The method could be implemented as part of the boiler automation, allowing risk assessment of the leak situation to be done safely from the control room. The introduction of tracer method could therefore significantly improve the operational safety of boilers utilizing AVT of boiler water.

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