

LAPPEENRANTA-LAHTI UNIVERSITY OF TECHNOLOGY LUT  
School of Energy Systems  
Degree Programme in Energy Technology

*Henri Matilainen*

**SIMULATION OF LIQUID WASTE TREATMENT DURING  
NUCLEAR POWER PLANT DECOMMISSIONING**

Examiners: Professor, D.Sc. Juhani Hyvärinen  
M.Sc. (Tech.) Aino Ahonen

## **ABSTRACT**

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### **Simulation of liquid waste treatment during nuclear power plant decommissioning**

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Examiners: Professor, D.Sc. Juhani Hyvärinen  
M.Sc. (Tech.) Aino Ahonen

Supervisor: M.Sc. (Tech.) Aino Ahonen

Keywords: Apros, boric acid, crystallization, evaporation, decommissioning, radioactive liquid waste

This thesis focuses on the treatment of process water at Loviisa nuclear power plant during the plant decommissioning. The objective is to study process water treatment and find out how a process simulation software Apros would help in the process water treatment planning.

The thesis goes through the origins of process waters, process water characteristics and current liquid waste treatment methods in Loviisa nuclear power plant. Apros modelling possibilities on the process water treatment chain are assessed. Apros simulation model is developed focusing on process water logistics in Loviisa nuclear power plant. The drain water evaporation process in Loviisa is modelled accurately and analyzed on the simulation model.

Simulations on the drain water evaporation process show that current plant operation results evaporator concentrates containing undesired amount of boric acid. Measurements from the evaporation process support the simulation results. Results indicate that the monitoring algorithm on the drain water evaporation plant needs adjustments prior to the decommissioning of Loviisa, but for the current operation as well.

Discussion addresses process water treatment planning and utilization areas for created simulation model in decommissioning planning and future projects. Recommendations are given on possible improvement areas in the physics of the simulation software to improve liquid waste treatment modelling capabilities in the future.

# TIIVISTELMÄ

Lappeenrannan-Lahden teknillinen yliopisto LUT  
School of Energy Systems  
Energiatekniikan koulutusohjelma

Henri Matilainen

## **Nestemäisten jätteiden käsittelyn simulointi ydinvoimalaitoksen käytöstäpoiston aikana**

Diplomityö

2021

106 sivua, 16 kuvaa, 6 taulukkoa ja 3 liitettä

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DI Aino Ahonen

Ohjaaja: DI Aino Ahonen

Hakusanat: Apros, boorihappo, kiteytyminen, haihdutus, käytöstäpoisto, radioaktiivinen nestemäinen jäte

Diplomityössä keskitytään prosessivesien käsittelyyn Loviisan voimalaitoksen käytöstäpoiston aikana. Tavoitteena on tutkia prosessivesien käsittelyn suunnittelussa huomioitavia asioita, sekä arvioida kuinka prosessisimulaatio-ohjelmisto Apros soveltuu prosessivesien käsittelyn suunnitteluun.

Diplomityössä käydään läpi prosessivesien lähteitä ja niiden ominaispiirteitä sekä nykyisiä nestemäisten jätteiden käsittelymenetelmiä Loviisan voimalaitoksella. Prosessivesien käsittelyketjun mallintamista Apros-ohjelmistolla arvioidaan. Diplomityössä kehitetään Aprosimulointimalli, keskittyen prosessivesien käsittelyketjun logistiikan simulointiin Loviisan voimalaitoksella. Simulointimallin osana oleva viemäri-vesien haihdutuslaitos mallinnetaan tarkemmin ja sen toimintaa analysoidaan simulointiajoilla.

Simuloinnit osoittavat, että viemäri-vesihaihduttimien nykyisellä käytöllä haihdutusjätteisiin konsentroituvan boorihapon pitoisuus ei muodostu toivotun suuruiseksi. Laitoksella aiemmin tehdyt mittaukset tukevat simulointiajojen tuloksia. Simulointitulosten perusteella viemäri-vesihaihduttimien toimintaa valvovaa laskenta-algoritmia tulisi säätää ennen Loviisan käytöstäpoiston aikaista vesienkäsittelyn aloittamista, mutta jo nykyistä käyttöäkin ajatellen.

Diplomityön lopuksi pohditaan prosessivesien käsittelyn suunnittelussa huomioitavia asioita sekä luodun simulointimallin hyödyntämistä käytöstäpoiston suunnittelussa ja tulevilla projekteilla. Myös kehitysehdotuksia simulointiohjelmiston mallinnusfysiikassa tunnistetaan työn perusteella. Niiden toteuttaminen parantaisi nestemäisten jätteiden käsittelyketjun mallintamismahdollisuuksia tulevaisuudessa.

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While the global pandemic still continues, things eventually seem to come to an end - just like the writing of this thesis.

Espoo, 6<sup>th</sup> September 2021

*Henri Matilainen*

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## LIST OF SYMBOLS AND ABBREVIATIONS

### Roman alphabet

$A$	activity, area	[Bq], [m <sup>2</sup> ]
$C_s, C_w$	solvent phase density	[kg/m <sup>3</sup> ]
$F$	force	[N]
$g$	gravity	[m/s <sup>2</sup> ]
$h$	specific enthalpy	[kJ/kg]
$K$	ion exchange capacity	[meg/g]
$K_D$	distribution coefficient	[-]
$m$	mass	[kg]
$N$	number of nuclides	[-]
$p$	pressure	[bar, Pa]
$Q$	heat flow	[W/m <sup>2</sup> ]
$T$	temperature	[°C]
$t$	time	[s]
$u, v$	velocity	[m/s]
$V$	volume	[m <sup>3</sup> ]
$x$	concentration, length	[ppm], [m]
$z$	spatial location	[m]

### Greek alphabet

$\alpha$	void fraction	[-]
$\Gamma$	mass transfer between phases	[kg/m <sup>3</sup> s]
$\lambda$	decay constant	[1/s]
$\rho$	density	[kg/m <sup>3</sup> ]

### Dimensionless numbers

$C$	Courant number
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### Subscripts

$b$	boron
$f$	final
$i$	interface, current node
$k$	phase
$s$	steam

$w$	wall, water
0	initial state
1	upwind value

### **Superscripts**

$n$	time step
$t-\Delta t$	previous time step value

### **Abbreviations**

APROS	Advanced Process Simulation Software
CFD	Computational Fluid Dynamics
DF	Decontamination Factor
EIA	Environmental Impact Assessment
EW	Exemption Waste
HLW	High-Level Waste
IAEA	International Atomic Energy Agency
ILW	Intermediate-Level Waste
LILW	Low- and Intermediate-Level Waste
LLW	Low-Level Waste
LOCA	Loss-Of-Coolant-Accident
LO1	Reactor unit 1 in Loviisa nuclear power plant
LO2	Reactor unit 2 in Loviisa nuclear power plant
PCP	Primary Circuit Pump
PMS	Process Monitoring System
PWR	Pressurized Water Reactor
SA	Severe Accidents
SAM	Severe Accident Management
SCL	Simantics Constraint Language
VLLW	Very-Low-Level Waste
VRF	Volume Reduction Factor
WWER	Water-Water-Energetic Reactor (VVER in Russian)
YVL	Finnish Regulatory Guides on nuclear safety

# 1 INTRODUCTION

Nuclear power has remained one of the biggest sources of carbon-free electricity for decades. By the end of year 2019, there were 443 operational nuclear reactors worldwide, corresponding total net electricity capacity being approximately 392 GW. In addition to that, 54 new reactors were under construction, with 57.4 GW of new net electric capacity to be added in the future. (IAEA 2020, p. 11.) Notably, almost 70 % of these 443 operational reactors are currently more than 30 years old. It has been estimated that around 200 reactors are to be shut down within the next two decades. Furthermore, a little more than 180 reactors are already in permanent shutdown, meaning that the actual number of reactors to be decommissioned before 2040's could lie anywhere between 200 and 400 reactors. (Iurchak 2020) Considering these facts, it is certain that more interest and focus ought to be addressed towards the world of nuclear decommissioning in the near future.

This thesis focuses on process water treatment during nuclear power plant decommissioning. This nuclear power plant in question is the first commercial nuclear power plant built in Finland, located on the southern coast of Finland, Loviisa. Loviisa nuclear power plant has two VVER-440<sup>1</sup> type pressurized water reactors (PWR), designed in the former Soviet Union. Reactor unit 1 (LO1) started its operation in 1977 and unit 2 (LO2) in 1980. The design and building of Loviisa nuclear power plant was an exceptional project at that time, because Soviet reactor design was historically combined with Western technology and safety standards. The annual load factors have been among the best of the PWRs in the world for decades. The units have provided electricity into the Finnish electricity grid for more than 40 years now, approximately 8 TWh annually - corresponding to over 10 % share in the current Finnish electricity production portfolio. (Fortum 2021a)

## 1.1 Background

Considering the ages of the two reactors in Loviisa, the decommissioning of Loviisa nuclear power plant is to receive more attention soon. Current operating license for LO1 is expiring after the end of 2027, and for LO2 the operating license expires after the end of 2030. The

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<sup>1</sup> VVER = *vodo-vodyanoi energetichesky reaktor* (transliterated from Russian). The English translation of VVER is WWER (*water-water energetic reactor*).

future of the two reactor units is not yet decided, but plant owner Fortum is assessing the possibilities to extend the commercial operation of the power plant by a maximum of 20 years beyond the current license periods. However, the decision concerning whether an application for the extension of the operating licenses is to be applied in the future, was not yet clear during the writing of this thesis. If extensions to licenses are not applied, then Loviisa will proceed to decommissioning phase, starting from LO1 in year 2028. Either way, a licensing procedure is required in accordance with Nuclear Energy Act, and consequently an environmental impact assessment procedure. As a result, Fortum initiated an Environmental Impact Assessment (EIA) procedure in August 2020 where the environmental impacts of the potential extension to lifetime or the decommissioning are reviewed. (Fortum 2020, p. 8-9.)

Detailed plans and preparations for power plant decommissioning are needed well before the actual decommissioning may start. Preliminary plans are already there: a decommissioning plan for Loviisa exists and it is updated regularly. Before the dismantling of reactor and large cutting procedures at the power plant may start, the primary circuit and other process systems must be drained from water and possibly decontaminated from radioactive material. The amount of process water and generated liquid radioactive waste to be treated is considerable, meaning that the handling of process water should be planned rigorously and executed in a proper, safe and cost-effective manner. Therefore, it is of interest to study and investigate the possible ways and constraints regarding radioactive liquid waste treatment during decommissioning. It should be remembered that the operation of LO2 is intended to continue three more years after LO1 is shut down, so the successful and safe operation of LO2 needs to be ensured as well.

## **1.2 Thesis objectives**

The focus on this thesis is on the treatment of process water in Loviisa nuclear power plant primary circuit. The stages that are covered in this thesis include the draining process and further treatment of that process water - until it can be safely disposed of. The objective of this thesis is to produce information on the treatment process - what needs to be known for the planning process. The capabilities of a process simulation software Apros are reviewed in this sense - could it be utilized as an effective tool in the planning of process water treatment options? Could process simulation give other benefits for liquid waste treatment planning during the decommissioning? Hence, a target is to create a simulation model for helping

in the systems draining and process water treatment planning. Also, the feasibility of current procedures in liquid waste treatment in Loviisa are reviewed regarding the decommissioning.

There are a lot of uncertainties and questions related to the upcoming decommissioning and liquid waste treatment. Thus, the scope of this thesis is limited to analyze only the possibilities of using dynamic simulation with Apros in liquid waste management planning. The study is limited to concern only internal processes at the power plant - further considerations on the long-term safety issues of nuclear waste or environmental regulations and aspects are not included in this thesis. Considering the systems in the power plant, only the biggest process systems are to be included here, since they clearly form the bulk of the treated liquid waste during decommissioning.

Plant information and process data from Loviisa nuclear power plant is used in the simulation model development. Scientific knowledge on the liquid waste management area is reviewed to understand the techniques, requirements and limitations in liquid waste management. Based on the findings, possible needs and improvements in modelling are discussed concerning liquid waste treatment modelling aspects in the future.

### **1.3 Thesis structure**

The further structure of this thesis is as follows: Chapter 2 starts by introducing the decommissioning of Loviisa nuclear power plant and principles in nuclear waste management. Chapter 3 focuses on the draining of process systems during the decommissioning of Loviisa nuclear power plant; sources of process water, process water characteristics and different treatment strategies are discussed. Chapter 4 starts the discussion on the process water treatment methods by presenting the evaporation process. Chapter 5 continues process water treatment by introducing the ion exchange process. In Chapter 6, it is explained how liquid wastes are immobilized and disposed safely. Chapter 7 starts the empirical part of this thesis by assessing modelling possibilities in the treatment chain and the development of a simulation model. Then, in Chapter 8, a specific plant issue in the liquid waste treatment chain is taken into consideration, where the developed simulation model is used in the analysis. The key results, findings and further studies to be conducted are discussed on Chapter 9, before the thesis is summarized on Chapter 10.

## 2 NUCLEAR WASTE MANAGEMENT IN DECOMMISSIONING

Before starting the process water treatment, principles in nuclear waste management should be familiarized, together with the decommissioning of a nuclear power plant. General waste management options for radioactive waste, specifically liquid radioactive waste, are presented.

### 2.1 Radioactivity

Radioactive waste is distinguished by the presence of radioactive material in it, which makes the management of it much more demanding compared to non-radioactive conventional waste. The presence of radioactivity means that radioactive waste cannot be exterminated by normal means; instead, it must be confined from environment. While radioactive waste is generated in nuclear power plants, hospitals and research institutes, our main concern lies on the radioactive waste arising from a nuclear facility. (Ruokola et al. 2004, p. 270 & 273)

What ultimately makes matter radioactive, is caused by unstable particles in the matter. The elements in the universe we know are formed from tiny atoms. Each atom has an atomic nucleus, composed of protons and neutrons, and an electron cloud surrounding the nucleus. Those atoms that have a specific number of protons and neutrons in the atomic nucleus are called nuclides. Now, nuclides are either stable or unstable; this unstable nature some nuclides possess, is the very cause of radioactivity. Unstable nuclides are also called radionuclides<sup>2</sup>, emphasizing the radioactivity of the nuclides. (Ojovan & Lee 2014, p. 7-8)

Unstable nuclides have excess nuclear energy in them, which they need to release to reach stability. To achieve it, they undergo a spontaneous radioactive decay scheme. The most encountered decay schemes are called alpha, beta, gamma and fission. Several other radioactive decay schemes also exist, e.g., electron capture, proton emission, neutron emission and cluster radioactivity. (Ojovan & Lee 2014, p. 8) A decay constant  $\lambda$  [unit 1/s] specifies the probability of a certain radioactive decay mode for every radionuclide. The decay constant is seen on the decay law, which states that the number of nuclei decaying per time

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<sup>2</sup> Notably, most of the known nuclides are unstable. Currently, there are more than 4000 known nuclides, of which only around 300 of them are stable. Many more new nuclides are likely to be discovered in the future. (Adamian et al. 2020)

interval is proportional to the decay constant. It leads to following equation (1), describing how the number of radionuclides change within time:

$$N(t) = N_0 e^{-\lambda t}, \quad (1)$$

where  $N(t)$  is the number of radionuclides at a given time  $t$  [s] and  $N_0$  is the number of radionuclides at  $t = 0$ . (Ojovan & Lee 2014, p. 8-9)

The power in exponential decay is seen on the half-live  $T_{1/2}$  [s] of a nuclide, that can be derived from the decay law (1). It tells the time interval during which the number of radioactive nuclei decreases to half from original: (Ojovan & Lee 2014, p. 9)

$$T_{1/2} = \frac{\ln(2)}{\lambda}. \quad (2)$$

The activity of a nuclide is a very important quantity to be known and it is frequently encountered in nuclear waste management. Activity describes the number of decays a nuclide has per unit time, defined as

$$A(t) = \lambda N(t). \quad (3)$$

The SI unit of activity is Becquerel [Bq], essentially meaning one disintegration per second [1/s]. In nuclear waste management, activity is often expressed as per unit of mass (Bq/kg) or per unit of volume (Bq/m<sup>3</sup>). (Ojovan & Lee 2014, p. 11)

The activity of a nuclide also follows exponential decay, since if equation (3) is solved for  $N(t)$  and substituted into equation (1), then a similar expression for activity  $A(t)$  is obtained than for  $N(t)$  in equation (1).

## 2.2 The decommissioning of Loviisa nuclear power plant

The term decommissioning might be understood just to mean the physical dismantling of the power plant. More precisely, IAEA (2014) has defined that decommissioning refers to both administrative and technical actions taken to allow the removal of some, or all the regulatory controls from a facility. Different aspects in decommissioning can be divided into the planning of decommissioning, conducting decommissioning actions and terminating the authorization for decommissioning. The decommissioning actions are different procedures,

processes and work activities, such as decontamination and removal of structures, systems and components. These actions are considered complete, when the approved end state of the facility has been reached. The end state is stated on national regulatory requirements, and usually leads to the release of the facility from regulatory control, with or without restricting its future use. (IAEA 2014, p. 1-2)

According to IAEA (2014), two strategies for the decommissioning of a nuclear power plant exist: immediate and deferred dismantling. Immediate dismantling means that decommissioning actions are started shortly after the reactor has been shut down permanently. All systems, components and structures containing radioactivity are removed or decontaminated, allowing the facility to be released from regulatory control. Deferred dismantling means that the nuclear facility, or parts of it where radioactive material are present, are placed in safe storage until the facility is eventually decontaminated and dismantled. Deferred dismantling might involve early dismantling of some parts of the facility to ensure safe storage for the remaining parts of the facility. (IAEA 2014, p. 2-3)

Requirement 8 in International Atomic Energy Agency's GSR Part 6 states that immediate dismantling shall be the preferred decommissioning strategy (IAEA 2014, p. 12). This way, the burden of decommissioning is not transferred to future generations' problem. IAEA (2014) also acknowledges that in some situations, immediate dismantling is not a practical strategy to fulfill, hence the deferred dismantling strategy could be chosen in those situations.

In addition to immediate and deferred dismantling, the entombment of a nuclear facility is possible. Entombment means that the facility or some parts of it are encased into a structurally long living material. However, entombment should be considered only under exceptional circumstances, such as after a severe accident, like it was applied after Chernobyl disaster. (IAEA 2014, p. 3)

Loviisa nuclear power plant decommissioning plan is following the suggested strategy, immediate dismantling. The decommissioning project of Loviisa nuclear power plant is divided into four phases:

1. Licensing phase (to be completed before final shut down)
2. Transition period (0-3 years after final shut down)

3. Dismantling of primary circuit and its auxiliary systems in the reactor building (3-8.5 years after final shutdown)
4. Dismantling of all contaminated structures in the auxiliary building, spent fuel storage, liquid waste storage and solidification plant (30-33 years after final shutdown) (Kaisanlahti et al. 2018, p. 18, 28)

The decommissioning of the power plant units requires a different license than the operational phase, and it must be granted before the operation license expires. Some activities may be carried under the operating license. Earlier mentioned EIA procedure, launched in the autumn 2020, is a step towards the decommissioning license. (Kaisanlahti et al. 2018, p. 28)

The actual decommissioning activities can be thought to start during the transition period, immediately after the plant shutdown. Several activities must be carried out at during this stage, such as:

- Transferring spent fuel from the pools in reactor building to interim storage of spent fuel,
- Draining of process systems from water and further treatment of process water and generated liquid waste,
- Possibly the decontamination of primary circuit,
- Constructing transport routes and hauling holes to allow large component transfers in the dismantling phase. (Kaisanlahti et al. 2018, p. 28)

In the third phase, the large and activated components of the power plant are dismantled. Large primary circuit components have been activated by neutron irradiation (e.g., the reactor pressure vessel, reactor internal parts, shielding elements, control rod absorbers, etc.). The pressure vessel is handled in one piece: the plan is to lift it into reactor hall, place it inside a radiation shield and transfer it into the on-site repository (Loviisa LILW repository) for final disposal. All other activated systems are also placed in Loviisa LILW repository. In addition to decommissioning waste, Loviisa LILW repository is used for operational LILW disposal. There are also many contaminated systems in reactor building, that are likely to be partially decontaminated or flushed, before their dismantling. Contaminated systems and components are cut into smaller pieces, packed into wooden boxes or concrete containers

depending on their activity levels and transferred to Loviisa LILW repository. (Kaisanlahti et al. 2018, p. 30-32, 37)

When the final phase begins, contaminated systems in other parts of the power plant are dismantled. Some parts of the power plant, like liquid waste solidification plant, Loviisa LILW repository and interim storage of spent fuel were left operating independently after plant shutdown. After the spent fuel has been transferred from Loviisa interim storage to the final repository in Olkiluoto<sup>3</sup>, the last contaminated systems in the power plant may be dismantled. The waste management obligation in Loviisa expires when the final disposal of nuclear waste and the decommissioning of a nuclear facility have been carried out, and the authority has confirmed the waste to be permanently disposed and the quantity of radioactive material inside the buildings and at the soil of the power plant site is within the requirements. (Kaisanlahti et al. 2018, p. 39)

### **2.3 Decommissioning waste from Loviisa**

The decommissioning of Loviisa nuclear power plant generates several waste streams, of which solid and liquid radioactive waste are the two main radioactive waste stream categories (Kaisanlahti et al. 2018, p. 40). A lot of non-radioactive conventional waste is generated throughout the project as well, but its management should be discussed elsewhere.

Solid radioactive waste consists of activated and contaminated material. Activated material contains previously mentioned large and activated components of the reactor. Contaminated material contains maintenance waste and a plenty of miscellaneous waste arising from the dismantling of contaminated systems in the reactor building, auxiliary building, interim spent fuel storage, liquid waste storage and in other contaminated buildings. Liquid radioactive waste accumulates during the whole decommissioning project. Liquid radioactive waste consists of various process waste streams, such as ion exchange resins, evaporator concentrates and by-products of concrete sawing (sludge). (Kaisanlahti et al. 2018, p. 40)

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<sup>3</sup> The Finnish Government made a decision-in-principle in year 2000 to carry out final disposal of HLW deep in bedrock. The final disposal site (ONKALO) is located nearby Olkiluoto nuclear power plant. The site is - currently under construction - the operational phase in final disposal is likely to begin in the 2020's. (Posiva n.d.)

From liquid wastes, a special attention should be paid on the handling of process water arising from the process systems of Loviisa nuclear power plant. Process systems of Loviisa primary circuit are filled with water, and they need to be drained before these systems can be dismantled. The draining of process systems is to be conducted on a 3 year-long transition period of the decommissioning. (Kaisanlahti et al. 2018, p. 43-44)

It has been estimated that the total volume of activated material from both LO1 and LO2 is nearly 3650 m<sup>3</sup> when packed and the volume of contaminated decommissioning waste for both units is estimated to be almost 19 000 m<sup>3</sup>. The activity inventories on the activated and contaminated waste have been evaluated as well to be used in long-term safety analyses. The total activity of activated material for both plant units at the time of the shutdown is estimated to be some 6.37E+8 GBq, whereas the activity inventory in contaminated waste is estimated to be some 4.41E+4 GBq (a number which have included radionuclides with half-lives more than 5 years). These numbers give a rough idea on the magnitudes and hazardousness of the decommissioning waste - while the activated material contains nearly 10<sup>4</sup> times more activity, contaminated material takes five times more space in volume. (Kaisanlahti et al 2018, p. 41; 41-45)

Anyway, of the many decommissioning waste streams, the treatment of process water shall be the main concern of this thesis and discussed a little bit on Chapter 2.5, but the total focus on this topic starts from Chapter 3 onwards.

## **2.4 Nuclear waste classification**

The most apparent way to classify nuclear waste is by its physical form: waste can be in solid, liquid or gaseous form. As far as authorities are concerned, measurable quantities are needed. Therefore, nuclear waste is divided into different classes according the activity levels in it. Nuclear waste may be classified also according to the decay period of the radionuclides in waste. This classification leads to waste with short-living radionuclides (half-lives less than 30 years) and waste with long-living radionuclides (half-lives more than 30 years). A third option to characterize nuclear waste could be to do it according to the management option, essentially meaning the type of storage or disposal means. (Besnard et al. 2019, p. 24; Ruokola et al. 2004, p. 274-275)

IAEA (2009) has provided a general framework on the classification. Finnish perspective on nuclear waste classification is stated on guide YVL D.4. It classifies nuclear waste into the following three categories by their levels of radioactivity, see Table 1.

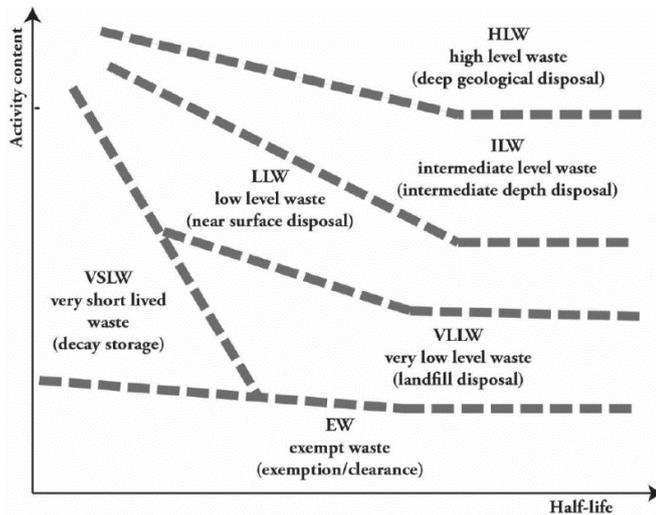
**Table 1.** Nuclear waste classification in Finland, according to YVL D.4 (2019).

<b>Class</b>	<b>Activity limit</b>	<b>Example</b>
High-level waste	more than 10 GBq/kg	Spent fuel
Intermediate-level waste	1 MBq/kg - 10 GBq/kg	Ion exchange resins
Low-level waste	less than 1 MBq/kg	Maintenance waste

High-level waste (HLW) is composed solely from spent nuclear fuel, due to the high activity level. The handling of HLW requires a strong protection from radiation and possibly the cooling of spent fuel. The handling of intermediate-level waste (ILW), like ion exchange resins, requires also proper radiation protection measures. The third category, low-level waste (LLW), usually does not involve any special arrangements considering the radiation protection. This waste category is encountered in the daily operation of a nuclear power plant as miscellaneous solid waste (a so-called maintenance waste). (Ruokola et al. 2004, p. 274)

IAEA (2009) has presented additional categories as well. Exempt waste (EW) is waste that meets criteria for clearance, exemption or exclusion from regulatory control for radiation protection purposes. In Finland, the exemption values for waste with different radionuclides are stated in a guide YVL D.4. Considering the most relevant radionuclides in nuclear waste, their exemption values vary in the range of 0.1 - 10 Bq/g. Very-short-lived waste (VSLW) is waste, that contains primarily short-living radionuclides; hence if it is stored to decay over a limited period (up to a few years), VSLW could be subsequently released from regulatory control. Very-low-level waste (VLLW) is waste that does not necessarily meet the criteria of EW, but VLLW does not need a high level of containment or isolation - making it possible to dispose VLLW near surface.

These categories are also seen in Figure 1, which combines both the activity content and the half-life of the radionuclides in nuclear waste. It also suggests possible final disposal options for each category.



**Figure 1.** Nuclear waste classification presented in terms of activity level and half-life of the radionuclides in the waste. (IAEA 2009, p. 7)

## 2.5 Nuclear waste management

Here, the treatment chain of LILW, waste that is generated in the daily operation of nuclear power plant, but during the decommissioning as well is discussed. As it was already mentioned, spent fuel (HLW) from nuclear power plant operation is currently stored on the interim storages on sites. In many places, it is still an open issue to be solved, although Finland is starting to address this matter soon (see also the Footnote 3 on page 16).

In nuclear waste management, the treatment options can be summarized with the following three principles:

1. Delay and decay,
2. Dilute and disperse,
3. Concentrate and confine.

Delay and decay can be understood so that nuclear waste is stored and radionuclides in it are let to decay - until the activity in waste reaches exemption levels. However, nuclear waste

often contains both long-living and short-living radionuclides; nuclear waste might still need treatment after the short-living nuclides have decayed away. Dilute and disperse is often applied when gaseous or liquid radioactive waste is treated. These two normally contain a little activity spread into a very large volume. By diluting the effluent, the activities released to environment are guaranteed to stay at low level, and the activity even further diminishes when the effluent disperses. Finally, concentrate and confine implies that nuclear waste should be concentrated into a compact, stable form and then confined from environment by disposing it into a final disposal facility. (Ruokola et al. 2004, p. 278-279)

Typically, the treatment of LILW starts from the pre-treatment phase: nuclear waste is collected, sorted, neutralized or adjusted chemically, decontaminated and radiologically characterized. It is important to sort the waste by its activity level: some waste might be clearable from regulatory control right away. This allows to treat it as non-radioactive waste, which makes the treatment of it easier compared to the treatment of radioactive waste. (Ruokola et al. 2004, p. 279)

The treatment of primary radioactive waste aims to change the properties of waste to improve safety, or possibly gain economic benefits from it. The basic objectives are: 1) a reduction in the waste volume, 2) the removal of radionuclides, 3) a change in the physical state and chemical composition of the waste. Numerous treatment methods exist for solid and liquid radioactive waste streams: solid waste may be incinerated or compacted, whereas liquid waste treatment methods include evaporation, filtration, ion exchange, chemical precipitation, etc.<sup>4</sup> Usually, several treatment methods are used in combination to increase the efficiency in the decontamination of the waste during its treatment chain. (Ojovan & Lee 2014, p. 120)

The reduction in the waste volume, defined as the volume reduction factor (VRF) is calculated from a simple equation (4):

$$\text{VRF} = \frac{V_0}{V_f}, \quad (4)$$

---

<sup>4</sup> Appendix I compares typical aqueous waste treatment methods. Of the typical methods, evaporation and ion exchange process are discussed in Chapters 4 and 5 of this thesis, since they are utilized in Loviisa nuclear power plant.

where  $V_0$  is the initial volume of the treated waste [ $\text{m}^3$ ] and  $V_f$  is the volume of the treated waste [ $\text{m}^3$ ], after the treatment process. The higher VRF is, the more efficient waste reduction process is thought to be. While a high VRF is often a desirable outcome, it leads to the concentration of potentially a dangerously high amount of radioactivity into a small volume. (Ojovan & Lee 2014, p. 171)

The removal of radionuclides in the treatment process is expressed with the decontamination factor (DF):

$$DF = \frac{A_0}{A_f}, \quad (5)$$

where  $A_0$  is the initial concentration of radionuclides in the waste [Bq] and  $A_f$  is the final concentration of radionuclides in the largest waste stream [Bq], e.g., in purified water after the treatment. Usually, DF is calculated from the activities of a specific nuclide in the waste, for example radiocaesium (Cs-137). A high DF effectively proves that the treatment method is good. If several methods are used in combination, then the overall DF can be obtained by multiplying the respective decontamination factors of the different treatment methods. (Ojovan & Lee 2014, p. 171-172; Ruokola et al. 2004, p. 280)

Nuclear waste usually needs further conditioning after the waste streams have been processed. Conditioning aims to transform nuclear waste into a suitable form for easing the further handling, transportation, storage and the final disposal of nuclear waste. Immobilization of the radionuclides in nuclear waste aims to convert the waste into a durable wasteform. Immobilization reduces the risk of dispersion of radionuclides from nuclear waste in later stages. The immobilization of solid waste might involve just a simple operation as the packing of waste into containers. The immobilization of liquid radioactive waste typically means that the waste is solidified into cement, bitumen or glass matrix. (Ojovan & Lee 2014, p. 120; Ruokola et al. 2004, p. 281)

The treatment chain ends on the final disposal of nuclear waste. Radioactive waste is placed in a repository or another location, where it is safe from unintentional disturbance while it is also prevented from escaping. The LILW from Loviisa nuclear power plant is placed on the site on Loviisa LILW repository, where the decommissioning waste shall also be placed in the future. (Ojovan & Lee 2014, p. 121; Ruokola et al. 2004, p. 283)

### 3 PROCESS WATER IN LOVIISA NUCLEAR POWER PLANT

This chapter covers the draining of process systems conducted in the transition phase of Loviisa decommissioning. The basics in WWER type reactor water chemistry is discussed first, and then the relevant process systems are mapped, containing water that needs to be treated. Arranging the logistics in the draining and possible strategies to treat the water are discussed.

#### 3.1 Water chemistry in WWER reactors

It is important to maintain proper water chemistry conditions in the primary circuit of a nuclear power plant. Proper conditions are essential in ensuring the integrity of the fuel cladding, minimizing corrosion in the primary circuit, suppressing the products of radiolysis and minimizing the formation and transportation corrosion product radionuclides - ultimately protection power plant personnel from radiation. (IAEA 2008, p. 23)

The water chemistry measures applied for nuclear reactors have an effect on the process waters, hence into the treatment process and generated liquid waste characteristics in the end. The main concern is related on the presence of boric acid in the process waters.

##### 3.1.1 pH value

First, let's familiarize ourselves with the definition of a very important quantity in water chemistry - pH value. It is important to know the pH value, since many chemical, physical and biological phenomena are either directly, or indirectly linked to it. (Ylén 2001, p. 5)

The pH value is used to describe the acidity or the alkalinity of an aqueous solution. Acidic solution contains more oxonium ions ( $\text{H}_3\text{O}^+$ ) than hydroxide ions ( $\text{OH}^-$ ), whereas for alkaline solution, hydroxide ions are dominating over hydroxide ions. If their concentrations equal in the solution, then that solution is neutral. The pH value is a value on a logarithmic scale describing the concentration of oxonium ions in the solution, hence its acidity: (Ylén 2001, p. 9-11)

$$\text{pH} = -\log_{10}\{\text{H}_3\text{O}^+\} \quad (6)$$

At a temperature of 25 °C, the pH value 7 corresponds to a neutral solution. When pH is less than 7, the solution is acidic and pH value greater than 7 means that the solution is alkaline.

The pH value varies typically between 1 to 14, although higher and lower values are possible too. (Ylén 2001, p. 11)

Temperature has a strong effect on the pH value of a solution. Taken demineralized water, pH value decreases when the temperature is increased - due to temperature affecting on the dissociation reactions in water. In the temperature region PWRs regularly operate (290 - 325 °C), the pH value of demineralized water varies from 5.7 to 5.9. In these conditions, the acidity in the water has increased roughly a tenfold more from the neutral conditions (pH = 7) existing at the temperature of 25 °C. (Lips 2005, p. 931-932)

### **3.1.2 Primary circuit chemistry**

The primary circuit of a WWER-440 reactor consists of a reactor pressure vessel and six main circulating loops. Each circulating loop contains a cold, leg, hot leg, horizontal steam generator and a primary circuit pump feeding coolant water into the reactor (Fortum Power and Heat Oy 2004a).

Good water chemistry conditions in the primary circuit rely on establishing mildly alkaline and reducing conditions there. This means that the pH value should be slightly above 7, or as the case is in Loviisa nuclear power plant, the pH value is kept in the region of 7.2 - 7.3 in the operating temperature (Fortum Power and Heat Oy 2004a). The reducing conditions are achieved by the addition of ammonia ( $\text{NH}_3$ ) in the primary circuit. Ammonia decomposes into hydrogen and nitrogen due to radiolysis in the reactor core: hydrogen not only establishes reducing conditions, but it suppresses the products of water radiolysis in the reactor by further reacting with oxygen. (IAEA 2008, p. 23)

As far as mildly alkaline conditions are concerned, there are many factors to be considered. The first is boric acid ( $\text{H}_3\text{BO}_3$ ), that is diluted in the primary circuit coolant as a chemical shim. Boric acid is used to control the reactivity in the reactor together with control rods (Schubert 2015, p. 27). Essentially, boric acid is an acid, so the acidity it causes in the coolant must be counteracted with the addition of a base - if neutral conditions are to be achieved. WWERs typically use potassium hydroxide (KOH) in the reactor coolant, whereas other PWRs commonly use lithium hydroxide (LiOH). (IAEA 2008, p. 23; Fortum Power and Heat Oy 2004a)

However, the concentration of boric acid does not remain constant during a fuel cycle. In the beginning of a cycle, the concentration of boric acid in the water needs to be higher than in the end of the cycle; more boric acid is needed to counteract the excess reactivity in the fuel. Before the start-up of a WWER-440 reactor, boric acid concentration in the coolant is somewhere above 12 g/kg, maintaining subcritical conditions. As the reactor start-up proceeds, the concentration of boric acid is diluted into a start-of-cycle concentration around 8 g/kg which also makes the reactor critical. The concentration is then decreased throughout the fuel cycle, until in the end, it is almost zero. (IAEA 2008, p. 49; Lips 2005, p. 930-931)

Besides boric acid, there are also three different alkali metals (K, Li, Na) affecting the alkalinity on the primary circuit water. Boric acid alkalizes the coolant itself a little, because boron-10 decomposes into lithium-7 and alpha particles due to neutron captures in the reactor core. Moreover, KOH contains a little sodium hydroxide (NaOH) in it, adding another component to consider. Therefore, the alkalinity is normally controlled in terms of total alkali metal concentration, or as is the case in Loviisa, in total equivalent potassium concentration. (IAEA 2008, p. 29)

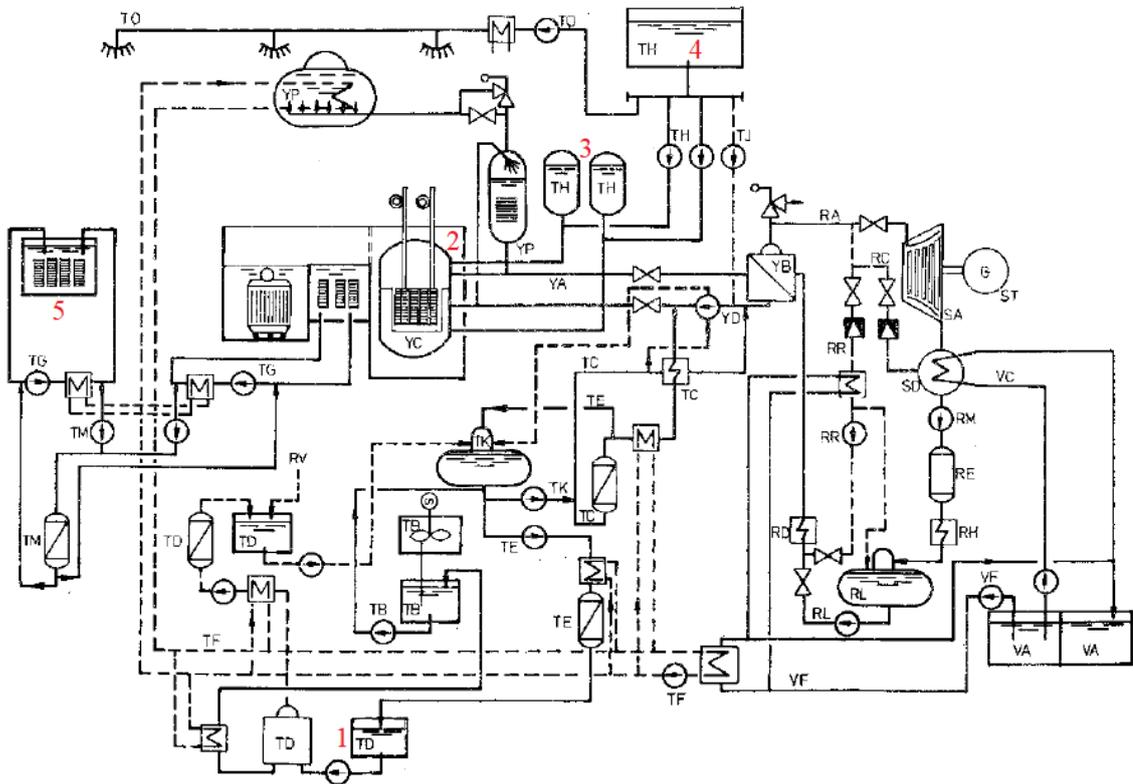
Ultimately, we are interested about the primary circuit and process system water, when the plant decommissioning starts. Before the reactor is shut down, the concentration of boric acid in the primary circuit is relatively low. Now, when the reactor has been shut down, the primary circuit is borated. This increases the concentration of boric acid in the water remarkably, being some 13-15 g/kg in the end. The high amount of boric acid present in the water means that the conditions in water are shifted towards acidic conditions and pH value will end up being around 4.8. (Fortum Power and Heat Oy 2004a)

## **3.2 Process water sources in Loviisa nuclear power plant**

Systems containing a significant amount of process water to be treated are presented next. It should be kept in mind, that only the systems located in the primary circuit systems of Loviisa are of interest. Other considerable sources of water are briefly discussed as well.

### **3.2.1 Process water in primary circuit systems**

To illustrate the systems that are needed to be drained, consider the main circulation chart of Loviisa nuclear power plant, presented in Figure 2.



**Figure 2.** Main circulation chart of Loviisa nuclear power plant. (modified from Leppäsalo 2021, p. 39)

The systems, that are known to contain significant amount of process water, and which possibly contain such substances that can further make their treatment process difficult (radioactivity or chemicals) are marked with red colored numbers on Figure 2. Systems, and their corresponding KZ-codes<sup>5</sup> shown in Figure 2 are listed below. (Kärkkäinen 2018, p. 13)

- 1) Primary water treatment system (TD)
- 2) Primary circuit (YA/YC)
- 3) Hydro accumulators (TH)
- 4) Emergency cooling tank (TH)
- 5) Spent fuel cooling system (TG)
- 6) Other systems (TB, TC, TE, TK)

<sup>5</sup> KZ-codes (from German word *Kennzeichnung*) are used to label the different systems in Loviisa NPP.

Reactor coolant purification system (TC) is an important water treatment system during the operation of the reactor. TC-system is responsible for removing impurities and radionuclides from the coolant (mainly corrosion products), and participates in the control of alkalinity in the primary circuit by removing potassium and ammonium from the coolant. The system consists of two loops, each loop connected to three of the primary circuit loops. The loops in TC-system are connected across the primary circuit pumps (PCP) on the primary circuit loops, operating at full primary circuit pressure. TC-system has no pumps; the primary coolant flow through the purification system is driven by the pressure difference developed across the PCPs. The ion exchange resins used in TC-system are changed once in a year, at the end of a fuel cycle. These resins form a major source of intermediate level waste at the power plant. Used ion exchange resins are transferred into the liquid waste storage of the power plant for storage; waiting for waste immobilization and final disposal. (Fortum Power and Heat Oy 2004a; IAEA 2008, p. 12)

The primary water treatment system (labeled with TD, number 1) is responsible for treating the let-down water. Let-down water is gathered from primary circuit during a fuel cycle, when the boric acid concentration in the coolant towards the end of cycle is decreased. Additionally, primary water treatment system collects process water from different system drainages, fillings and sampling lines. The let-down water is stored in two large tanks, with a volume of 350 m<sup>3</sup> each. Typically, only one of them is used for let-down water collection during the operation while the other is used to feed diluted boric acid into reactor make-up water system. (Fortum Power and Heat Oy 2004b)

The water volume in the primary circuit (YA/YC, number 2) is approximately 200 m<sup>3</sup> (Kärkkäinen 2018, p. 13). The four hydro accumulators (TH, number 3) are connected into reactor each with separate pipeline. They are used to feed emergency cooling water into the reactor core in case a loss-of-cooling-accident (LOCA) occurs. Each hydro accumulator is pressurized with nitrogen, containing approximately 45 m<sup>3</sup> of water with boric acid concentration of 14 g/kg. Emergency cooling tank (TH, number 4) provides water for both low- and high-pressure safety injection systems (TH and TJ) and for containment spray system (TQ) for accident mitigation scenarios. Emergency cooling tank contains some 900 m<sup>3</sup> of water, with boric acid concentration of 14 g/kg. There is also another emergency cooling tank in reserve, with a capacity of 1000 m<sup>3</sup> shared with both plant units. This tank is common for both units,

and therefore not meant to be drained when LO1 has been shut down, since it is kept in reserve for the operation of LO2. (Fortum Power and Heat Oy 2004c)

The fuel pool cooling (TG, number 5) system has four different pools: reactor pool, fuel pool and two wells. The reactor pool is filled with water when the reactor is defueled, since water offers a protection from radiation. The spent fuel is loaded into racks in the fuel pool to cool down a certain period. Of the two wells in the reactor hall, the other one is used when spent fuel is loaded into transferring gaskets - used to transfer spent fuel into the interim storage. The other well contains "clean" water, hence the water in it does not need to be treated similarly than systems. The pools in the reactor hall have a connection to the emergency cooling tank. Emergency cooling tank can be used either to provide water for the pools or to receive water from the pools. (Fortum Power and Heat Oy 2004b)

The interim storage of spent fuel also contains pools that are filled with water. These pools are drained after the spent fuel has been transferred to the final disposal facility in Olkiluoto, currently planned to happen in the mid 2060's (Kärkkäinen 2018, p. 15). The other systems (number 6) contain primarily chemical control systems (TB) and normal make-up water and drains collection (TK) systems. (Fortum Power and Heat Oy 2004b; Fortum Power and Heat Oy 2004c)

Table 2 summarizes the key information concerning the process systems needed to be drained from process water in the primary circuit systems of LO1.

**Table 2.** Process systems, their estimated volumes and chemical conditions in the primary circuit systems of LO1. (Adapted from Kärkkäinen 2018, p. 13)

<b>System</b>	<b>Liquid volume [m<sup>3</sup>]</b>	<b>Estimated boric acid concentration [g/kg]</b>	<b>pH value</b>
Primary water treatment system	350	14	> 4,2
Primary circuit	200	14	> 4,2
Hydro accumulators	180	14	> 4,2
Emergency cooling tank	900	14	> 4,2
Fuel pool cooling system	820	14	> 4,2
Other systems	160	0-9	5-10,5

*Total volume* 2610 m<sup>3</sup>

Note that the boric acid concentration in the systems presented in Table 2 correspond to conditions after the primary circuit has been borated. The liquid volumes presented here are estimations and should not be taken as exact values. As an example, of the two large tanks in the primary water treatment system, only one of them is assumed to be full. Later, it is explained why it is such, since this action is needed to be done to allow the draining of the process systems.

Considering the decommissioning of LO2, the list of drained systems would be almost the same in Table 2, but additionally the common emergency cooling tank is added on the list. As a result, when the water is treated in LO2, the total amount of treated water would be somewhere around 3610 m<sup>3</sup>. (Kärkkäinen 2018, p. 13)

It needs to be remembered that the amount of water to be treated in LO1 during the transition period is probably more than Table 2 estimates. Additional sources of water and liquid waste are coming from the potential decontamination of primary circuit and the flushing of primary circuit and its systems with water. Therefore, Loviisa nuclear power plant should be prepared to treat more water than it is currently estimated to lie on the process systems alone.

Next, a few additional systems containing water, or at least in some point, are presented.

### 3.2.2 Ice condenser

Another source of process water can be thought to come from the ice condensers in Loviisa nuclear power plant. They are designed for severe accident management (SAM): ice condenser, together with the containment spray system, are designed to prevent the pressure increase inside the containment during an accident (e.g., a loss-of-coolant-accident in the primary circuit). Together, they ensure that the integrity of the containment is preserved. (Fortum Power and Heat Oy 2004c)

Ice condenser is located inside the containment, consisting of two annular shaped halves that are filled with ice. One ice condenser contains approximately 835 000 kg of ice inside it. The ice in the ice condensers of Loviisa contain boron, as in the form of sodium tetraborate ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot \text{H}_2\text{O}$ ), also known as borax (Tuunanen 1994, p. 15). When an accident occurs, the erupting high-pressure liquid from primary circuit flashes to steam. Flashing steam is led into the ice condenser to condense, as it melts the ice in it. As the steam condenses into water, pressure increase inside the containment is effectively prevented. As the ice melts, water (containing boric acid) flows down to containment sumps. Emergency cooling systems can utilize the water in the containment sumps by pumping it into the reactor. This way, ice condensers also have an important role in the long-term mitigation of a LOCA. (Fortum Power and Heat Oy 2004c)

### 3.2.3 Drain water

Besides the process water in the primary circuit systems Loviisa, there is another source of water needing treatment during the decommissioning. As we already know, liquid waste sources in the nuclear power plant consist of ion exchange resins, evaporator concentrates, sludges, precipitates etc. These are not only generated when process waters are treated, but also, or pretty much greatly from the treatment of active drain water in the power plant. (Ropponen 2014, p. 7)

Active drain water arises from miscellaneous liquid waste sources, that are led into drains in the power plant, and collected. At this point, the solution contains a lot of active solid particles in it, making it inhomogeneous source of liquid waste and difficult to treat. The raw liquid waste solution is initially collected into tanks located underneath the reactor and auxiliary buildings. Then, the raw liquid waste solution is led into the liquid waste storage

facility of the power plant for temporary storage and clarification. After the clarification, the aqueous solution, called as active drain water now, is pumped into drain water storage tanks. Drain water is stored there until it is treated in an evaporation process. (Fortum Power and Heat Oy 2004b; Ropponen 2014, p. 7)

It has been estimated that approximately 12 000 m<sup>3</sup> of active drain water is treated annually in LO1 and LO2 combined (Ropponen 2020). This number varies depending on the length of the outage and activities carried out during it. However, the final volume of liquid waste that is left from this 12 000 m<sup>3</sup>, after the evaporation process, is remarkably less. Annually, some 50-70 m<sup>3</sup> of evaporator concentrates are left over after drain water evaporation. This means that majority of the drain water is eventually purified and discharged back into sea as a pure condensate water (Ropponen 2014, p. 7). The evaporation process for both drain and process waters is discussed on Chapter 4.

### **3.3 Process water treatment strategies**

In the decommissioning plan of Loviisa nuclear power plant, the draining of process systems from water and the treatment of generated liquid waste has been planned to be executed during the three-year transition period of decommissioning. It is a tight schedule, meaning that the treatment process should be accomplished successfully to prevent delays before the dismantling starts. Next, it is discussed how the process water is planned to be drained from the systems and what are the possible treatment options.

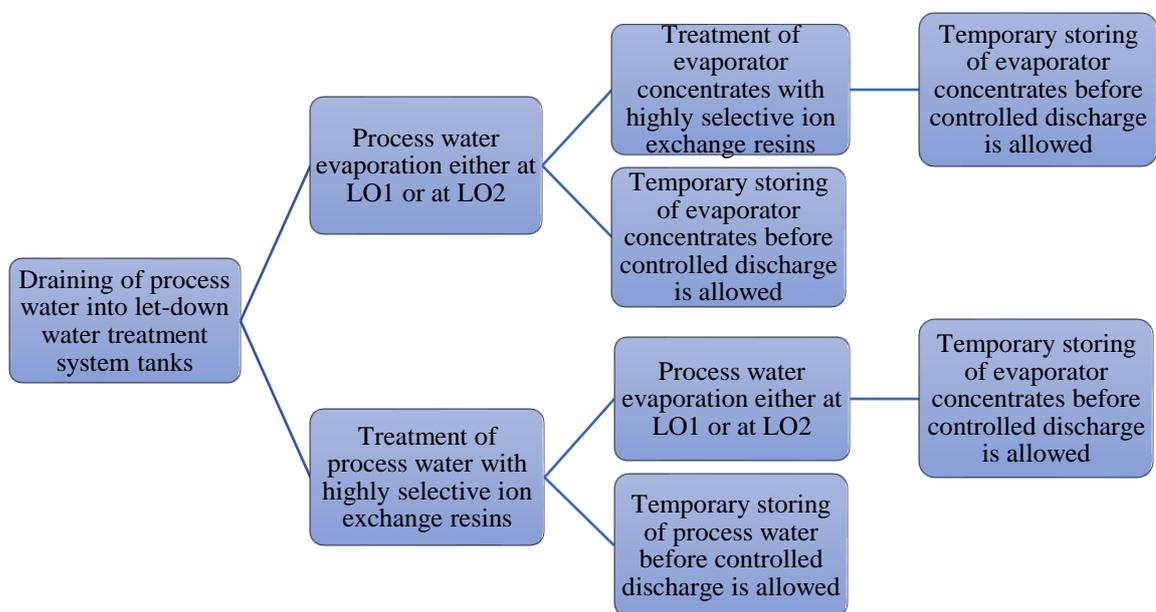
The process starts with the draining of reactor pool, primary circuit and the four hydroaccumulators. Reactor pool is the first to be drained: the process can start when spent fuel has been transferred from the reactor core to fuel pool, and this pool is separated from the reactor pool with a gate. A drainage line (TY) is used to drain the systems. It is connected to each primary circuit loop, but also in the hydroaccumulators. At this point, PCPs cannot be operated anymore, making the draining process relatively slow. It should be noted that around 50 m<sup>3</sup> of water will be left on the bottom of the reactor, because the cold leg circulating loops are connected several meters above the bottom of the reactor. An external pump or such is needed to finish the draining process. (Kärkkäinen 2018, p. 12-14)

On the next phase of the draining process, the process water in emergency cooling tank is drained. Once the emergency cooling tank is empty, the contents of fuel pool and the well

in the reactor hall are transferred there as well. However, fuel pool may be drained only after some 18 months have gone from the final shutdown of the power plant. The reason for this is that the spent fuel must be transferred to interim storage, before fuel pool can be drained. All other minor systems in the primary circuit of Loviisa should be drained whenever they are no longer needed. (Kaisanlahti et al. 2018, p. 29; Kärkkäinen 2018, p. 14).

So where is the water transferred from the process systems? The drainage line in the primary circuit leads the water first into a small primary circuit collecting tank, from which it is further pumped into the let-down water treatment system tanks. We noted that one of these tanks is needed to be available for receiving process water when the draining process starts. Process water from fuel pools and the emergency cooling tank are also transferred into the let-down water system tanks. (Fortum Power and Heat Oy 2004a; Fortum Power and Heat Oy 2004b)

How the process water treatment is progressed from this point on, is still under investigation. Currently, several different strategies to treat the process water have been proposed in internal plans (Kärkkäinen 2018). Figure 3 shows possible strategic pathways to treat the water.



**Figure 3.** Different options to treat the process waters. Detailed plans (plant specific information) on the treatment logistics are presented in Kärkkäinen (2018).

As can be seen on Figure 3, the first choice is related to the treatment method. The process waters are transferred to be evaporated either in LO1 or LO2. After the evaporation process, evaporator concentrates (the leftover liquid waste) containing the radioactive material is treated with highly selective ion exchange resins, if that is necessary. Opposed to starting the process water treatment with evaporation, process waters could be treated with highly selective ion exchange resins directly, after which their volume is reduced with evaporation, if necessary. In both cases, evaporator concentrates, or process waters (liquid waste) probably needs to be stored temporarily in the site. After a suitable time of storing, the discharge of the concentrates or process (waste) water can be executed in a controlled manner. Or, if the discharge is not allowed, then some liquid waste originating from the process water might need solidification in the end. At very least, any ion exchange resin material used in the purification of water end up being solidified.

Whichever strategy is finally chosen, modifications in the power plant and further investigations are still needed. Process water is drained to let-down water system, but there is no connection to drain water evaporation plant of LO1 yet. The system has a connection to let-down water evaporators in LO2, but the problem is that concentrates cannot be transferred to liquid waste storage from LO2 evaporators. It should be ensured that the liquid waste storage of the power plant is reached during the process water treatment, since it contains virtually the only available storage place for all liquid wastes accumulating in the power plant. (Kärkkäinen 2018, p. 25)

Concerning the ice in the condensers, there is no concrete plans made for that operation yet. Here, the author of this thesis has presented two possible alternatives to treat the ice. A direct approach would be to let the ice melt on its place: this way, water would flow down on the floor drains and containment sumps. The benefit here is that ice could be transformed into liquid phase easily - into a form that the liquid waste treatment systems of the power plant can handle. Now, the ice in the ice condensers is virtually free from radioactivity or contains just a little amount of radioactive material in it, hence it is probably better not to melt the ice on its place. If such an amount of ice would be melted, generated water could cause a lot of problems by flooding floors, drain water collection or process lines. Hence, another way to handle the ice would be to detach the ice from the ice condensers, transfer it outside where it melts and then continue the processing with now clean water. This requires more effort

and equipment, but in the end, it might be worth not the mix clean boron water from the ice condensers with the active process waters of the power plant.

### 3.4 Boric acid in the process water

It has been seen that the presence of boric acid on the process waters is significant, when the decommissioning starts. Boric acid has some important features to be considered in liquid waste management, so these are the next topics to be discussed.

Natural boron in boric acid comprises its isotopes boron-10 and boron-11. Of these two, only boron-10 absorbs neutrons in the core, although its natural abundance is slightly less than 20 % - the rest being boron-11 (Schubert 2015, p. 27). Usually, reactor physicists have their interest on the quantities of boron in the reactor (expressed as ppm, parts per million). In liquid waste management, it is much more important to know the amount of boric acid dissolved in the water. Based on the atomic masses of boron and boric acid, a simple relation between boron and boric acid can be formulated:

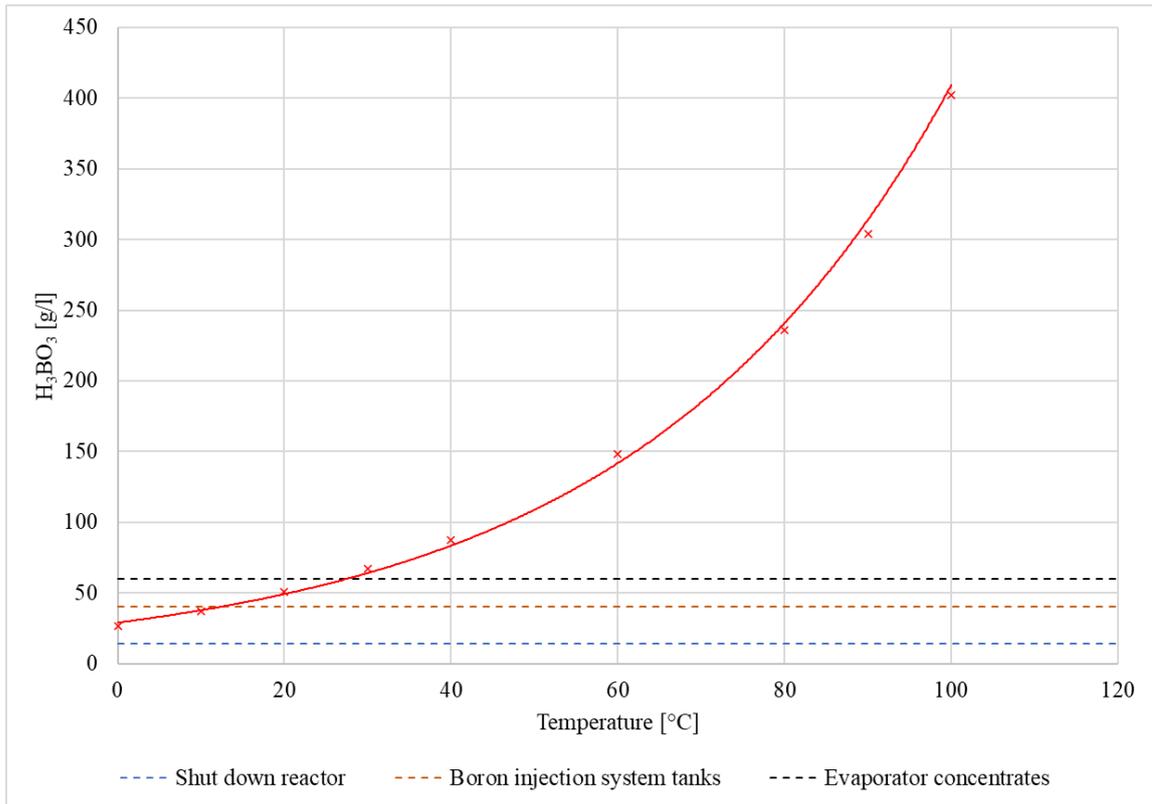
$$1 \text{ wt. \% boric acid} = (10\ 000) \times \frac{10.81}{61.83} \text{ ppm boron} = 1784.34 \text{ ppm boron} \quad (7)$$

According to equation (7), 1 wt. % of boric acid (10 g/kg) dissolved in water is equivalent to having 1748.34 ppm of boron - meaning that 1 g/kg of boric acid corresponds to approximately 175 ppm of boron. (Birch 2015)

#### 3.4.1 Solubility of boric acid

The solubility of a substance tells how well it dissolves in a solvent. A saturated solution is reached (at a given temperature and pressure) when the solute does not dissolve in that solution anymore.

Literature contains a lot of information on the solubility of boric acid. Typically, the effect of pressure on the solubility is weak, and can be said to be negligible for solids and liquids. However, the effect of temperature on the solubility of a substance can be significant. Figure 4 presents how the temperature affects the solubility of boric acid in water. Also, some typical concentration values encountered in Loviisa nuclear power plant have been plotted on the same graph.



**Figure 4.** The influence of temperature on the solubility of boric acid in water shown on the red curve. Solubility is expressed as the amount of boric acid (in grams, per 1000 g of water) making the solution saturated in the given temperature. Data for the chart is taken from Dean (1992). Additionally, some typical boric acid concentrations encountered in Loviisa nuclear power plant have been highlighted on the graph using horizontal dashed lines.

As can be seen on Figure 4, by increasing the temperature of the solution, the solubility of boric acid in water greatly increases. The solubility of boric acid at 20 °C is approximately 50 g/l. At 20 °C, the pH value in a saturated solution of boric acid is approximately pH = 3.7 (Schubert 2015, p. 8). The solubility of boric acid is almost doubled, when the temperature is increased from 20 °C to 40 °C, since the solubility increases to 87 g/l. Further increase in the temperature leads to an exponential growth in the solubility of boric acid.

Besides from water, boric acid may dissolve in steam. The solubility of boric acid in steam is typically expressed by using a distribution coefficient  $K_D$ . It is defined as the ratio of solvent phase densities, or from

$$K_D = \frac{C_s}{C_w} = \left( \frac{\rho_s}{\rho_w} \right)^n, \quad (8)$$

where  $C_s$  is the concentration of boric acid in the vapor phase,  $C_w$  is the concentration of boric acid in the liquid phase,  $\rho_s$  and  $\rho_w$  are the densities of steam and water [ $\text{kg/m}^3$ ], respectively. (Morozov et al. 2018) For the exponent  $n$  in equation (8), appropriate value seems to be 0.9. In the following Table 3, the distribution coefficients of boric acid have been calculated according to the relation presented in equation (8), using the properties of saturated water and steam and  $n = 0.9$  as the exponent.

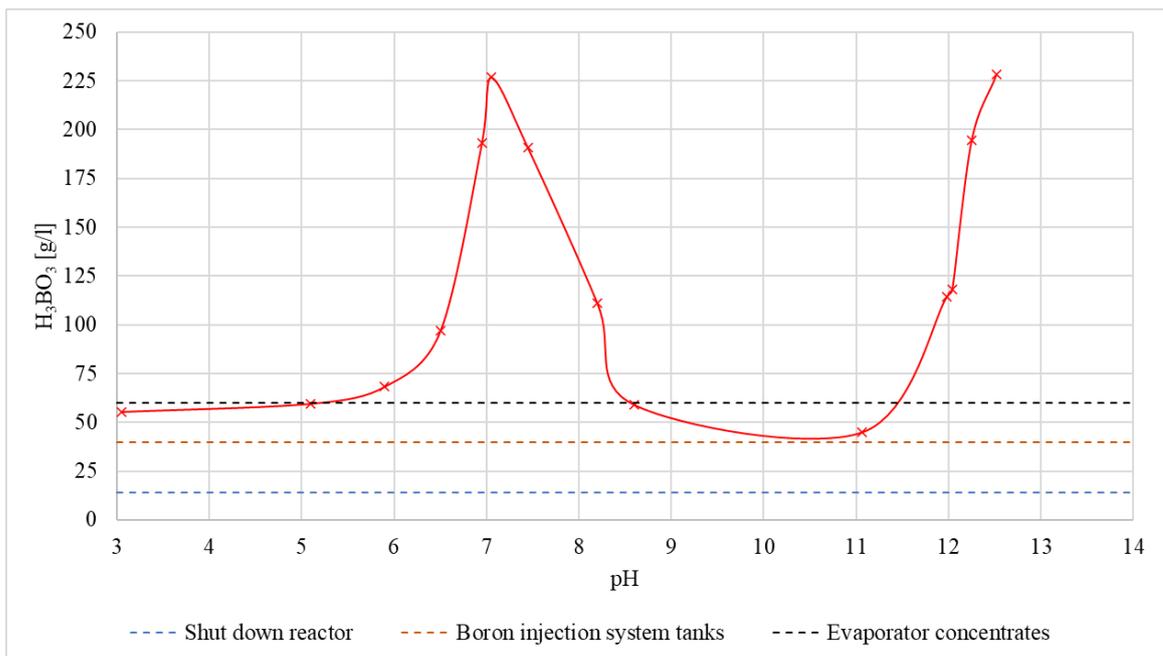
**Table 3.** The distribution coefficient  $K_D$  of boric acid in various temperatures. Values in the second row are calculated from equation (8), whereas third row presents empirically obtained values of distribution coefficients: originally by Reeder (1979) but obtained here as presented in Hyvärinen (1993).

Temperature [ $^{\circ}\text{C}$ ]						
121	177	204	260	316	343	374
$K_D$ , calculated from eq. (8)						
0.0024	0.009	0.016	0.043	0.11	0.20	1.00
$K_D$ , as presented in Hyvärinen (1993), originally from Reeder (1979)						
0.025	0.033	0.04	0.056	0.095	0.15	1.00

The calculated distribution coefficients of boric acid in Table 3 are noticeably small on low temperatures and even until temperatures above 300  $^{\circ}\text{C}$ . Eventually, the distribution coefficient increases to 1, when the critical point of water is reached (374  $^{\circ}\text{C}$ ). Compared to values by Reeder (1979), equation (8) seems to underestimate the solubility of boric acid in steam on the lower temperature region. For example, at 121  $^{\circ}\text{C}$ , equation (8) gives roughly a tenfold smaller value than Reeder (1979). A much better agreement between equation (8) and empirical results is achieved on the higher temperature area.

Table 3 indicates that at low temperatures, the solubility of boric acid in steam is only a fraction compared to that of water. Even at the temperature of 260  $^{\circ}\text{C}$ , the solubility of boric acid in steam is only about 4.3 % (calculated) from the solubility of boric acid into water. Concluding, the solubility of boric acid in steam should not be significant at low temperatures compared to its solubility in water but becomes considerable when the temperature increases to 300  $^{\circ}\text{C}$  or more.

In addition to temperature, there is another interesting factor to be accounted on the solubility of boric acid. Langfelderová et al. (1993) investigated the solubility of boric acid in aqueous solutions of sodium, potassium, calcium and barium hydroxides at various pH values between 5.5 to 12.5. They created conditions for boric acid flowing in similar wastewater compositions than it would be exposed to in WWER reactor type nuclear power plants. They prepared saturated solutions by adding a specified volume of NaOH (or KOH) into weighted amount of boric acid, greater than the anticipated solubility of the product. The mixture was then filled up to 50 cm<sup>3</sup> using redistilled water. Solutions were transferred into glass-joint jacketed vessels, where they were stirred, tempered until a small portion was filtered off after a predetermined time had elapsed. From the filtrate, the contents of boric acid and pH were analyzed. This procedure was repeated until both values stayed constant. Figure 5 presents the results they obtained for the solubility of boric acid in aqueous sodium hydroxide (NaOH), at various boric acid and NaOH ratios, consequently in different pH values.



**Figure 5.** The solubility dependence of boric acid on the pH value of a saturated solution, in the presence of NaOH (at 22 °C). Data taken from the study by Langfelderová et al. (1993). As in Figure 4, typical boric acid concentrations encountered in Loviisa nuclear power plant have been highlighted on the graph.

The higher pH values in Figure 5 correspond to higher concentration of NaOH compared to boric acid in the solution. Figure 5 shows that on the acidic region (pH < 5), the solubility

of boric acid remains slightly less than 60 g/l. On the acidic region of Figure 5, the solubility values are obtained for solutions where mostly boric acid is present. Values in the acidic region of Figure 5 are also in agreement with Figure 4: the pH value in a saturated solution of boric acid at 20 °C is pH = 3.7 and Figure 4 presented that the solubility of boric acid is approximately 50 g/l at 20 °C. In Figure 5, the solubility of boric is increased remarkably, when the pH value in the solution approaches neutral (pH = 7) region. On this region, the solubility of boric acid has a local maximum value of 225 g/l. The solubility of boric acid is also enhanced when the solution becomes strongly alkaline (pH > 11), when more NaOH is present in the solution. Interestingly, pure boric acid has a buffering maximum when pH = 9.24 at 25 °C (Birch 2015). Figure 5 shows that in a solution of boric acid and NaOH, buffering maximum seems to be on the neutral region.

Langfelderová et al. (1993) did not obtain as good solubilities of boric acid with other hydroxides (KOH, Ca(OH)<sub>2</sub> or Ba(OH)<sub>2</sub>) present in the system than they obtained with NaOH. Only one exception to this was noticed in the solution of KOH and boric acid: the solubility of boric acid with KOH present was higher on a pH value greater than 9, than the solubility of boric acid with NaOH present at that pH value. Langfelderová et al. (1993) explained that the solubility differences of boric acid in the presence of various cations and at different pH values is caused by the formation of polyborates, that have different solubilities. In any case, the solubility dependence of boric acid with respect to pH value of the solution seems to be difficult to predict accurately.

### 3.4.2 Crystallization of boric acid

Now, it is important to keep the boric acid dissolved in the solution - otherwise, it might crystallize. Crystallization as a process is a physical transformation: a liquid, solution or gas transfers into a solid form, crystal, in which the atoms or molecules are highly organized. Boric acid crystallizes from an aqueous solution as white-colored, waxy platelets (Schubert 2015, p. 7).

Crystallization occurs through nucleation and growth mechanism. In the crystallization process, stable molecular aggregates, nuclei, are formed first. The nuclei can grow into macroscopic crystals, which constitutes the growth period then. Crystallization may occur only when a thermodynamic driving force is present in the solution: for the crystallization in a

solution, the driving force is supersaturation. Supersaturated conditions in a solution are reached when the concentration of a solute (here, boric acid) exceeds its equilibrium solubility. Equilibrium solubility is a condition, where the solute concentration in a solution is in equilibrium with its solute crystals. Practically speaking, this happens when the concentration of boric acid in water exceeds its solubility limits, seen also on the solubility curves in Figures 4 and 5. (Yu & Reutzel-Edens 2003, p. 1698)

Since PWRs use boric acid for the reactivity control, there might be situations when the concentration of boric acid increases high, even up to supersaturated conditions that would lead to the realization of the crystallization threat. Severe consequences on the crystallization of boric acid could be followed by such a loss-of-coolant-accident, where borated water in the reactor core is boiling, but the boric acid in the water could not be transferred out of the core together with steam. It was seen that the dissolving of boric acid in steam effectively requires to have a high temperature, so boric acid could very well stay on the core without dissolving in steam. Another boric acid transport mechanism, entrainment (spoken on Chapter 4), is thought to be negligible in this situation. Anyway, at some point, the concentration of boric acid in the core following the accident could exceed its solubility limits, crystallize in the core area and possible block some flow paths; eventually leading to overheating or failure in some fuel rods. (Tuunanen 1994, p. 5)

A more likely scenario is not related to such an accident but could be encountered in normal operation conditions. Boric acid may crystallize in the process lines of a power plant, especially if it gets mixed with cold water. Those flow paths, that inject boric acid with high concentrations, should be heated to prevent any crystallization threat in the pipelines (Tuunanen 1994, p. 10). As shown in Figure 4, at the temperature of 20 °C, only some 50 g of boric acid dissolved in 1000 g of water is needed to reach the solubility limit. If the temperature in the water decreases to 10 °C, then the solubility limit is decreased to under 40 g/kg. This a concentration level, that can be encountered in normal operation. For example, Loviisa nuclear power plant has storage tanks on the boron injection system, where the boric acid concentration in these tanks is in a level of 40 g/kg. The crystallization threat is prevented by keeping these two tanks in temperatures between 50-60 °C; this prevents the crystallization of boric acid in these tanks or whenever boric acid is injected to reactor make-up water system lines. (Fortum Power and Heat Oy 2004a)

### 3.5 Radioactivity in the process water

The presence of radioactive material in the process water, consequently in the liquid waste is the reason for the specific treatment methods in liquid waste management. The radioactive material encountered in nuclear waste can be divided into fission products, activation products, or naturally occurring radioactive material, while the last one is not particularly relevant here. (Ruokola et al. 2004, p. 270).

Fission products originate from uranium fissions in the reactor. They emit beta and gamma radiation while decaying. Some fission products stay in gaseous phase in reactor operation temperatures, such as different noble gases and isotopes of iodine, accumulating inside the fuel cladding. Some fission products (such as Cs-137) may dissolve in the coolant. (Lytz et al. 2004, p. 148)

Activation products are born when different material captures neutrons. They are further divided into actinides<sup>6</sup> and neutron-activation products. Operation of the reactor leads to activations in fuel claddings, reactor core structures, reactor internal components and in coolant. Some examples of the activation products encountered in process water are strong gamma emitter N-16 ( $T_{1/2} = 7$  s) that is born in water radiolysis, and beta emitter tritium (H-3,  $T_{1/2} = 12$  a) that is born when boron in the reactor water reacts with neutrons. (Lytz et al. 2004, p. 149)

A special case of activation products are corrosion products. They are activated metal particles, appearing as impurities or dissolved species in the coolant. Corrosion products encountered in the nuclear power plant are characterized by the type of materials that are used in the components of the power plant. In WWER-440 reactors, notable corrosion products are Co-60, Co-58, Ag-110m and Sb-124. While these corrosion products are responsible for most of the radiation hazard, radionuclides Cr-51, Mn-54 and Fe-59 are also common. Corrosion products tend to attach on the surfaces of the primary circuit forming a "crud" on the surface. (Lytz et al. 2004, p. 149-150; IAEA 2008, p. 35)

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<sup>6</sup> Actinides are radioactive elements, having an atomic number from 89-103. Transuranium elements are a special group inside the actinides - they are elements heavier than uranium, having an atomic number greater than 92. (Lytz et al. 2004, p. 146)

### 3.5.1 Radionuclides encountered during the decommissioning

Radionuclides that have relevance considering the plant decommissioning or the times beyond it have long half-lives. It is caused by the exponential decay law, since short-living radionuclides will decay away in the time that is taken after the plant has been shut down for the final time and no more new radioactive material is born in the reactor core. What is finally left for consideration are the transuranics (bound mostly in spent fuel), various corrosion products and some fission products. (Dyer & Bechtold 1994, p. 6-8)

The radionuclides found in the primary circuit water prior to process water treatment should be known considering the planning. Indications on the activity levels can be determined by measuring the water activity levels. For example, Dyer & Bechtold (1994) reported on primary circuit radionuclide activity concentrations, measured from 8 PWRs in the US. It seems that tritium dominates the activity concentration in the coolant in long run. After 1000 days of decaying, the activity concentration of tritium was calculated to be  $1.7\text{E-}1 \mu\text{Ci/g}^7$ , while the other radionuclides combined had only activity level of  $9.76\text{E-}3 \mu\text{Ci/g}$ . The activity level of other radionuclides after 1000 days constituted mainly from radiocaesium (its nuclides Cs-134 and Cs-137) with an almost 90 % share, while the rest (10 %) of the other products were mainly covered by corrosion product activities, such as the nuclides Co-60 and Fe-55.

This report gives a good hint on the most relevant radionuclides to be encountered when the process water is treated in Loviisa. After the time frame of 1000 days (comparable to three-year transition period in Loviisa), only the long-living radionuclides have relevance anymore. These radionuclides are encountered in the liquid wastes accumulating from the process water treatment, assuming that liquid waste that is stored at the site to continue decaying, and not discharged immediately into the sea. It seems evident that tritium will dominate the activity concentration, but more uncertainty is related to the shares of other products. It is known that the used plant material affects the corrosion product fleet, but the presence of radiocaesium in the coolant may be significantly higher, if fuel failures have been common.

Of course, the best way to evaluate the composition of radionuclides in the process waters of Loviisa is to monitor their concentrations on the site itself. An instant and up-to-date

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<sup>7</sup> The activity unit Curie (Ci) is a non-SI unit.  $1 \text{ Ci} = 3.7\text{E+}10 \text{ Bq}$  (Ojovan & Lee 2014, p. 11). Therefore,  $1.7\text{E-}1 \mu\text{Ci/g} = 6290 \text{ Bq/g}$ .

information on the situation is available, since the primary circuit activity in Loviisa nuclear power plant is measured and reported on a weekly basis (Ollas 2021). Another hint on the radionuclides to be considerable is found by looking at the composition of accumulated and stored liquid wastes in Loviisa. In the evaporator concentrates stored in Loviisa nuclear power plant, the major contributors in activity levels have come from the radionuclides Cs-137, Cs-134, Co-60, Ag-110m, Sb-124 and Ni-63, apart from the evident source tritium. (Ropponen 2014, p. 38)

### **3.5.2 Regulation insights on activity levels**

In Loviisa nuclear power plant, small amount of radioactive substances are released in air and sea in a controlled way, that is in accordance with legislation as well as licenses and regulations concerning the operations. Before discharging any water into the sea, the activity level is measured: the release is allowed only when the activity is below set limit values. When the effluents are eventually discharged, they are diluted by mixing them with cooling water flow in the cooling water discharge channel. (Fortum 2020, p. 29-30)

Currently, the emission limits concerning aqueous releases into water systems are divided into two categories: tritium emissions and other fission and activation product emissions. Tritium emission limit is approximately 150 TBq/a, whereas the limit for other products is approximately 0.9 TBq/a. These limits have never been even approached, at least in the past ten years or so. Since in between years 2008-2018, the reported highest tritium emissions were approximately 14 % from the set limit value, whereas other emissions reached only 0.2 % from the limit. (Fortum 2020, p. 31)

Why it is important to address these activity levels prior to decommissioning? One of the principles in nuclear waste management stated that dilute and disperse is a viable option to treat low activity level effluents. Process water treatment follows a similar procedure, considering that concentrating and confining all liquid waste streams by solidification is extremely tedious, yet unnecessary. Of course, the release of effluents is, and must be regulated.

In Finland, guide YVL D.4 addresses the predisposal management of LILW and the decommissioning of a nuclear facility. General clearance levels for unlimited amounts of material, for common radionuclides, are given there as activity concentrations (Bq/g). These values

are probably not applicable as such that process waters could be released directly from regulatory control, or at least not immediately. Therefore, a similar controlled discharge procedure is likely to be followed than it is the current practice with wastewater discharges. Considering the decommissioning phase, different emission limits are likely to come into force then. How much they differ from the current limits, is not certain. However, should they differ much from the current limits, these limits need to be set such that at least the requirement 302 in YVL D.4 is fulfilled. The following statement gives an idea on the requirement: "*--- the decommissioning of the nuclear facility shall be designed such that annual dose constraint for the member of the public arising from planned processing and storage is 0.01 mSv*". (YVL D.4 2019)

### **3.5.3 Decontamination of primary circuit**

In addition to just the radioactivity bound in the process waters of Loviisa, the surfaces in the primary circuit of Loviisa have been contaminated from corrosion products (crud). This might drive for a need to decontaminate the primary circuit before its dismantling.

Previous experience from the decontamination dates to year 1994, when the primary circuit in LO2 was decontaminated. Back then, all loops in the primary circuit, reactor pressure vessel, pressurizer, steam generators and most of the auxiliary systems in the primary circuit were decontaminated. The method was based on the use of chemical decontamination: the process involved the use of permanganic acid, oxalic acid and hydrogen peroxide. The decontamination resulted an average decontamination factor of 40. Some 290 kg of corrosion products were removed, with an activity level of 41.5 TBq in total. (Seitomaa 2021, p. 12-13)

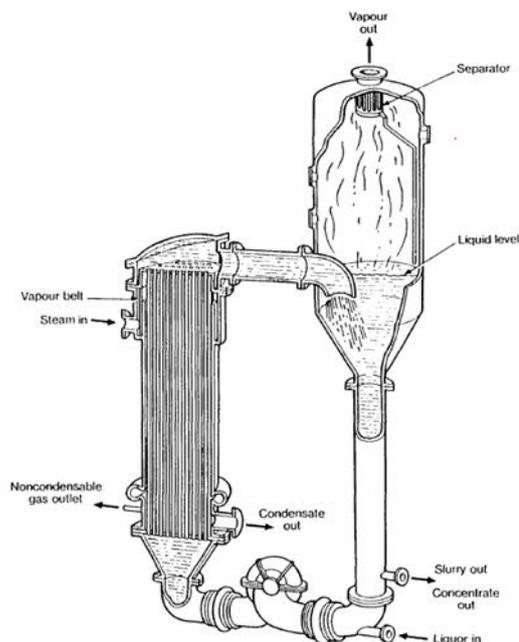
The ultimate decision on whether the decontamination is needed, or what will be the chosen technology will be made prior to decommissioning. Initial estimations indicate that the decontamination has a potential reduce radiation doses for plant personnel significantly, and it is therefore recommended to be done. As a downside, the decontamination generates a lot of liquid waste needing treatment: a lot of ion exchange resins, but also waste water needing evaporation. These should be accounted whenever process water treatment during the decommissioning is planned further. However, this, or the estimations on the radioactive levels in primary circuit are not evaluated more in this thesis. (Seitomaa 2021, p. 18, 30, 34)

## 4 EVAPORATION OF PROCESS WATER

This chapter introduces a treatment method for liquid radioactive waste that effectively reduces the volume of liquid radioactive waste and concentrates the radioactivity. The fundamentals of evaporation process are discussed, focusing especially on how radioactive liquid waste management utilizes evaporation. The evaporation process in Loviisa nuclear power plant is taken into deeper consideration, and how it is currently utilized in the power plant.

### 4.1 Principles on evaporation

Evaporation is a thermal separation technique that concentrates a feed stream by removing a solvent, in vapor form, from a solution or slurry that is fed in the evaporator. Fundamentally, the evaporator apparatus itself is a heat exchanger that uses thermal energy in the process, so that evaporation in the solution is possible. Normally, dry and saturated steam is used as a source of heat in the evaporation, although other sources of heat are also available. Figure 6 presents a simple evaporator apparatus and the associated process streams in it. (Freese 2014, p. 239)



**Figure 6.** A simple long-tube vertical evaporator. (Collier 1991, p. 2)

Figure 6 shows the different process streams in a long-tube vertical type evaporator apparatus: the solution that is fed inside the evaporator is heated with steam, which produces

vapor going out from the evaporator and concentrated product taken out from the bottom of the evaporator. Figure 6 also underlines the three main elements a typical evaporator apparatus has: 1) a heating unit, 2) a region where liquid-vapor separation occurs, and 3) a structural body to house the elements, but also separating the evaporating fluid and heating medium from each other. (Freese 2014, p. 245)

## 4.2 Evaporator types

Evaporators can be divided into two main types: there are evaporators in which the evaporating fluid and the heating medium are separated from each other and then there are evaporators in which the evaporating fluid and the heating medium are brought into direct contact (Collier 1991, p. 2).

Evaporators with tubular heating surfaces are the common in process industry (Freese 2014, p. 245). Shell and tube evaporators form a common evaporator category. A shell and tube evaporator consists of a large cylindrical shell with a bundle of tubes, arranged either horizontally or vertically inside the evaporator. Depending on the application, the evaporated solvent might flow on the shell side, or inside the tubes. Plate type evaporators form another common category where evaporating fluid and heating steam are separated. These evaporators use plates to divide the two streams from each other. The plates are often corrugated or ribbed, to improve heat transfer inside the evaporator. (Collier 1991, p. 2)

Evaporators rely either on natural or forced circulation in the operation. In natural circulation evaporators, boiling induces the movement of the evaporating liquid across the heating surface inside the evaporator by natural circulation; it is caused by the density difference between the liquid-vapor solution and the fluid behind it. Some thicker fluids or fluids with high solids content may require the use of forced circulation when natural circulation is too weak. Usually, a centrifugal pump is installed on the evaporator to take care of the circulation of evaporating fluid inside the evaporator. (Freese 2014, p. 245)

Evaporators may be characterized according to evaporating fluid film behavior. Falling film evaporators are evaporators where the fluid is fed from the top of the evaporator, resulting a gravity driven film flow down the heating surface. The advantage in falling film evaporators comes from the gravity induced flow: the pressure drop is often low or negligible. Long-tube evaporators are often called climbing film evaporators: the evaporating fluid is

introduced from the bottom of the evaporator and carried upwards as a thin film with the generated vapor. Falling film evaporators achieve generally higher heat transfer coefficients than climbing film evaporators. (Collier 1991, p. 9 & 22; Freese 2014, p. 248)

### **4.3 Evaporation in nuclear industry**

Our interest lies on the treatment of process waters with evaporation, where the removed solvent is water vapor. As the vapor is removed from the solution, the concentrated product, "bottoms", is left on the evaporator. The produced solvent vapor is condensed back into liquid in a condenser. The condensate, often called as the distillate, can be discharged into environment after conditioning, since it is mostly free from radioactivity. Evaporator concentrates, that were left on the bottom of the evaporator, is a thick liquor solution. The concentrates contain all non-volatile components, various salts and non-volatile radionuclides (such as the corrosion products). In optimal conditions, evaporators are expected to reach high decontamination factors, even numbers varying from  $10^4$  to  $10^6$ . Some volatile radionuclides, like tritium, ruthenium and iodine may volatilize during the evaporation, and be carried away from the evaporator. Volatilization, together with excessive entrainment, might reduce the overall decontamination of the process. (Freese 2014, p. 239; Ojovan & Lee 2014, p. 172-173)

Apart from volatilization, another important factor affecting the decontamination factor in liquid radioactive waste evaporators is the entrainment. Entrainment is a phenomenon where liquid droplets are carried out from the evaporator together with the rising vapor (Freese 2014, p. 239). Two mechanisms for the formation of liquid droplets are believed to exist. Small droplets (a diameter of few micrometers) are formed when steam bubbles rise in the boiling liquid but burst at the liquid surface. Bigger droplets (a diameter of few hundred micrometers) originate from rising jets of liquid that break up at the liquid surface. Bigger droplets are virtually responsible for the weakening in the decontamination factor of the process. The entrainment caused by those bigger droplets can be mitigated by having large flash chambers in the evaporators: it ensures that the droplets will have enough time to settle down, since the velocity of rising vapor is decreased by having a larger chamber. In addition to enlarging the chamber, de-entrainment devices are usually incorporated into evaporators to remove the droplets that have not settled back. (Godbee & Kibbey 1978, p. 68)

Other than the volatilization or the entrainment, foaming and splashing might also reduce the overall decontamination factor in the evaporation. Foaming tends to increase the entrainment phenomena by raising the liquid level in the evaporator, decreasing the volume in the disengagement space and providing bubbles to be carried away. Foaming is mitigated with the addition of antifoam agents in the evaporator. Splashing can occur, if the boiling in the evaporator is inconsistent and wild. Usually, it is not significant, if there is enough space between the evaporating liquid surface and at the exit of the vapor. (Moghissi et al. 1986, p. 238)

#### **4.4 Evaporation in Loviisa nuclear power plant**

In Loviisa nuclear power plant, the evaporation of aqueous solutions is divided into the evaporation of drain water collected from uncontrolled and controlled leakages of the power plant and the evaporation of primary circuit let-down water<sup>8</sup>. Drain water evaporation produces concentrates have no use anymore; they are further treated as liquid waste. In contrast, the let-down water evaporation is designed to recover boric acid from the process waters to allow its reuse in the power plant processes. (Ropponen 2014, p. 10)

Drain water is more inhomogeneous type of water than process water, since it often contains various dissolved solid particles in it. In contrast, process water should be as pure as possible because it is used in the primary circuit. The main difference comes from the amount of boric acid in them: process water may contain a lot more dissolved boric acid than drain water, especially if we consider process water, that is going to be treated in the plant decommissioning.

##### **4.4.1 Evaporation processes**

Drain water evaporation system consists of a main evaporator, an auxiliary evaporator, a condenser-degasser, a gas cooler and other necessary process components like pumps, valves and control circuits. Drain water evaporation is handled in two stages. The purpose of carrying drain water evaporation in two stages is to concentrate the liquid waste bottoms on the

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<sup>8</sup> These two evaporation processes are arranged such that LO1 is responsible for the evaporation of drain water and LO2 is responsible for the evaporation of primary circuit let-down water. (Fortum Power and Heat Oy 2004b)

auxiliary evaporator - from where the evaporator bottoms are further transferred to the liquid waste storage. (Ropponen 2014, p. 14-15)

Both the main and auxiliary evaporators are constructed such that the heating steam for the process is introduced through a coil that is placed inside the evaporators. The steam for the process is taken from auxiliary steam supply system TN at a pressure of 5 bar, from which the pressure is further reduced to a level suitable for the process, normally into 2.3 bar (temperature of 125 °C). The temperature in which the evaporating liquid boils is approximately 105 °C (pressure on the liquid side about 1.2 bar). (Fortum Power and Heat Oy 2004b & Ropponen 2014, p. 43)

The let-down water evaporator system contains similar components than the drain water evaporator system, apart from not having an auxiliary evaporator. So, the let-down water evaporation is handled in one unit. The evaporator in the let-down water system is identical to the main evaporator of the drain water evaporation plant system. Moreover, these two processes reach similar process values and conditions. Thus, the evaporation process in Loviisa is explained by going through the drain water evaporation. It is also noted if any noticeable differences exist between the drain water evaporation and let-down water evaporation. (Fortum Power and Heat Oy 2004b)

Drain water in the power plant was collected into the drain water storage tanks, located in LO1. Before the contents in the tank are evaporated, the evaporation process begins first by mixing the contents of the tank. After that, the contents in the drain water solution are analyzed to determine the pH value, boric acid concentration, waste concentration<sup>9</sup> and the activity level of the solution. Based on the analyses, pH value in the drain water solution is usually adjusted above pH = 11.5 with NaOH (sodium hydroxide) (Fortum Power and Heat Oy 2004b).

The pH value is adjusted due to a few different reasons. First, the solubility of boric acid is dependent on the pH value (remember Chapter 3.4). The adjustment in the pH value ensures that a higher concentration of boric acid can be left on the evaporator concentrates, and less

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<sup>9</sup> In Loviisa nuclear power plant, the "waste concentration" in a solution is defined as that "waste" consists of the residues of a solution, left when water is removed from that solution. These residues are consisted of many undefined salts, but there might be some solid particles as well. (Mäkinen 2021)

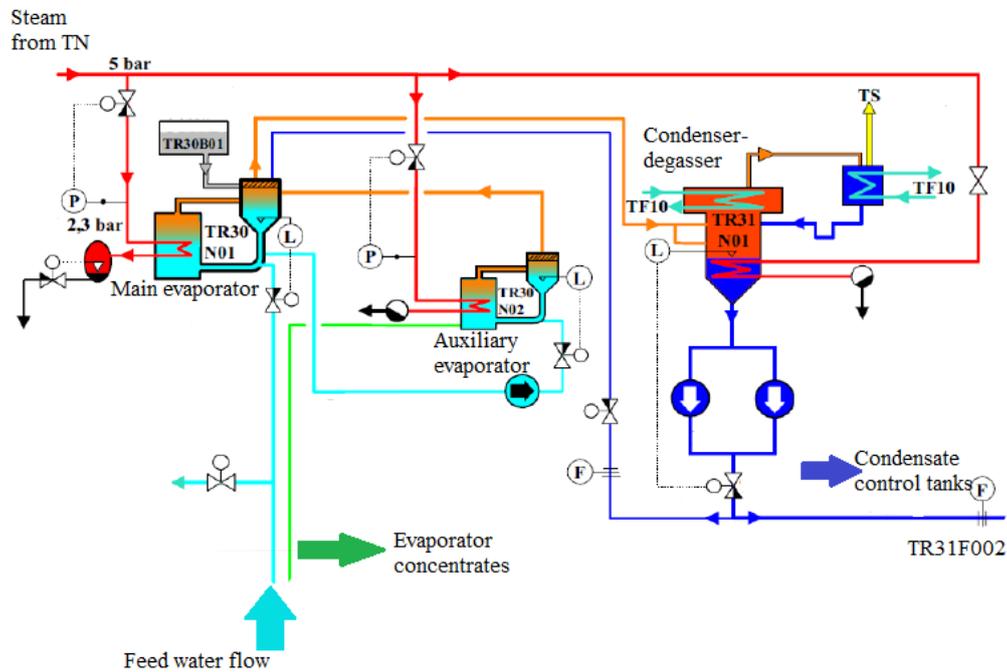
liquid waste is generated. A higher pH value is also a requirement for the further treatment of evaporator concentrates, when they are treated from radiocaesium (Cs-137 and Cs-134) using highly selective inorganic ion exchange resins. The optimal performance on these resins is linked to having a pH value above 11, although having a highly alkaline solution in that process is not desired. (Fortum Power and Heat Oy 2004b; Ropponen 2014, p. 33). The evaporation in the let-down water system does not currently involve a similar adjustment in the pH value of the feed solution. Nevertheless, the solubility limits of boric acid in the water must be considered in that process as well.

Once operator starts the drain water evaporation process, a feed water pump starts pumping water from a drain water storage tank into the main evaporator. The evaporated water is further led into the auxiliary evaporator from the main evaporator via a booster pump. Heating steam for the process is taken from the auxiliary supply system. The heating steam condenses into water inside the heating coils of the evaporators, transferring heat into the evaporating liquid. Control circuit is maintaining the liquid levels in main and auxiliary evaporators constant during the evaporation process. (Fortum Power and Heat Oy 2004b)

As the liquid in the evaporators boil, generated secondary steam is taken out. The temperature at the evaporating liquid side is approximately 105 °C. The secondary steam generated in the auxiliary evaporator is led into the main evaporator. From the main evaporator, the secondary steam flow from both evaporators rises into a demister section. There, a small portion of the condensate water is sprayed into the secondary steam, enhancing the droplet separation and reducing the entrainment. (Fortum Power and Heat Oy 2004b)

After droplet separation, secondary steam flow goes into the condenser-degasser. The steam is first let to condense, but it is immediately vaporized a little again. This ensures that non-condensable gases are efficiently separated from the secondary steam flow. The non-condensable gases are further led into gas-cooling section of the condenser-degasser and then absorbed into active gas treatment system. Finally, the condensate (or distillate at this point), free from non-condensable gases, is pumped into condensate control tanks through a heat exchanger, carbon filters and ion exchangers. Remember also that a small portion of the condensate was recirculated back into the main evaporator. The condensate from the evaporated solvent is now dischargeable into sea, if activity levels permit it, or reused in the plant make-up water systems. (Fortum Power and Heat Oy 2004b & Ropponen 2014, p. 16)

The drain water evaporation process schematic is shown in Figure 7.



**Figure 7.** Drain water evaporation process in Loviisa nuclear power plant. (modified from Fortum Power and Heat Oy 2004b)

#### 4.4.2 Evaporator concentrates

The composition of the evaporator concentrates resulting from the two processes differ. The let-down water evaporation should produce concentrates that are pretty much uniform in composition, since the evaporation process involves the recovery of boric acid from process waters into reuse. The boric acid concentration in the let-down water evaporator concentrates is in the range of 40 g/l. (Fortum Power and Heat Oy 2004b)

The concentrates from drain water evaporation have had much more variety in them. Drain water evaporation concentrates are a highly alkaline solution, containing different salts and compounds of boric acid. In Loviisa nuclear power plant, a typical pH value in these concentrates have been reportedly in the range of 11.5 - 13.3, whereas some 60 g/l of boric acid compounds and 145 to 225 g/l of dissolved salts have been found in stored concentrates (Ropponen 2014, p. 8). By looking on these values, a slight risk of boric acid crystallization is possible, should the concentrates have a low pH value (pH = 11.5). Figure 5 indicates that

the solubility limit of boric acid with a pH = 11.5 is close to 60 g/l. To avoid the crystallization risk in the concentrates, pH value should preferably be near, or over pH = 12. At least right after evaporation, the risk of crystallization even on the lower pH value (11.5) is overcome, judging by the temperature of the solution in that process (evaporation in a temperature near 100 °C). But when the temperature in the concentrates decreases, the risk of crystallization on a low pH value is possible again; Figure 4 shows that the solubility approaches the value of 60 g/l when the temperature decreases under 30 °C.

#### **4.4.3 Evaporation process control**

The two evaporation processes in Loviisa nuclear power plant have different control systems.

Drain water evaporation plant is controlled by a process monitoring system (PMS). Before the evaporation process is started, operators specify the initial concentrations of boric acid and waste in the evaporating liquid and set these values manually into monitoring system computer. Once the evaporation is started, process is let to be monitored by PMS. The control algorithm in the PMS is based on the calculation of boric acid and waste concentrations in the auxiliary evaporator. The calculation routine in PMS integrates the amount of outgoing condensate from the process, measured from a flow after the condenser-degasser. When the routine in PMS has calculated that either boric acid or waste concentration has exceeded predefined concentration limits, it gives a command to empty the auxiliary evaporator. Operators may also manually operate and empty the auxiliary evaporator, if PMS is not available or used. (Finnilä & Taberman 2020, p. 55 & 62-63)

The control system in the let-down water evaporation plant is more autonomous: once the evaporation process has started, evaporator concentrates are circulated through a sampling line. There, evaporator concentrates are analyzed in an analyzer, that continuously measures the boric acid concentration in the evaporator concentrates. As soon as the boric acid concentration in the solution reaches a target value (normally 40 g/kg), a control valve in the outlet line of the evaporator opens, allowing to transfer the concentrates out of the evaporator. A control circuit maintains the outflow such, that the concentration measured in the sampling line stays within the target value. The concentrates are flown into a collecting tank through a heat exchanger, after which they are further gathered into boron injection system

storage tanks, feeding boric acid (at 40 g/l) for plant processes. (Fortum Power and Heat Oy 2004b)

#### **4.4.4 Anomalies on Loviisa drain water evaporation**

In between years 2018 and 2019, some experiments were executed in Loviisa nuclear power plant drain water evaporator system. The objective in these experiments was to find out an optimal pH value to be used in the drain water, before it is fed for the evaporation. Here, "optimal" refers to such a pH value in the drain water feed flow, that results a readily suitable pH value in the evaporator concentrates, i.e., a pH value that is optimal for the further treatment of the concentrates with ion exchange resins ( $\text{pH} > 11.5$ ). Finding an optimal pH value means that there would be no need to adjust the pH value on the concentrates anymore after the evaporation process, making it simpler and potentially saving in the use of chemicals in the future. (Mäkinen 2019)

During these experiments, it was observed that the concentration values PMS calculates for boric acid and waste in the solution inside auxiliary evaporator were different than in samples taken from the auxiliary evaporator bottoms concentrates. Generally, the samples indicated that boric acid concentration in them was lower than PMS had calculated and estimated (Mäkinen 2019). Appendix II contains a portion of the taken samples and corresponding PMS estimations. On average, the boric acid concentration in these samples was 19 % lower than PMS had calculated. However, not all samples presented in Appendix II are following similar behavior: some samples had concentration values above the one PMS estimated.

In any case, these experiments raised the concern that there might be something wrong in the calculation routine of PMS, but no clear explanation for its behavior was ever presented or investigated further. This problem was raised again during this thesis work and was investigated together with the model development. These evaporation plant issues are addressed again in Chapter 8.

## 5 ION EXCHANGE PROCESS FOR LIQUID RADIOACTIVE WASTE

The use of ion exchange process in nuclear industry is a well-established technology. It has been used to fulfill the following duties:

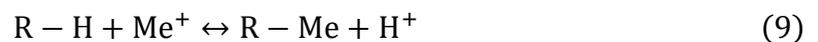
- Provide demineralized make-up water into power plant processes,
- Reduce oxygen levels in the coolant,
- Control the levels of different additives in the coolant,
- Remove radioactive contaminants, such as corrosion and fission products, from the coolant. (Wang & Wan 2015, p. 48)

Of these various applications, our interest lies on the treatment of radioactive contaminants in the water or liquid effluents with ion exchange resins. The fundamentals of ion exchange process and its usage on the treatment of radioactive contaminants are discussed next.

### 5.1 Principles in ion exchange process

Ion exchange process belongs to sorption processes. Sorption occurs when water is pumped through a layer of granulated load material. The impurities in water, such as ions and surface-active particles, are extracted as a result of their physical and chemical interaction with the load material. In contrast to chemical or physical sorption, ion exchange occurs via an electrostatic sorption: attractive coulombic forces between the ions in the solution and ions in the matrix of granulated load drive the process. As a result of ion exchange, the ions from the solution are bound in the solid matrix of the granulated load, while the ions from solid matrix are released into the solution. (IAEA 2002, p. 4-7; Ojovan & Lee 2014, p. 176)

The ions in the solid matrix are bound to different functional groups. Functional groups having a negative charge, exchange ions with positively charged cations of the solution. Correspondingly, functional groups with positive charge, exchange ions with negatively charged anions of the solution. The reactions occurring in cation and anion exchangers are presented in equations (9) and (10), respectively. (IAEA 2002, p. 4; Ojovan & Lee 2014, p. 176-177)





In a cation exchanger, the insoluble part of the cation exchanger (R) releases a hydrogen ion ( $H^+$ ) into the solution and picks up a cation ( $Me^+$ ) from the solution. In an anion exchanger, the insoluble part of the anion exchanger ( $R^a$ ) releases a hydroxide ion ( $OH^-$ ) into the solution and picks up an anion ( $A^-$ ) from the solution.

Sometimes anion and cation exchangers are combined to form a mixed bed system, allowing to remove both positively and negatively charged ions from the solution. As a hydrogen and a hydroxide ion are released in an ion exchange process, they combine to form a water molecule ( $H_2O$ ). Since water is only weakly dissociated, the reactions shown in (9) and (10) are driven to the right-hand side of the equation, so the ion exchange process proceeds. (IAEA 2002, p. 4-5)

## 5.2 Ion exchange efficiency

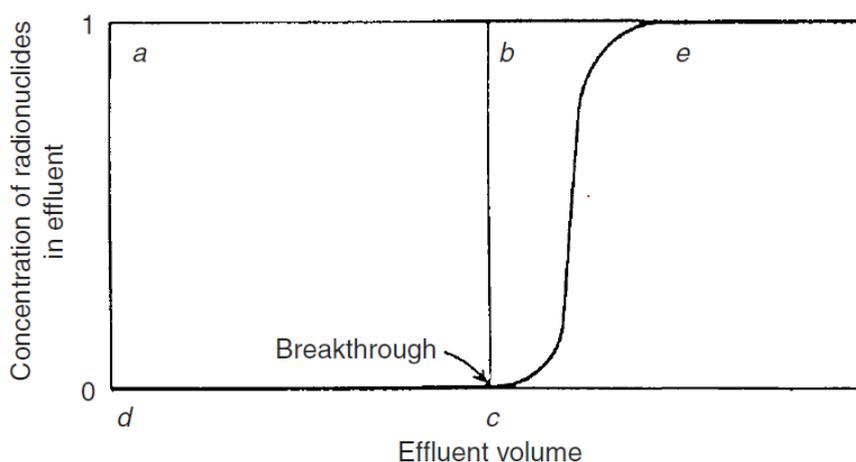
There are many different factors affecting the ion exchange efficiency, such as the ion exchange capacity, ion exchange isotherm, separation factor, selectivity coefficient and the distribution coefficient. (IAEA 2002, p. 5-6)

The ion exchange capacity describes how many functional groups are available on an ion exchange resin, consequently telling how many counterions it has. The ion exchange capacity  $K$  (meq/g, milli-equivalents per gram) is constant for a given ion exchange material. The distribution coefficient  $K_d$  (ml/g) is a parameter, that characterizes the capability of an ion exchanger with a mass of  $m$  (g) to absorb ions from a water having a volume of  $V$  (ml). Obviously, the higher the distribution coefficient is, the better. (IAEA 2002, p. 7-9)

Ion exchange materials react differently with different ions in the solution. The selectivity of a sorbent ( $K^{M1/M2}$ ) is defined as the ratio of two distribution coefficients:  $K_d(M1)$  and  $K_d(M2)$ .  $M1$  and  $M2$  are used to name two different ions here. The selectivity coefficient depends on the concentration, temperature and the presence of other ions in the solution. Because the selectivity is not constant, only general "rules of thumb" on the selectivities of different ionic species can be given. An example: in cationic organic ion exchange resins and conditions applicable for waste processing, selectivity typically increases with an increase on the charge on the exchanging cation and an increasing atomic number of the

exchanged cation. This means that for example  $\text{Cs}^+$ -ion has a higher selectivity over  $\text{Na}^+$ -ion, while  $\text{Co}^{2+}$ -ion has even higher selectivity than these two. Hexacyanoferrates have a very high selectivity towards caesium in solutions where sodium is present, thus the selectivity coefficient  $K^{\text{Cs}/\text{Na}}$  in hexacyanoferrates is high. (IAEA 2002, p. 6; Ojovan & Lee 2014, p. 178)

The operating capacity, or the breakthrough capacity in a column type ion exchange process is important. Breakthrough refers to the volume of the solution that can be treated, before a noticeable increase is observed on the concentration of the species on the treated solution (effluent). In an ion exchange process applied to the treatment of radioactive liquid wastes, the species is, of course, the radionuclides in the solution. See Figure 8, where a schematic representation of a breakthrough curve is presented. (IAEA 2002, p. 8)



**Figure 8.** Schematic representation on an ion exchange breakthrough curve. (IAEA 2002, p. 11)

The horizontal axis (effluent volume) in Figure 8 is usually represented as the cumulative resin bed volume (BV), which is the ratio between volume of processed liquid to the volume of ion exchange resin bed size. The vertical axis shows the concentration of radionuclides downstream the ion exchanger. The values are normalized: 0 means that virtually every radionuclide has been captured from the treated solution, whereas 1 refers to the situation when radionuclides are no longer captured from the solution.

The breakthrough in Figure 8 begins on point *c*. It keeps increasing steeply until at point *e*, no more ion exchanging occurs, since the ion exchange bed has been saturated. The shape

of the breakthrough curve depends on operational conditions (such as on the used particle size in the bed material or the liquid flow rate), but also on the diffusion coefficients of the exchanging ions in the system. The shape of the breakthrough curve presented in Figure 8 represents an ideal situation. It would be a desirable outcome for real processes, since steep increase in the breakthrough curve maximizes the column utilization rate, in contrast to steadily increasing breakthrough would yield. (IAEA 2002, p. 8-11)

When designing and operating ion exchange resin beds, there is a need to optimize the flow rate in the process, since operation conditions influence the breakthrough. With a high flow rate, the throughput from the process is increased, but simultaneously the pressure drop in the process is increased. More importantly, high flow rate decreases residence time inside the ion exchanger. The residence time should be long enough to ensure that the diffusion of the ions in the solution into the particles of the resin occurs desirably. A high flow rate leads to a need to increase the depth of the ion exchange bed, which means that more bed material is needed. Apart from decreasing the flow rate, the residence time could be increased by using a smaller particle size in the resin. However, smaller particles in deep bed systems may also introduce higher pressure drop in the flow. (Moghissi et al. 1986, p. 243)

### **5.3 Using ion exchange for the treatment of radioactive liquid waste**

There are certain prerequisites that the treated liquid waste should fulfill, if ion exchange process is thought to be applied. First, the very nature of ion exchange process requires that the radionuclides in the solution are in a suitable ionic form. Nonionic forms, such as insoluble particulates, colloids, neutral molecules and neutral complexes, are not captured in an ion exchange process (Moghissi et al. 1986, p. 241). Preferably, the treated liquid waste should contain only a little amount of dissolved salts in it (less than 2 g/l); to avoid the competition between nonradioactive ions and radioactive ions of the solution in ion exchange process. However, highly selective ion exchange resins can overcome this problem: they are designed to be selective towards the radioactive species in the solution, while letting the nonradioactive species in the solution pass through them. Thus, highly selective ion exchange resins could be used to treat also solutions where high amount of dissolved salts are present. (IAEA 2002, p. 12, 24; Moghissi et al. 1986, p. 250)

Various ion exchange materials are available. Ion exchange resins can be divided into organic and inorganic ion exchange resins. The resins can be manufactured either using naturally occurring or synthesized materials. Natural inorganic ion exchangers have used natural mineral compounds, such as clays and zeolites. Natural organic ion exchange materials have used polysaccharides, proteins and carbonaceous materials (such as charcoals and lignites). Synthetic inorganic ion exchangers have used synthetic zeolites, titanates, silico-titanates and hexacyanoferrates. (IAEA 2002, p. 12-19)

Inorganic ion exchangers are usually favored in liquid waste management, since they have shown good durability and immobilization properties. Even though the ion exchange process is reversible and would allow the regeneration of the ion exchange bed, it is not normally applied in the treatment of radioactive liquid waste. Instead, once an ion exchange bed has saturated, the resin is removed from service and further treated as radioactive waste. (Ojovan & Lee 2014, p. 179)

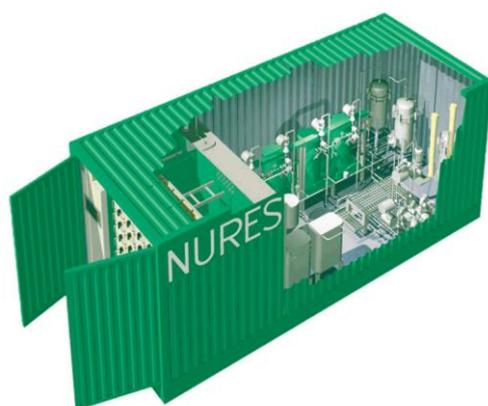
In Loviisa nuclear power plant, the treatment of radioactive liquids with ion exchange resins is applied on the treatment of evaporator concentrates, originating from drain water evaporation. The concentrates from evaporation process are stored into the active liquid waste storage of the power plant. Radionuclides in these concentrates are known to consist mostly of short-living radionuclides, that decay away in few years. However, the presence of long-living radiocaesium (its isotopes Cs-134 and Cs-137) has been the biggest concern and a limiting factor concerning the controlled release of the concentrates. After the concentrates have been stored for a few years or so, a treatment campaign is started: concentrates are treated from the radiocaesium using a highly selective ion exchange resin. After the treatment process, a controlled discharge of the concentrates is possible to conduct. (Ropponen 2014, p. 8, 31)

This highly selective ion exchange resin (market name CsTreat®) used in Loviisa was specifically developed to be used in the treatment of evaporator concentrates. CsTreat® is an inorganic ion exchange resin, made from hexacyanoferrates. It is highly selective towards caesium in solutions where potassium or sodium are significantly present (common for WWER-440 liquid wastes). In addition to CsTreat®, similar highly selective ion exchange resins have been developed to be used in the treatment of radioactive liquids. Fortum's NURES® portfolio contains highly selective ion exchange resins to be used for the treatment

of previously mentioned radiocaesium, but also cobalt (CoTreat®, based on titanium oxide), strontium (SrTreat®, based on titanium oxide) and antimony (SbTreat®, based on zirconium oxide). Apart from their market name indicates of the target nuclide, resins can be selective towards other nuclides as well. For example, CoTreat® has been used to remove other corrosion products from the solution, such as Mn-54, Fe-59 and Ni-63. (Fortum 2021b; Tusa et al. 2007)

Reported decontamination factors (DF) achieved in the ion exchange process vary, remembering that the increase in the breakthrough leads to the saturation of the bed in some point. Eventually, the decrease in DF leads to the need to change the ion exchange medium. Concerning these previously mentioned highly selective ion exchange resins, reported DF for CsTreat® have been between  $10^4$  -  $10^5$ , CoTreat® has reached DF between 10 - 2000, SrTreat® has reached DF between 200 - 2000 and SbTreat® has reached DF between 20 - 1000. (Fortum 2021b; Tusa et al. 2007)

When the process waters are treated during plant decommissioning, options are to either use ion exchange process to evaporator concentrates, or to process water directly. The treatment of radioactive liquid waste using highly selective ion exchange resins could be conducted using a mobile unit that is installed on the site, see Figure 9. (Kärkkäinen 2018, p. 10-11)



**Figure 9.** A mobile NURES container for active liquid waste treatment. The system typically contains highly selective ion exchange resins, prefilters and a carbon filter. After the treatment process, resins are treated as radioactive waste and purified liquid can be discharged into sea. (Ruokola et al. 2004, p. 280)

## **6 IMMOBILIZATION OF LIQUID RADIOACTIVE WASTE**

This chapter briefly goes through the final step on the process water treatment chain - liquid waste immobilization. Waste immobilization is used to convert liquid or semi-liquid nuclear waste form into a solid form. It allows to handle, store, and dispose nuclear waste more conveniently and safely. Immobilization of liquid radioactive waste sources involves mainly ion exchange resins, sludges, precipitates and those evaporator concentrates that cannot be discharged into environment. By immobilizing nuclear waste, the risk of radionuclides escaping into the geosphere after final disposal is reduced. (IAEA 2001, p. 88-89)

### **6.1 Immobilization methods**

There are a variety of techniques and matrix materials available for the immobilization of nuclear waste. Currently, the three main immobilizing technologies are cementation, bituminization and vitrification. These techniques can be divided into thermal methods, requiring a significant heat input (vitrification) in the process or into non-thermal methods, done at close to room temperatures (cementation). The physical and chemical nature of the waste and the acceptance criteria for long-term storage should be considered when choosing a suitable technology. (Ojovan & Lee 2014, p. 205)

#### **6.1.1 Cementation**

Cements are used to immobilize both solid and liquid radioactive waste. Cementation has shown its greatness in the immobilization of nuclear waste. Of the many advantages it has, some of them include:

- it is a simple, low-cost technology at ambient temperature,
- the cement matrix acts as a diffusion barrier,
- it is suitable for sludges, liquors and dry solids,
- the wasteform is non-flammable,
- the wasteform provides a good protection from radiation, and it is not degraded by radiation itself. (Ojovan & Lee 2014, p. 206)

Hydraulic cements are the most frequently used cement matrixes. Hydraulic cements are inorganic materials that set and harden when mixed with water (in ambient conditions): this reaction is called hydration. Hydration consists a series of chemical reactions, eventually

leading to the hardening of the cement - which usually takes several days to complete. The hardened mixture of hydrated cement is called concrete. (IAEA 2001, p. 90; Ojovan & Lee 2014, p. 208-209)

For liquid and solid radioactive waste immobilization, Portland cements are the most common type of cement. Portland cement is produced by heating clay materials with lime in high temperature (over 1500 °C). The formed solid mass is cooled, mixed with gypsum (calcium sulphate) and pulverized. Different Portland cements can be made by varying the compositions of its basic compounds: tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium aluminoferrite. Five basic types of Portland cement have been identified internationally; of which three of them are considered suitable for the solidification of radioactive waste. (IAEA 2001, p. 90-92)

Some types of nuclear waste have shown difficulties when regular Portland cement has been used in the immobilization process. Essentially, the chemical composition of the waste to be immobilized affects the hydration reaction, meaning that the water chemistry conditions of the power plant affects the success of immobilizing different liquid wastes (Ropponen 2020). The success rate in the immobilization of liquid wastes has been improved using additives in Portland cement. For example, masonry cement (additive slaked lime) has been used to solidify successfully wastes such as boric acid, borate salts and bead resins. Several other special combinations exist too. (IEAE 2001, p. 93-95)

In Loviisa nuclear power plant, radioactive liquid waste is solidified into reinforced concrete packages (with a net volume of 1 m<sup>3</sup>) in Loviisa nuclear power plant solidification plant (LOKIT). LOKIT is designed to handle all liquid radioactive wastes generated throughout the operational and decommissioning phases of Loviisa nuclear power plant. The solidification process in LOKIT follows in-drum mixing. Liquid radioactive waste (dosed 0.4 - 0.5 m<sup>3</sup> per one concrete package) is mixed with binding ingredients (cement and blast furnace slags) into a final disposal package, after which the contents are mixed. After the mixture has solidified (usually takes some 24 hours), the package is sealed by casting a concrete lid on top of it. The concrete packages are taken to a buffer storage and let to harden about a month, before they can be transferred into the final disposal facility of Loviisa. (Ropponen 2019)

### 6.1.2 Bituminization

Bituminization is a process in which radioactive waste is embedded in molten bitumen and encapsulated after the bitumen has cooled. Bitumen is obtained as a residue from petroleum or coal tar refining processes. Bitumen (asphalt) is a mixture of heavy molecular weight hydrocarbons. It is thermoplastic material and depending on its temperature, behaves either as a viscous liquid or a solid. (IAEA 2001, p. 96; Ojovan & Lee 2014, p. 233)

Bituminization process is very energy intensive, since it requires energy to heat the equipment, bitumen storage tanks and feed lines. Bituminization can be done continuous or batch-wise manner. Batch process is usually applied when small waste volumes are treated. In a batch process, radioactive waste is typically first dried, and fed continuously into a metered volume of molten bitumen that is kept in a high temperature (200-230 °C). Water evaporates, and solid residues in the waste are mixed with the bitumen. When the desired composition for the wasteform is reached, no more waste is added anymore. Then, the resulting mixture is heated and stirred to evaporate the residual water away. The mixture is placed into containers to cool and solidify as a final step. (IAEA 2001, p. 100; Ojovan & Lee 2014, p. 237)

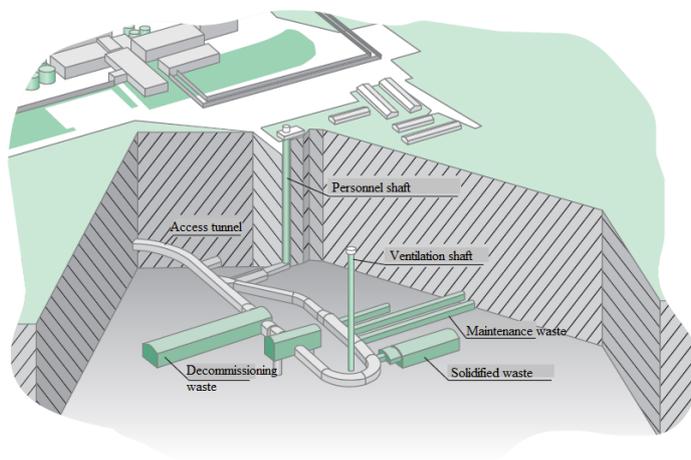
Continuous processes are usually preferred over batch processes, due to higher process throughput. In an extrusion, waste concentrates are fed into a heated extruder screw together with bitumen (at a temperature of 130-200 °C). As waste and bitumen pass through the extruder, they become not only well mixed, but the water in the waste also evaporates. The mixture is then placed into containers to let to cool and solidify. Another typical continuous process uses film evaporators. In this process, bitumen and preheated waste are fed separately on top of an evaporator apparatus. The streams become mixed as they flow down the heated wall of the evaporator. Water in the waste also evaporates away, and the remaining mineral residue can be mixed with bitumen. (Ojovan & Lee 2014, p. 237)

Compared to cementation, bituminization can achieve higher waste loading: bitumen can bind nearly twice as many resins than cement. The weakness in bituminization process is related to its fire hazard: several fires have occurred whenever nuclear waste has been embedded in bitumen. Bitumen is also more vulnerable to radiation than cement. (Ojovan & Lee 2014, p. 241-244)

## 6.2 Nuclear waste disposal

The disposal of nuclear waste is the final step in the waste treatment chain. Ideally, radioactive waste is placed into a dedicated disposal facility. The purpose is to isolate nuclear waste from both human action and natural processes. As the time passes on, radionuclides eventually escape from nuclear waste. This is inevitable, and it must be accounted in the design phase; it must be ensured that escaping radionuclide concentrations shall remain low, and that it will not pose a hazard to human health or to environment. (Ojovan & Lee 2014, p. 321)

Options for the final disposal of nuclear waste include near-surface disposal facilities, boreholes and cavities at intermediate depth and geological disposal facilities including deep boreholes. Depending on the type of nuclear waste to be disposed, all these options have their own benefits but also limitations (Ojovan & Lee 2014, p. 323). In Loviisa nuclear power plant, nuclear waste from the solidification plant and the maintenance waste are placed into the Loviisa LILW repository, in an intermediate depth (approximately 110 m in depth) cavern (see Figure 10). The decommissioning waste shall be placed there as well in the future.



**Figure 10.** Loviisa LILW repository. The repository presented here will be enlarged before the decommissioning of Loviisa nuclear power plant starts. (modified from Ruokola et al. 2004, p. 284)

## **7 DEVELOPING A SIMULATION MODEL FOR PROCESS WATER TREATMENT PLANNING**

To gain a better understanding on thermal power plant processes, modelling the processes comes into question. Those models are based on the conservation equations of mass, momentum and energy. Models could represent either the steady state or the dynamic behavior on the thermohydraulic process. In nuclear power industry, not only the thermodynamics in the power plant systems have been of interest regarding modelling. Nuclear safety has remained a main concern: models and codes have been developed and used to demonstrate that nuclear power plants and their safety systems are able to mitigate different (both realistic and postulated) transient and accident situations. Another common application area is the training of the plant's licensed staff in simulators: training has focused on the daily operation of a nuclear power plant, but also training to mitigate under transient and accident situations. (Alobaid et al. 2017, p. 136)

This thesis work introduces a relatively different dynamic simulation application in nuclear industry, or at least compared to where dynamic simulation has been traditionally used. The following chapters present the simulation software and then the simulation model development and usage with this software.

### **7.1 Apros simulation software**

Apros® (Advanced Process Simulation Software) is a dynamic simulation software jointly developed by VTT and Fortum. It is a system code, treating the thermohydraulic problem in one-dimensional form (Apros n.d.). 1D-approach for the modelling is often enough to be applied for nuclear power plant safety analyses, since flow in the axial direction is usually dominating. Many of the dictating regions for heat transfer can be well analyzed with one-dimensional codes, while also saving a lot of computational resources compared to modelling the whole power plant in 3D. Examples of those regions where axial flow dominates are the hot and cold leg, steam generator tubes or fuel bundle sub-channels. (Vihavainen 2014, p. 33-34)

Apros is managed via a graphical user interface, making modelling and running simulations with it easy. Apros contains a set of predefined component models, e.g., pipes, pumps, valves

and heat exchangers readily available to be used in models. Automation and electrical systems of a power plant can be also modelled with Apros. These will add the presence of dynamic power plant behavior into process models. (Apros n.d.)

Apros sets up the calculational model from the predefined components modeler has defined into his or her own model. Apros automatically generates calculation level objects, nodes and branches, from the process components of the simulation model. Nodes and branches are the elementary components of Apros, where the physics of the problem is modelled and solved. Apros treats the simulation model as a network of nodes (i.e., control volumes) and branches (connecting the nodes) at the calculation level. The spatial discretization of the computational grid follows a staggered grid approach: pressures, enthalpies and component mass fractions are solved in thermohydraulic nodes, whereas flow velocities are solved in the branches that connect the thermohydraulic nodes together. Composition network (in parallel with thermohydraulic network) is used for the concentrations of substances and material properties flowing in the thermohydraulic network. Concentrations in the composition network are solved by using flows obtained from the solution of the thermohydraulic network. (Apros n.d.)

### 7.1.1 Conservation equations

Apros has a few different ways to model the conservation of mass, momentum and energy. The two most frequently used are the homogeneous equilibrium model and the two-fluid six equation model. The two-fluid six equation model consists of six different equations, since the conservation equations are written separately for liquid and gas phases. The homogeneous equilibrium model treats the flow as a mixture of gas and liquid, in which the phases have equal velocities and temperatures. Hence, the number of conservation equations for homogenous two-phase model reduces to three.

The conservation of mass, momentum and energy in the two-fluid six equation model of Apros, written for phase  $k$ , are presented here in a differential form, respectively:

$$\frac{\partial \alpha_k \rho_k}{\partial t} + \frac{\partial \alpha_k \rho_k u_k}{\partial z} = \Gamma_k, \quad (11)$$

$$\frac{\partial \alpha_k \rho_k u_k}{\partial t} + \frac{\partial \alpha_k \rho_k u_k^2}{\partial z} = -\alpha_k \frac{\partial p}{\partial z} + \Gamma_k u_{i,k} + \alpha_k \rho_k g + F_{w,k} + F_{i,k}, \quad (12)$$

$$\frac{\partial \alpha_k \rho_k h_k^*}{\partial t} + \frac{\partial \alpha_k \rho_k h_k^* u_k}{\partial z} = \alpha_k \frac{\partial p}{\partial t} + \Gamma_k h_{i,k}^* + Q_{i,k}''' + Q_{w,k}''' + F_{i,k} u_{i,k} + \alpha_k \rho_k u_k g. \quad (13)$$

In these equations,  $\alpha$  refers to the volume fraction [-] (of the phase),  $\rho$  to density [kg/m<sup>3</sup>],  $t$  to time [s],  $u$  to velocity [m/s],  $z$  to spatial location [m],  $\Gamma$  to mass transfer between the phases [kg/m<sup>3</sup>s],  $p$  to pressure [Pa],  $g$  to gravity [m/s<sup>2</sup>],  $F$  to different friction forces acting on the fluid [N/m<sup>3</sup>],  $h$  to specific enthalpy [J/kg] and  $Q$  to heat flow [W/m<sup>2</sup>]. Subscript  $k$  refers to the phase (gas or liquid), subscript  $i$  to interface and subscript  $w$  to wall. In the energy equation,  $h_k^*$  is defined as the total enthalpy:  $h_k^* = h_k + \frac{1}{2}u_k$ . (Kurki et al. 2019, p. 9; Hänninen 2009, p. 6-8 & 22)

The conservation equations must be discretized in respect to time and space, and non-linear terms in them must be linearized to allow the numerical solution of pressures, void fractions, phase velocities and enthalpies. The discretization process is presented for example in the publication written by Hänninen & Ylijoki (2008). To close the system of equations, liquid and gas phase are coupled to each other using various empirical friction and heat transfer correlations. (Hänninen & Ylijoki 2008, p. 15-18)

### 7.1.2 Boron concentration

On the composition network of Apros, boron concentration is calculated. Calculating and tracking the concentration of boron in reactor core is vital for safety analyses, since boron is needed in controlling the reactivity in a nuclear reactor.

In the concentration equation of boron, Apros assumes that boron stays only in the liquid phase. Therefore, the concentration equation is written as:

$$\frac{\partial (1 - \alpha) \rho_1 x_b}{\partial t} + \frac{\partial (1 - \alpha) \rho_1 u_1 x_b}{\partial z} = 0, \quad (14)$$

where  $x_b$  is boron concentration [ppm],  $(1 - \alpha) \rho_1$  refers to upwind void fraction density of liquid [kg/m<sup>3</sup>] and  $u_1$  velocity of the flow [m/s]. (Hänninen & Ylijoki 2008, p. 37-38)

Hänninen & Ylijoki (2008) presented the discretization of equation (14), that follows a similar procedure than the discretization of energy equation (13). The boron concentration equation (14) is first multiplied with the average cross section of node  $i$  and then integrated over

the node  $i$ . The first term (accumulation of mass) in the newly obtained equation is discretized as follows:

$$V_i \frac{(1 - \alpha_i)\rho_1 x_{b,i}^n - [(1 - \alpha)\rho_1 x_{b,i}]^{t-\Delta t}}{\Delta t} \quad (15)$$

Where  $V_i$  is the volume of node  $i$  [ $\text{m}^3$ ],  $\Delta t$  is the time step size [s],  $x_{b,i}^n$  is boron concentration at new time step on node  $i$  [ppm]. Superscript  $t-\Delta t$  refers to old time step value.

The second term (convection) is discretized using upwind discretization scheme, to yield:

$$\begin{aligned} & A_{i+1/2}[(1 - \alpha)\rho_1]_{i+1/2}[u_{1,i+1/2}, 0]x_{b,i}^n \\ & - A_{i-1/2}[(1 - \alpha)\rho_1]_{i-1/2}[u_{1,i-1/2}, 0]x_{b,i-1}^n \\ & - A_{i-1/2}[(1 - \alpha)\rho_1]_{i-1/2}[-u_{1,i-1/2}, 0]x_{b,i}^n \\ & - A_{i+1/2}[(1 - \alpha)\rho_1]_{i+1/2}[-u_{1,i+1/2}, 0]x_{b,i+1}^n \end{aligned} \quad (16)$$

Here,  $A$  is the flow area [ $\text{m}^2$ ]. Subscript  $i + 1/2$  means the branch located between current node  $i$  and  $i + 1$ , the node on the right side of current node. Subscript  $i - 1/2$  means the branch located between current node  $i$  and  $i - 1$ , the node on the left side of current node. A special notation  $[u, 0]$  means that greater of  $u$  or 0 is used as the value for velocity [m/s].

It is assumed that boron has no effect on the flow conditions: the concentration solution is made after the pressure, void fraction, non-condensable gas density and enthalpy solutions have converged. It can be seen on equations (15) and (16) that boron is advected only along the liquid phase. It is a reasonable approximation, although a small amount of boron could be advected with steam via droplet entrainment.

The phase change occurring in water evaporation inside a node leads to increase in the void fraction ( $\alpha$ ). The phase change is not seen on the concentration equation (14), but it does not mean that boron would disappear from the node when water evaporates. When the void inside a node increases, then boron concentration inside the node must also increase since boron is mixed to smaller water volume after evaporation.

### 7.1.3 Numerical diffusion

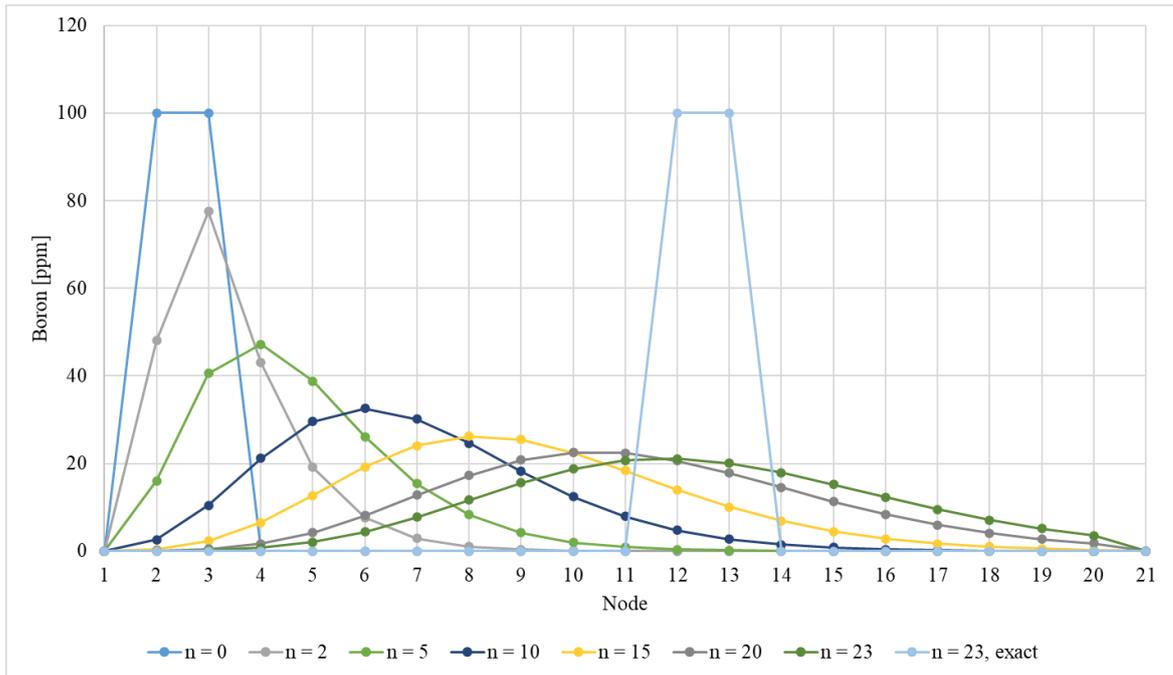
In one-dimensional system codes, such as in Apros, numerical diffusion is a feature arising from the discretization and solving of the partial differential equations. Numerical diffusion tends to even out sharp distributions of solved variables. (Hänninen 2009, p. 19)

How numerical diffusion affects the boron concentration calculation in Apros, is illustrated with a simple example. Before that, let us define a dimensionless number  $C$ , the Courant number with:

$$C = \frac{v\Delta t}{\Delta x} \quad (17)$$

where  $v$  is the velocity of the flow [m/s],  $\Delta t$  is the timestep size [s] and  $\Delta x$  is the length between mesh elements (nodes) [m]. The Courant number represents the time, that information (say, an advected particle) stays inside a node. If  $C > 1$ , it means that information (particle) skips a node completely. Courant criteria,  $C \leq 1$  is important to fulfill when explicit schemes are used; otherwise, the numerical scheme cannot be guaranteed to stay stable. (Caminha 2019)

Now, consider a pipe with a diameter of 40 mm and a length of 6 m. The pipe is divided into 21 calculation nodes, where the two outmost nodes have a length of 0.15 m and the rest 19 nodes have a length of 0.3 m. Flow, with a constant velocity of 1.327 m/s flows through the pipe, advecting the substances in it. According to equation (17), the Courant number is then  $C = 0.44$ . Initially, a boron "plug" is inserted in the beginning of the pipe on nodes 2 and 3, with an initial concentration of 100 ppm. The plug is advected for 2.3 seconds, with a time step of 0.1 s. Results from the calculation are shown in Figure 11, for some time steps.

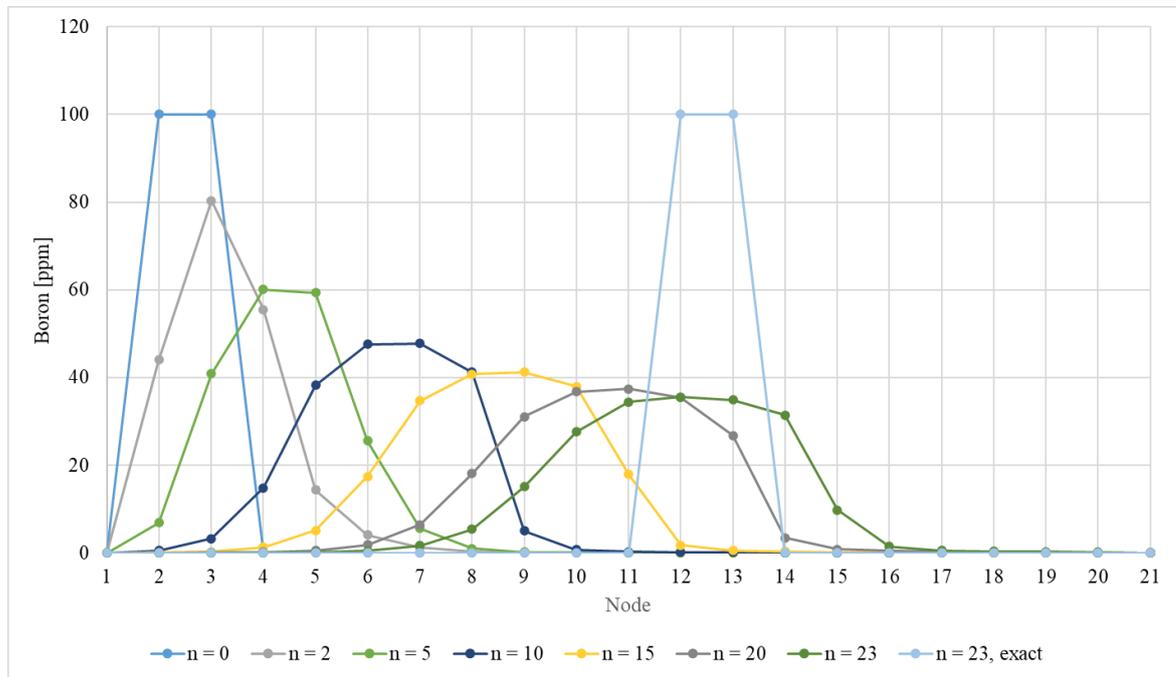


**Figure 11.** An example of numerical diffusion in pipe flow boron concentration calculation. Solved in Apros using first-order discretization scheme. Time steps are referred with the letter n. Here, the Courant number, calculated according to equation (17) is  $C = 0.44$ .

Figure 11 shows how the boron concentration is distributed within the pipe. In the beginning (time step  $n = 0$ ), the profile shows the initial boron front shape on nodes 2 and 3. As the simulation proceeds, the distribution profile in the boron front flattens: it does not preserve its original shape. The maximum value in the boron front has decayed to 20 % from its original value on the final time step ( $n = 23$ ). Approximation on the exact solution is also shown at the final time step, assuming that boron front would be advected through the pipe preserving its shape, as it should. Although the boron front diffuses into a wider area, mass in the system is conserved - the area under the curves stays constant from time step to time step.

Numerical diffusion might affect safety analyses and should be considered carefully if proper tracking of boron front is needed. This phenomenon can be mitigated by using denser nodalization and smaller time steps, but cannot be fully eliminated (Hänninen 2009, p. 37). Hänninen (2009) describes how a higher order discretization scheme was added in Apros to improve the calculation of enthalpy and the boron concentration as well, by reducing the

numerical diffusion. Here, the same case as presented in Figure 11 was recalculated, but this time using a second-order discretization scheme, see Figure 12.



**Figure 12.** The same pipe flow case as in the previous figure, but this time second-order discretization scheme was used in the calculation of boron concentration. The Courant number is  $C = 0.44$ .

In Figure 12, the boron front preserves its shape much better than in Figure 11, but still, numerical diffusion is present. At time step  $n = 23$ , the maximum value in the boron front has now decayed to approximately 35 % from original. This value is almost a factor of two larger than the first-order scheme produced, so the accuracy on the boron front tracking can be improved remarkably by using a second-order scheme.

To conclude this section, numerical diffusion might have a significant effect on the calculation of the boron concentration. Depending on the application of the model, it should be considered and noted that it might bring limitations for analyses. Concerning analyses on the crystallization of boric acid, the maximum concentration on a boron front should be tracked accurately. It is inevitable that the threat arises first on a higher boric acid concentration area, seen for example in a similar boron plug problem than Figures 11 and 12 presented. If significant amount of numerical diffusion is present on the calculation, then the threat of crystallization might be left unnoticed. In this sense, a higher order scheme should always be chosen whenever accurate tracking of the front is needed.

## 7.2 Modelling the liquid waste treatment chain with Apros

Let's think about the modelling of the liquid waste treatment chain with Apros. Generally, the whole liquid waste treatment chain in Loviisa nuclear power plant can be thought to consist of the following aspects:

- process systems containing the water to be treated,
- piping work and components in the power plant process lines for transferring the water,
- evaporation plant(s),
- liquid waste storage,
- ion exchange/highly selective ion exchange resins for the treatment of concentrates,
- solidification plant,
- final disposal facility for nuclear waste.

The capabilities of a process simulation software are mainly limited to solve fluid flow problems, which automatically rules out the final parts of the treatment chain: liquid waste solidification process and waste disposal deep underground. But how about the others? Can they be modelled in Apros? What could be modelled there?

Consider first the nature of the problem. The process water in the process systems of Loviisa nuclear power plant is made up of ordinary water, dissolved boric acid, other dissolved chemical substances and salts, as well as radionuclides as corrosion products (solids) or dissolved ionic species. We have seen that boron concentration calculation is included in Apros, meaning that Apros could be used to investigate issues where boric acid is present. Chemical substances in the water are not included, nor possible chemical reactions in them. An exception to this is the possibility to model combustion processes, but it is certainly not interesting regarding liquid waste management. The absence of chemical reactions means, unfortunately, that Apros does not have currently the abilities to conduct analyses on the water chemistry of the liquid, or to use it in the ion exchange process studies.

Yet another deficiency concerning analyses where radioactive liquid waste is present, is not to have radionuclides behavior modelled thoroughly in Apros. Apros Severe Accidents (SA) module is an extension to the normal thermohydraulic solver, containing fission product

models (such as noble gases, iodine and cesium etc.). However, only the fission products have been included there. Moreover, mainly the gaseous phase and aerosols are tracked accurately - since they are likely to be spread into the environment in a nuclear accident. Although caesium is included in Apros SA, it is grouped together with rubidium. (Ylijoki 2019).

The needs in liquid waste management analyses in radionuclide behavior investigations should be placed on the modelling of corrosion product and radiocaesium behavior. This also rules out the current use of Apros as an analysis tool for radionuclide behavior analyses in liquid waste treatment. However, there are a lot of other possibilities in modelling the treatment chain with Apros, as discussed next.

### **7.2.1 Process water logistics**

The logistical route from process systems to water treatment systems consists of pipes, and different components such as pumps, tanks and valves. Automation systems of the power plant need input from the process conditions, so a variety of different measurements along the route should be taken such as measurement on the flow rate, water temperature and pressure. Dynamic simulation with Apros (system code) is a good choice for modelling the logistical route: considering that the process lines needed in the logistics covers a long route, the flow inside the route occurs mainly in the axial direction and there is virtually no interest to capture any complex phenomena with accurate modelling (such as with CFD codes). Apros contains many process components readily in it, making the construction of the logistical route easy and visually explanatory. Of course, information is needed from the pipe dimensions, pump capacities, valves and automation system logics to model or to simulate the behavior of a real power plant.

The process systems can be physically modelled in Apros. Some systems, such as tanks or storages can be easily modelled using predefined Apros components. Bigger systems involving complex geometry - like primary circuit, should be divided into several calculation nodes. If complex geometries like reactor pressure vessel wants to be modelled accurately, then a more detailed approach is needed. For example, the downcomer section, the upper and lower plenum should be modelled with tools where three-dimensional flows are included, because mixing and recirculating flows inside them are present. Certainly, these phenomena are not of interest regarding the modelling of process water treatment. Considering

process water treatment in plant decommissioning, water in the reactor or in the primary circuit should be just removed and transferred elsewhere, where the real interests in the process are.

When it comes to the physicality in the model, several things should be considered. How pressure or heat losses along the route should, or could be calculated? Pressure losses in a flow are calculated from wall friction, friction caused by the form loss coefficient, irreversible losses due to change in flow area and change in momentum flux between branches (Apros 2020). Apros calculates the losses based on user input data: pipe length, diameter, roughness of the pipe surface and form losses on the pipe must be given. Form losses are given as coefficients: they describe the losses in a pipeline due to elbows, sudden changes in flow areas, inlet or outlets losses to tanks, etc. Typical loss coefficient values are listed in many fluid engineering handbooks<sup>10</sup>. Or, if one wants to investigate the heat losses along the route, there are also opportunities for that as well. Heat pipes can be used to calculate heat fluxes into or out from a pipe. Storage tanks with heat structures could be modelled as well, if heat losses there are of interest. Again, user needs to specify the used material and their dimensions.

Now, whether these two are important for a simulation model representing the process water draining and water treatment during the decommissioning or not, is another question. After the power plant has been shut down, temperature of the water in the process systems should be close to a room temperature, but not much more; considering that the primary circuit has cooled down a while and the water in the process systems is not warm anymore, nor that there would be specific needs to warm it anymore. So, when the systems are drained and process water is transferred forward in the power plant, heat losses in the process lines are probably negligible. However, the temperatures that are encountered in the evaporation process can be considerable: Loviisa uses hot steam (125 °C) in the evaporation process, so that water is boiling at a temperature of 105 °C. When it comes to modelling of the pressure losses along the route, it must be noted that it often requires quite a lot of work to get there. Information concerning pipe dimensions, geometry or process data from the power plant is not very often particularly well available, which makes the accounting of all losses in the

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<sup>10</sup> See for example White, F. M. 2011. *Fluid Mechanics*. Published by McGraw-Hill. 7th edition.

model difficult. Nevertheless, both pressure losses or heat losses can be modelled and analyzed, if such information is needed and important.

The message to take from here is that it should be first determined whether the model requires such an accuracy to be applied in it entirely. In the early design process for process water treatment, these are not the first things to consider. What is more important, is to understand the bigger picture, after which is easier to move towards more detailed understanding and representation of the process. Or, as the case is in the evaporation plant or such, then accuracy is justified and might be worth to investigate more. Finally, a better way to proceed with detailed understanding on the treatment process is to separate those parts into their own dedicated models, rather than building a simulation model containing everything and using it to investigate the possible issues that are concerning just small parts of a bigger picture.

### **7.2.2 Evaporation process**

Although not every corner of the model has an importance for conducting analyses in the treatment of process system water, evaporation plant is a distinction to this. Fundamentally, it is a simple thermohydraulic process where water is fed into an evaporator apparatus and heated with steam. As a result of the radioactive wastewater evaporation, two different process streams are created: 1) steam, that is condensed into liquid form and discharged into environment after conditioning, 2) evaporator concentrates left on the bottom of the evaporator. The concentrates contain all non-volatile substances, boric acid and salts, and needs to be conditioned or immobilized.

The interests in the evaporation process are strongly linked to the separation of boric acid from the feed stream. Although the crystallization of boric acid is a real threat, there is no way to analyze it on Apros as of now. In any case, a simulation model could be created to provide information that supports analyses on the crystallization threat: for example, user might want to know the temperature on the evaporator concentrates and wants to estimate the heat losses as evaporator concentrates are further processed. Other possible interests in this process are linked to the thermodynamics of the process. One can start by investigating basic mass and energy balances during the evaporation and move on to analyses where plant dynamics is introduced: for example, investigating evaporation process response to changes in the pressure of the heating steam, changes in feed flow rate, changes in the condenser

pressure etc. Or, one might want to investigate how the process throughput could be increased, and by what means: for example, how heat transfer area size affects the process throughput, etc.

When the evaporation process is modelled, it should be remembered that the process involves phase changes both in the heating steam and in the evaporating fluid. One approach to model the evaporation process is to start by selecting a suitable predefined heat exchanger component that represents the evaporator. For example, plate heat exchangers, shell and tube heat exchangers and crossflow heat exchangers are readily available. These can be used effectively, if the correct dimensions and exact structure of the evaporating apparatus are known. However, user should make sure that the predefined component is able to calculate the process correctly, such that phase changes truly occur for both fluids, or at least for the evaporating liquid. If not, then user might need to modify settings on the calculational level. Possible modifications are described on the following chapters when another modelling approach is gone through. (Apros 2020)

Another way to approach the evaporation process modelling is to start by defining two separated nodes, or possibly multiple nodes, but such that the heating steam and evaporating fluid flow are not mixed (if the process does not involve their mixing). Nevertheless, the heat that is generated in nodes where heating steam condenses is transferred to those nodes where evaporating fluid flows and boils. The heat can be transferred using a heat structure component. Then, user specifies the dimensions of the evaporator apparatus by entering relevant data concerning the heating structure: for example, stating the thickness and radius of a pipe, the length of a pipe and the number of pipes in a tubular heating structure. Information like this is needed when the model calculates correct heat transfer coefficients using correlations that depend on the structure and its dimensions, but also on the flow conditions.

Sometimes, it might happen that the dimensions of the evaporator or some other crucial information is missing. If the user is more interested on simulating the evaporation plant behavior, rather than conducting analyzes where conditions might alter, then it is still possible to proceed the modelling without knowing all details. User may modify various calculation level settings on the heat structures or in the nodes. The aim on these modifications is to affect into the efficiencies in heat structures and in the calculation of the heat transfer

coefficients, such that the desired performance level or conditions in the evaporation are reached.

### **7.2.3 Ion exchange process**

The actual ion exchange process is not modellable in Apros, but it does not mean it should be entirely abandoned from a simulation model. Simply a pipe (branch) or a valve component in a process line can be used to represent an ion exchanger for a simulation model. The weakening in the ion exchange process (breakthrough) cannot be calculated with Apros, but could be simulated, if that is desired. If measurement data is available from a breakthrough curve of some known ion exchange medium and process conditions, then it is possible to model this behavior artificially. This could be simulated by measuring the cumulative flow through the ion exchange medium, and then connecting the cumulative flow data into experimental knowledge on the evaluation of the breakthrough. Then, the model could inform whenever the breakthrough has increased too high, requiring further actions to be done. Now, the monitoring of the breakthrough evaluation is usually something that is measured on the field, not on the operator level, so the usage of such simulation is limited.

In many times, the plugging of an ion exchanger and the decrease on its performance level is indicated by increased pressure losses in a flow. There might be application areas, such as training simulators where such a phenomenon wants to be simulated, since plugging in a process line may require further actions from the operators.

## **7.3 Setting requirements for a simulation model**

The treatment of process water during the decommissioning of Loviisa nuclear power plant has been seen to involve many steps; it is not as straightforward as it would appear on the first thought. While the process systems in LO1 are drained, the operation of LO2 is still intended to continue at the same time. Traditionally, engineers tend to rely on static PI-diagrams when new processes or procedures for operation are planned. However, this approach is undeniably a bit challenging and inflexible - better ways to understand the whole process water treatment chain during the decommissioning is needed. How one could easily present and demonstrate the complexity of such process? What if there are various modifiable parameters that can affect towards the sufficiency of the whole process? These questions have underlined that there is a need to investigate whether the process water treatment during the

decommissioning could be better understood and studied with more flexible means than by using pen and paper, possibly by the means of simulation.

Originally, the idea for building a simulation model to investigate the process water treatment during the decommissioning came from the engineers working with liquid waste management in Loviisa nuclear power plant. They recognized that it is important to understand how the treatment chain as whole works, but also underlined that there is a room for new tools to be used in the decommissioning planning.

The simulation model should be visual and let engineers, operators and plant personnel easily get the impression on how the process water treatment is executed. The model should allow the variation in the key parameters related to the draining process, such as process system capacities or to allow somehow affecting into liquid waste volume optimization. It would be beneficial if the model could run a real-time simulation, faster than real-time for demonstration and analyses purposes.

One alternative for the process water treatment simulation model would have involved using an Apros based Loviisa nuclear power plant training and testing simulator model (LOKS2 in Loviisa). This simulator model is divided into 3 main models:

- 1) Primary circuit, secondary circuit, automation and electrical systems,
- 2) Containment,
- 3) 3D-reactor core (divided into one model containing the neutronics and eight thermo-hydraulic models). (Viljakainen 2020)

Training simulator model seemed to be too heavy and complex, considering that process water treatment during plant decommissioning does not need to have the secondary circuit of the power plant, reactor core neutronics or any other parts that are needed in the normal operation of the power plant. Considering how complex that model is, it is not only difficult to manage, but to operate, because the real-time simulation speed of it is limited. And to add that many plant automation systems are integrated as emulations to that model, which also effectively restricts the usage of the model as a stand-alone version. And finally, that model does not include all required systems for process water logistics and process water treatment; hence developing a new simulation model from scratch was the best option.

Essentially, the developed model (see Appendix III) is intended to be a design simulator model. In this first stage of the model development, the simulation model was not intended to be too complex, that might prevent its efficient creation, modification or operation. Visually, the target was to ensure that the simulation model is easily understandable for liquid waste management planning purposes. This way, the model illustrates the different systems that are needed in plant decommissioning and in the draining process, and it allows to simulate the draining process effortlessly. This approach differs from the approach that would aim to build a full simulator model to be used in operator training or compared to creating a model where all aspects from the process thermohydraulics should be captured. Nevertheless, this approach does not deny later improvements in the model accuracy.

Although the first stage of the simulation model development did not involve physically accurate modelling, one part of the model was taken into deeper investigation - the evaporation process. The interests towards this process were also shown by the engineers working with Loviisa liquid waste management. They had noticed the issues on the drain water evaporation plant, when they arranged experiments on the evaporation plant (see Chapter 4.4). Considering the decommissioning phase of the power plant, evaporation of process water might form one of the cornerstones in process water treatment: smooth operation there should be ensured. Apros provides the possibility to model thermohydraulic processes such as the evaporation accurately, so accurate modelling and analyzes there should be possible.

#### **7.4 Creating the simulation model**

The simulation model development can be divided into two different parts, so this chapter concentrates on the overall modelling process and the choices around it. Chapter 8 is then solely dedicated on the evaporation plant model, and for the results obtained from the calculations and analyzes around it.

The systems to be included for the whole logistical simulation model involved those systems that are to be drained and the most important functions needed in the whole process water treatment, see earlier chapters. Of course, the solidification process was not to be included, since it cannot be simulated with Apros or process simulation means. Not every branch in the power plant pipelines was to be included for this model: the model is meant to cover the route of the process water from Loviisa primary circuit systems to the end, as it has been

currently proposed and is known to be done in the power plant. The "end" means here either a liquid waste storage or a discharge to environment. There is an endless number of options to arrange the process water logistics during plant decommissioning; the one modelled here is mostly relying on current plant procedures, schematically presented in the internal plans as well (Kärkkäinen 2018). In any case, the logistical route was modelled "accurately". In this context, accurately means that operators and power plant personnel would understand what the route for the water is that it needs to travel from process systems to treatment. Not every system in the power plant was included for the model: for example, drain water evaporators were included in the model, but let-down water evaporators were not. As mentioned, drain water evaporation was to be investigated more in detail.

Information from plant documentation and the existing simulator model was used for the model. The basic components needed in the logistical route (pumps, tanks and valves) can be included in the simulation model by simply using predefined Apros components. Not every valve on the logistical route is needed - only the most necessary ones for the draining process or water logistics were included. It should be remembered that valves in the power plant field can be manually or operator operable: these were not separated from each other in this model but needs to be kept in mind if simulation model is used in any further planning.

Automation components were also used in the model. Automation in this model is needed to maintain liquid levels of tanks or to ease the simulations in many ways. Especially in the evaporation plant, automation is needed. The control logics behind the automation models were kept simple, bringing only the most relevant functions for the simulation model, thus skipping for example plant protection signals, or other signals encountered in real power plant, but not necessary here.

Some simplifications for the model were needed, since the drained systems and their route to the end covers a lot of modelling work to do. For example, the primary circuit and hydroaccumulators were not physically modelled as control volumes (nodes), since that would have not brought any extra value here. Therefore, they were replaced by defining a boundary condition set on the drainage line of the primary circuit loop. The six-equation model was selected as the flow model accuracy, although the homogeneous model would probably satisfy the needs as well. Working fluid in the model was selected to be WSB, a mixture of water/steam and boron, to allow analyses on the evaporation process.

In this model, nodalizations on the process lines were created by choosing pipes with correct dimensions (length), and then connecting them together with points set on different elevation levels. This way, Apros creates the nodalization automatically. The nodalization can be thickened by modifying an attribute that defines the number of nodes generated from a pipe. Judging by the numerical diffusion seen on Figures 11 and 12, nodalization should be always deliberately chosen. If a boron front is to be tracked accurately, then too coarse nodalization leads to loss in the information. Nodalization could also need thickening when pressure or temperature is to be measured from a specific place in a process line. It should be remembered that increasing the nodalization too much leads inevitably to the decrease in simulation speed. Therefore, the places where denser nodalization is to be applied should be optimized to achieve both the needed accuracy level and simulation requirements.

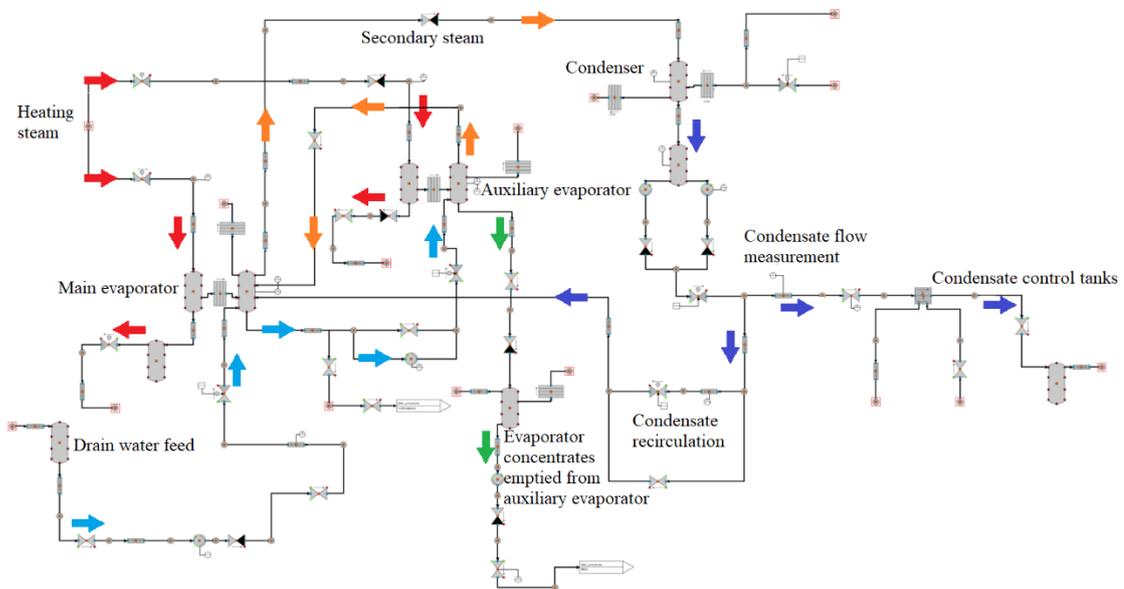
The simulation model can be operated manually, where one manages the simulation logistics by opening and closing valves, starting pumps and starting the evaporation process. This is similar to operating the power plant like operators would do. For demonstration and analysis purposes, it is convenient to create scripts for running through the water draining and treatment process sequentially. Apros utilizes SCL (Simantics Constraint Language) for scripting. With SCL scripts, one can parametrize the model running by defining the actions that are needed in the process - like opening valves and starting pumps at correct times.

## 8 ANALYZING LOVIISA DRAIN WATER EVAPORATION

This chapter is dedicated to present a real use and analysis case of the simulation model: the part of model involving drain water evaporation plant was used to investigate the reported issues on drain water evaporator plant process monitoring system, as presented in Chapter 4.4.

### 8.1 Evaporation plant simulation model

Before going on the analysis, the evaporation plant simulation model and modelling principles behind it are first presented here in detail. The whole evaporation plant Apro-s-model, and the associated process streams are shown in Figure 13.



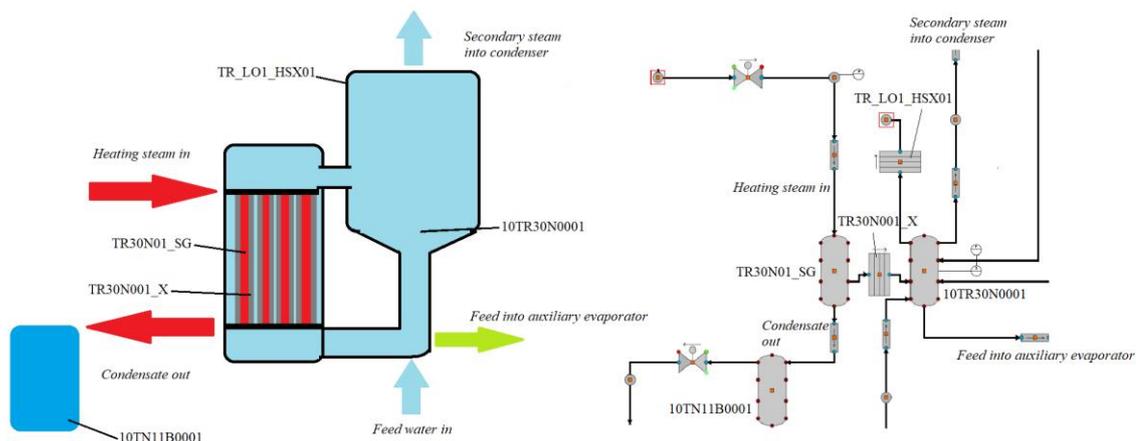
**Figure 13.** Apro-s-model representing the drain water evaporation plant in Loviisa.

Figure 13 shows how the process flows are arranged in the evaporation plant: drain water is introduced from the tank on the bottom left corner, from where it is pumped into the main evaporator. Heating steam for the main evaporator is taken from upper left corner, where a boundary condition point is defined. From the main evaporator, drain water is further led into the auxiliary evaporator via a booster pump. The auxiliary evaporator utilizes the same boundary condition point for process heating steam as the main evaporator does. Control circuits are also included on the model; they are maintaining the liquid levels constant during the evaporation process in both evaporators.

As the drain water boils, secondary steam from the auxiliary evaporator is led into the main evaporator. From the main evaporator, the combined secondary steam flow from both evaporator units is led into the condenser, that is located on the upper right corner of Figure 13. In the condenser, the secondary steam condenses into water and flows into a hotwell. From the hotwell, the condensate (or distillate at this point) is pumped into condensate control tanks. A small portion of the condensate flow is returned to the main evaporator, although, it is not used to enhance droplet separation here. In this model, secondary steam is already dry, but in saturated condition.

The purpose of the evaporation in the power plant is to concentrate the radionuclides from the feed stream in evaporator bottoms. At the same time, various salts and boric acid in that feed stream are concentrated on the bottoms as well. Process control is explained on the next subchapter, but in short, when the concentration of boric acid or waste exceeds a limit value, auxiliary evaporator is emptied. Then, the concentrates are led into the liquid waste storage of the power plant. In this model, concentrates are just transferred into a boundary condition point; only the state in concentrates after evaporating a batch was of interest.

Figure 14 shows a schematic of the nodalization idea in main evaporator.



**Figure 14.** On left: schematic on the main evaporator nodalization, and associated process flows in it. Corresponding part from the Apros-model is shown on right.

As shown on Figure 14, the main evaporator is modelled by two separated nodes that are connected with a heat structure (TR30N001\_X) in between them. Node TR30N01\_SG represents the heating coil, in which heating steam is introduced in the evaporator. The other node (10TR30N0001) represents the part of the evaporator filled with drain water, where drain water eventually boils. Heat structure TR30N001\_X is representing the inner and outer surfaces of the heating coil, transferring heat from the heating steam to evaporated drain water. The other heat structure (TR\_LO1\_HSX01) represents the outer surface of the main evaporator, from which heat flows into environment. The heat flow into environment is not significant during the evaporation but is needed when the evaporator is shut and cooled down. Finally, there is also a condensate tank 10TN11B0001 collecting condensates from the heating steam side.

The auxiliary evaporator is modelled in a similar fashion as the main evaporator, by using two separated nodes connected with a heat structure between them. The condenser is modelled with two nodes: from the node where secondary steam condenses and from the node representing the hotwell for condensate water. Non-condensable gases were not included in this model. Pressure in the condenser is maintained in the node where secondary steam is condensed; a control circuit alters the cooling water flow rate based on the pressure in the condenser.

The model needed also relevant input data on the evaporation plant capacities, process values and dimensions of the evaporators. The key process values of the drain water evaporation plant are presented on Tables 4, 5 and 6, corresponding the nominal conditions in evaporation. However, only heat transfer areas inside the evaporators were found: no specific information on the dimensions of heat transfer coils inside the evaporators was documented.

**Table 4.** Key process values of main evaporator in nominal conditions (Finnilä & Taberman 2020, p. 11-13; Fortum Power and Heat Oy 2004b & Ropponen 2014, p. 43).

<b>Parameter</b>	<b>Value</b>	<b>Unit</b>
Heat transfer area	150	m <sup>2</sup>
Pressure at the liquid side	1.25	bar
Pressure of the heating steam	2.3	bar
Temperature at the liquid side	105	°C
Temperature of the heating steam	125	°C
Feed flow into evaporator	1.5 - 1.7	kg/s
Heating steam flow	2.0 - 2.5	kg/s
Condensate return flow	0.2	kg/s
Volume of liquid in the evaporator	5.4	m <sup>3</sup>

**Table 5.** Auxiliary evaporator process values in nominal conditions (Fortum Power and Heat Oy 2004b & Ropponen 2014, p. 43).

<b>Parameter</b>	<b>Value</b>	<b>Unit</b>
Heat transfer area	18	m <sup>2</sup>
Pressure at the liquid side	1.25	bar
Pressure of the heating steam	2.3	bar
Temperature at the liquid side	105	°C
Temperature of the heating steam	125	°C
Heating steam flow	0.10 - 0.15	kg/s
Volume of liquid in the evaporator	1.2	m <sup>3</sup>

**Table 6.** Condenser-degasser process values in nominal conditions (Fortum Power and Heat Oy 2004b).

<b>Parameter</b>	<b>Value</b>	<b>Unit</b>
Condenser pressure	1.15	bar
Pressure of the cooling water	5	bar
Condensate flow out	1.5-1.7	kg/s
Cooling water flow	56	kg/s

Because only the sizes of heat transfer areas were known, some calculation level tuning was needed in the model. Tuning ensures that model calculates correct process values

(temperatures, pressures and mass flows) in nominal conditions - when the evaporator plant is run with the rated maximum capacity. This way, it was not even necessary to know correct dimensions for the heat exchanger coils inside the evaporators for this application.

Calculation level tuning was applied in the main evaporator, in the auxiliary evaporator and in the condenser. Tuning was executed by trial and error: interfacial heat transfer efficiencies were modified in nodes where steam is condensing (for example in node TR30N01\_SG) and heat structure efficiencies (for example in node TR30N001\_X) were increased, until satisfying process values during the evaporation were achieved.

## **8.2 Evaporation plant control in the simulation model**

Process monitoring system (PMS) calculates and monitors process parameters in the drain water evaporation plant of Loviisa nuclear power plant. Based on the calculations, PMS can give two commands for the automation system to execute at the field: to give a protection command for auxiliary steam system, or to give a command to empty the auxiliary evaporator (Ahonen 2015). For this model, we are specifically interested on how the auxiliary evaporator emptying is monitored and controlled.

The concentrations of boric acid and waste (salts) in the auxiliary evaporator are calculated on PMS. The calculation routine is based on the integration of outgoing condensate flow to the condensate control tanks. The condensate flow going out from the condenser-degasser is measured in a point, that is located right after a portion of the cleaned condensate has been returned to main evaporator (see also Figure 13 for the location). That part of the calculation routine in PMS, which is responsible for the monitoring of the concentrations in auxiliary evaporator (originally written as a Pascal code) works as follows:

1. PMS integrates the amount of evaporated clean condensate (t) from the outgoing condensate flow measurement TR31F002 (kg/s), using a 5-minute average value taken from the flow measurement.
2. PMS determines the amount of evaporated solid waste (kg) and boric acid (kg) in this 5-minute span by multiplying the concentrations in the evaporated liquid (g/kg) with the amount of evaporated clean condensate (t).
3. PMS determines the liquid volume (m<sup>3</sup>) in the auxiliary evaporator from a liquid level measurement in the auxiliary evaporator.

4. PMS calculates the concentrations of boric acid and waste in the auxiliary evaporator (g/l) by dividing the amount of evaporated solid waste (kg) and boric acid (kg) with the volume of the auxiliary evaporator (m<sup>3</sup>). (Ahonen 2005)

This routine is executed in every 5 minutes. When either of the two monitored concentrations exceeds a predefined limit value, a command to empty the auxiliary evaporator is given. If the evaporation is continued further, auxiliary evaporator is filled again with evaporated liquid, signals and integration values are initialized and the calculation routine starts again. (Finnilä & Taberman 2020, p. 64-65.)

At first glance, the computer code behind this routine seemed reasonable. By imagining it on pen and paper, no clear sign of its incorrectness could be identified. It was recalled that Apros has the feature to calculate boron (hence boric acid) concentrations in liquid: so, what if the evaporation process is simulated with Apros such that Apros is let to calculate the concentration of boric acid in the process, but the simulation model (evaporation) is left to be operated following the PMS routine? This way, boric acid concentration values in the process calculated by Apros could be compared to the ones that are estimated in the PMS routine and maybe, a better understanding of the evaporation process behavior could be achieved.

Since the original PMS calculation routine was written with Pascal, an appropriate way to mimic its behavior was needed for the simulation model. Luckily, the automation components in Apros provided a way to model its behavior. A slight difference between the original code and the one created for this simulation model comes from the way Apros treats the problem: Apros updates the values in every computer time step (for instance, this model used 0.2 seconds), whereas the routine in the power plant is executed in every 5 minutes. The modelled PMS routine for the simulation model (see also Appendix III, p. 4) works as follows:

1. When evaporation is started in the model, signal TR30U020 is changed to FALSE state, enabling the beginning of integration in the model.
2. Momentary flow measurement TR31F002 (kg/s) is multiplied with user defined values on boric acid and waste concentrations (g/kg) in the tank under evaporation.

3. Total amount of evaporated solid waste and boric acid are integrated in modules TR30F803 and TR30F802 by summing the result from current calculation round into cumulative result from previous calculation rounds.
4. Liquid volume in the auxiliary evaporator ( $\text{m}^3$ ) is determined from a volume measurement. As in the original code, the volume must be greater than  $1 \text{ m}^3$ , otherwise next step uses a value of  $1 \text{ m}^3$ . In nominal conditions, the liquid volume in the auxiliary evaporator is kept at  $1.2 \text{ m}^3$ .
5. Boric acid concentration (g/l) and waste concentration (g/l) in the auxiliary evaporator are calculated by dividing the amount of boric acid and waste with the liquid volume in auxiliary evaporator.
6. Steps 2-5 are executed as long as boric acid concentration or waste concentration in the auxiliary evaporator are below predefined limit values. When either of these concentrations exceed a limit, simulation is paused.

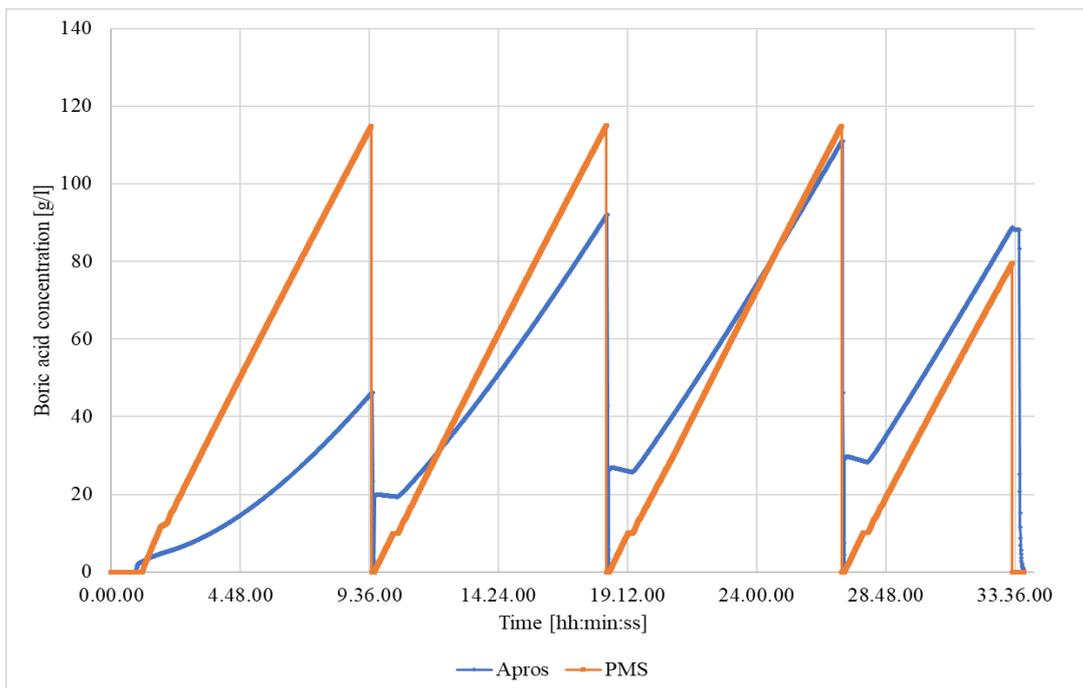
PMS routine was built such that, instead of giving a direct control to empty the auxiliary evaporator, the simulation is paused whenever the concentration is exceeded. After that, the auxiliary evaporator is emptied manually in the simulation model. Concentrations and integral values are initialized whenever auxiliary evaporator is emptied - by changing signal TR30U020 into TRUE state. When the evaporation is continued, the routine is executed again.

### **8.3 Results from drain water evaporation simulation**

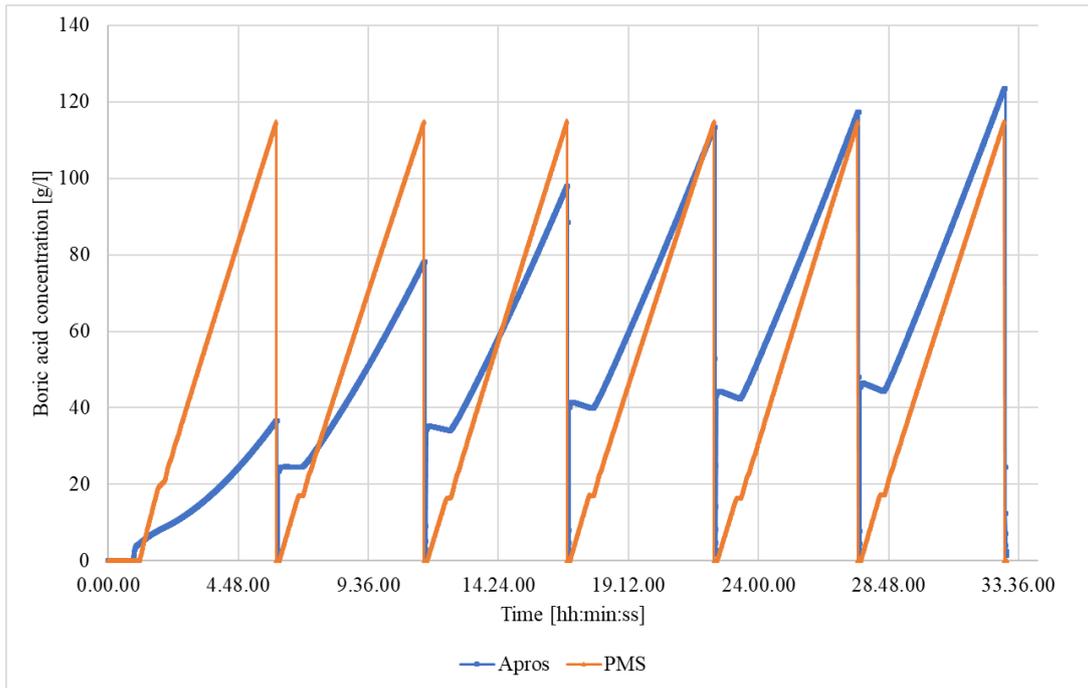
Two different cases were selected for the analysis to compare results with Apros and PMS: the evaporation of water with initial boric acid concentrations of 3.0 g/l and 5.0 g/l. They represented typical values in the evaporation plant experiments (Appendix II): the concentration value 3.0 g/l represents average concentration of boric acid in the evaporated water, whereas 5.0 g/l is close to the upper limit value. Remembering the relation presented in equation (7), these values correspond approximately 524 ppm and 874 ppm of boron to be used in Apros calculation. In both cases, the amount of drain water to be evaporated was selected to be approximately  $180 \text{ m}^3$  - a reasonable value compared to real evaporation process in Loviisa nuclear power plant.

In the simulation, the process was left to be controlled by PMS routine. Limit value for boric acid concentration in the evaporator bottoms was set to 115 g/l - corresponding to evaporation plant experiments in 2018-2019. The other control parameter, "waste concentration" in the auxiliary evaporator, was not important here, nor even monitored. In fact, the waste concentration value was seemingly below its limit value during the experiments, so boric acid anyway was the limiting factor and needing the attention.

Results from the simulations are presented in Figures 15 and 16.



**Figure 15.** First case - evaporation of drain water with the initial boric acid concentration of 3.0 g/l. Blue line represents Apropos calculated boric acid concentration and orange line PMS integrated boric acid concentration. Boric acid concentration is measured from the auxiliary evaporator.



**Figure 16.** Second case - evaporation of drain water with the initial boric acid concentration of 5.0 g/l. Blue line represents Apropos calculated boric acid concentration and orange line PMS integrated boric acid concentration. Boric acid concentration is measured from the auxiliary evaporator.

Figures 15 and 16 show how the drain water evaporation process behaves. The orange line, representing PMS calculated boric acid concentration, increases from 0 to 115 g/l, marking that boric acid is concentrated on the auxiliary evaporator. When PMS reaches the value 115 g/l, auxiliary evaporator is emptied, and the concentration is initialized back to 0 g/l. This pattern is repeated until no more water is left for evaporation; auxiliary evaporator is emptied for the last time and integrals are initialized.

When water with initial boric acid concentration of 3.0 g/l was evaporated (Figure 15), PMS reached the limit value three times. The fourth vertical line marks the time when all water had been evaporated and auxiliary evaporator was emptied for the last time. When water with initial boric acid concentration of 5.0 g/l was evaporated (Figure 16), PMS reached the limit value five times, although sixth time was not far away. Stronger initial boric acid concentration in the evaporated liquid in the second case also meant that the auxiliary evaporator needed more frequent emptying than in the first case.

Blue line represents the actual evolution of boric acid concentration in the auxiliary evaporator, calculated with Apros. In both Figure 15 and Figure 16, it is observed that the actual boric acid concentration (blue line) stays under the PMS integrated boric acid concentration (orange line) in the beginning of the evaporation, but towards the end of the evaporation, it crosses the orange line. The actual boric acid concentration peak value, before auxiliary evaporator is emptied, increases from pattern to pattern in both cases. In the first case (Figure 15), Apros calculated maximum boric acid concentration increases from 46 g/l to 92 g/l, and then increases to 110 g/l on the third time when auxiliary evaporator is emptied. In the second case (Figure 16), maximum concentration increases from 38 g/l to 78 g/l and then steadily keeps increasing: a concentration value of 117 g/l is reached on the fifth time auxiliary evaporator is emptied. The growth in the maximum value seems to follow a logarithmic asymptote. If a curve would be fitted on the maximum values, that curve would approach infinity, should the evaporation process be continued further.

#### **8.4 Interpretation of the results**

How these results relate to the plant experiments, and explain the results obtained there? During the experiments, the evaporator bottoms samples were taken once per an evaporation batch: when approximately half of the drain water from the tank under evaporation had been evaporated. Simulation results showed that the samples taken in the experiments should represent the conditions in evaporation concentrates in only one point of the evaporation batch, in the middle point. In the first simulated case (Figure 15), this "middle" point of a batch corresponds to the second or the third time auxiliary evaporator was emptied. In the first case, boric acid concentration in evaporator concentrates is somewhere around 90 g/l in the second emptying time and 110 g/l in the third emptying time. Now, in the second simulated case (Figure 16), the middle point of the batch could be the third or the fourth emptying time. For example, the third time auxiliary evaporator is emptied, the boric acid concentration is around 100 g/l.

Anyway, in both cases, it is certain that the boric acid concentration is below the PMS calculated limit value of 115 g/l, when the evaporator was emptied in the middle point of the evaporation. This result corresponds to the observations made during the experiments - the samples had a lower boric acid concentration than PMS estimated! Evaporator bottoms samples in the experiments had approximately 19 % lower boric acid concentration than PMS

had calculated (see Appendix II). The calculations from the simulation model resulted approximately 21 % lower concentration in the first case (90 g/l taken for comparison) and 13 % lower concentration in the second case.

If average values for boric acid concentration in the evaporator bottoms are calculated, concentration values of 84 g/l for the first case and 94 g/l for the second case are obtained. They are not terrible, but there is still a room for improvement and optimization to achieve exactly the wanted outcome from the evaporation. And yet to consider the decommissioning of the power plant: there is tons of water waiting to be evaporated. If the accuracy in evaporation cannot be ensured, problems are likely to arise - we should remember that the crystallization limits for boric acid in water should not be exceeded. With a boric acid concentration of 84 g/l, the crystallization might already happen in a temperature slightly over 40 °C, assuming that no NaOH is present in the solution. That temperature is certainly reached when the concentrates from the evaporation process cool down, if concentrates are not kept warm.

Simulation results clearly helped to understand how the calculation routine in PMS is operating. Simulations showed that in the beginning of the evaporation process, the actual boric acid concentration in auxiliary evaporator is well below PMS integrated concentration value. As the evaporation batch proceeds further, the actual boric concentration value becomes more and more closer to the integrated value, until the calculation routine seems to estimate the concentration on the auxiliary evaporator correctly. The reason for this behavior comes from the assumptions made in PMS monitoring code. PMS does calculate how much boric acid and waste are removed from the drain water feed, but that amount is concerning both the auxiliary and main evaporator. Somehow, PMS code assumes that all boric acid and waste are concentrated only on the auxiliary evaporator. The monitoring code does not calculate how much boric acid is removed already on the main evaporator before the solution is fed into the auxiliary evaporator. Therefore, in the beginning of the evaporation batch, PMS monitoring code leaves the concentrates in the auxiliary evaporator dilute, but results stronger and stronger concentrates towards the end of the batch.

To improve the accuracy in PMS routine, the calculation routine should be able to monitor the change in the concentration of evaporated liquid in the main evaporator. A problem comes from the current instrumentation on the evaporation process: currently, the only measurement that is used in the calculation routine is taken from the condensate flow going into

the condensate control tanks. This measurement cannot be the only one to be used in the calculation routine, if the accuracy in the routine wants to be improved. Introducing a continuous sampling line for evaporator bottoms concentrates as in the evaporators of LO2 would of course be a definite solution.

Finally, it must be mentioned that the samples taken in the experiments in 2018-2019 had a lot of variations and contradictions between them. Uncertainty comes from the documentation of the experimental conditions. It is not certain whether the conditions in different evaporations were comparable: for example, it is highly uncertain what was the amount of water that was evaporated in every evaporation occasion, but it is also uncertain what was the exact time when the evaporator samples were taken, or are they even comparable to each other. To confirm these results obtained with Apros simulation model, a set of new experiments should be conducted in the power plant. In these new experiments, evaporator bottoms samples should be taken whenever auxiliary evaporator is emptied and multiple evaporations should be executed. The evaporation conditions should be kept as identical as possible: a same amount of water should be evaporated with same limit values kept in PMS and plant conditions should be close to nominal. Later, simulation model could be used to verify the results from the new evaporation experiments.

## 9 DISCUSSION

This thesis focused on the treatment of process water in the primary circuit of Loviisa nuclear power plant. The treatment of process water is one of the earliest operations during the decommissioning of Loviisa. The objectives set for this thesis were to study the process water treatment and review whether the use of process simulation software would help in the planning of process water treatment, or whether simulation could offer other benefits considering the decommissioning planning.

The target in process water treatment is to treat the water into such an extent, that the bulk volume of generated liquid waste could be discharged in a controlled manner, while the smaller portion where radioactivity is concentrated can be immobilized and confined from environment. Currently, these elements in Loviisa nuclear power plant consist of process water evaporation, treatment of evaporator concentrates using a highly selective ion exchange resin towards radiocaesium and liquid waste solidification process for liquid wastes needing confinement.

The main focus on this thesis was placed on the first element of the liquid waste treatment chain: evaporation process. Process waters can be evaporated either by using the evaporators of LO1 or LO2 during the decommissioning of Loviisa nuclear power plant. Currently, evaporation process in LO1 is used to evaporate active drain water, while evaporation process in LO2 is used to recover boric acid from primary circuit process water. Concerning the plant decommissioning, process water evaporation in LO2 would follow current plant procedures. However, its future usage in process water evaporation compared to evaporation in LO1 is restricted; LO2 lacks the storage space for resulting evaporator concentrates, whereas evaporation in LO1 would give an instant access to the liquid waste storage of the power plant. Using either of the two evaporation plants during plant decommissioning requires still process modifications, such as building new process lines in the power plant.

It was found that drain water evaporation process needs more important improvements than just new process lines. This was revealed on the simulations with AproS: simulations on the drain water evaporation plant gave results that are different than drain water evaporation plant monitoring system (PMS) assumes. Simulations showed that not all boric acid gets carried instantaneously on the auxiliary evaporator bottoms, in contrast to what PMS

assumes. Measurements taken from the drain water evaporation process in Loviisa a few years ago seem to support Apros simulation results.

Simulation results mean that there is a need adjust the drain water evaporation plant control system. With current control, evaporation in the auxiliary evaporator stops too early in the beginning of an evaporation campaign. As a result, boric acid concentration in auxiliary evaporator bottoms concentrates is left milder than planned; the evaporation in auxiliary evaporator could still be continued. When the evaporation campaign proceeds further, boric acid concentration in auxiliary evaporator bottoms concentrates increases higher than it is desirable in the end. The adjustments in the monitoring code should take into account the changing boric acid concentration of the evaporating solution in the main evaporator, before it is fed into the auxiliary evaporator. Another solution could involve the introduction of a new continuous monitoring line on the drain water evaporation system. A similar system is already utilized in the let-down water evaporators in LO2.

Now, throughout the process water treatment, the amount of boric acid in water and evaporator concentrates needs to be known. It is known that process waters in Loviisa contain a lot of boric acid. The biggest concern boric acid poses for process water treatment is related to its potential to crystallize, if the concentration of boric acid in water exceeds its solubility limits. The crystallization of boric acid might lead to blockages in the process lines or in the components there, resulting unnecessary delays during the process water treatment. The biggest concerns are to be placed on the treatment of evaporator concentrates, since boric acid is concentrated on the concentrates.

It was found that the solubility of boric acid in water is strongly dependent on the temperature of the solution, but also on the pH value of the solution. For solutions where boric acid and sodium hydroxide are present, it seems that a neutral pH value yields the highest solubility of boric acid in water, slightly more than 200 g/l. This value is some four times higher, than the solubility limit value is in process waters with their current pH value (after the plant has been shut down). It was understood that alkaline pH values in the solution of sodium hydroxide and boric acid increases the solubility of boric acid. This practice is followed currently in Loviisa: drain water is adjusted to an alkaline pH region, before they are evaporated.

The differences in the solubility limits of boric acid in different pH values should be considered when process water evaporation is planned. By adjusting the pH value into a suitable region, a higher amount of boric acid can be concentrated in the evaporator concentrates without the risk of crystallization. As a result, more condensates could be discharged into the sea immediately while less liquid waste would be left for further treatment. The downside in adjusting the pH value of process waters is the increased consumption in chemicals, and a prolonged time taken to treat the process waters.

It must be understood that the presented solubility limits for boric acid are not exact. There might be other substances present in the water than just boric acid and sodium hydroxide affecting on the solubility. The pH value of the solution is also dependent on the temperature of the solution. Therefore, when the process water treatment with evaporation is planned, sufficient margins under the known solubility limits of boric acid should be left - to be on the safe side to avoiding the threat of crystallization. In any case, it would be beneficial to find such tools that could be used to evaluate the crystallization of boric acid accurately, that would consider not only the temperature in the solution, but other variables as well.

What should be evaluated more is whether the treatment methods in Loviisa remove the radioactivity from process waters into a level allowing a controlled discharge of the effluents. Operational experience has shown that radiocaesium is the limiting nuclide in radioactive liquid wastes, as far as the evaporator concentrates from drain water evaporation are concerned. Although the activity level in process water remains probably low, it needs to be addressed. Active monitoring of activity levels in primary circuit water and process systems is needed. It should be evaluated how effectively the current processes (evaporation, ion exchange) decontaminate the waters, and then compare the activity levels to known emission limits. This gives a quick hint on whether the discharge is possible, but more importantly whether there are needs for further treatment measures. Nevertheless, the possible decontamination of primary circuit forms a bigger concern than the process waters alone. Decontamination will produce a lot of active corrosion products and liquid wastes to be treated. This might ultimately drive for the need to invest in new systems, albeit the primary circuit process waters could be treated with current measures. These factors should be evaluated more: there might be a chance to optimize the amount of liquid waste ending up for the

solidification process, which is a tedious and more expensive process, rather than producing well treated liquid effluents that could be discharged in a controlled manner.

## **9.1 Using simulation on process water treatment planning**

The decommissioning is a whole new phase in the power plant lifecycle. Processes that will be operated and monitored in the power plant then no longer focus on the operation of the reactor or in the electricity generation: it is the process water treatment and other decommissioning duties that dictate the operation actions. Let's discuss a little on which ways does simulation help in the liquid waste management planning now or in the future.

The most quantifiable results of using dynamic simulation in the liquid waste management chain of Loviisa nuclear power plant were gained from the analyzes in the evaporation process. The problems encountered in the drain water evaporation plant of Loviisa could be well analyzed, since the main issues on that process were related to evaporation plant control automation. The evaporation process itself could be easily modelled at the same time - it is a simple thermohydraulic process where water is evaporated, and boric acid is concentrated from a feed stream. Simulations confirmed the suspicions in the evaporation plant's process monitoring system: the monitoring system algorithm contains a flaw, which results in inaccuracy when it calculates the concentration of boric acid in evaporator concentrates. Applying dynamic simulation in the evaporation process clearly helped to understand how that system behaves in the power plant.

Should drain water evaporation be reliably utilized for process water evaporation during the decommissioning and in the current operation as well, adjustments in the plant monitoring system algorithm or a completely new control system is needed. Plant decommissioning involves the treatment of many tons of process water, with a significant amount of boric acid present in them; the outcome from evaporation needs to be predicted correctly. If the evaporation process is predicted incorrectly, then either not all potential in reducing the volume of process waters is reached, or worse, the process waters are evaporated into such an extent that the risk of boric acid crystallization increases. Simulations on the drain water evaporation process proved that dynamic simulation could reveal risks beforehand, whenever any future operation or procedures are planned. With simulation, potential problems can be spotted in the early design stage and corrective actions can be started on time.

The other parts in the simulation model have focused on illustrating the relations and needed systems for process water treatment, but it forms a basis for later development. It contains the systems that are needed in the decommissioning, albeit many automation systems have not been included there yet. Some parts of the model could be refined to provide more information for the key areas in the liquid waste treatment chain, if some new or crucial information is needed for planning. For example, the concentration of boric acid and the temperatures encountered during the evaporation process and in the further treatment of concentrates are important to know. If processes are modified, then it is justified to investigate those modifications with simulation. The problems that currently can be solved with process simulation are related to thermohydraulic problems encountered in the treatment of process waters; not for example investigating the kinetics of the ion exchange process, the crystallization of boric acid or the activity levels in process water.

However, many other benefits from simulation are not as quantifiable or measurable as the simulation on the drain water evaporation process offered. The first point comes from the interactivity that the created simulation model offers: it is much easier to present and demonstrate different plans or strategies concerning process water treatment with the help of a model. The simulation model offers a tool for engineers, where one can plan, experiment and train the draining and process water treatment on his or her own. Process water treatment planning becomes much more interactive than it would be just by relying on static PI-diagrams or other plant documentation. The simulation model offers an effective way to study the needed process modifications concerning the process water treatment: the designer can be creative and build and experiment with those modifications freely, and possibly calculate whether some upgrades in the power plant are needed - such as evaluating the pump capacities, performance levels in heat exchangers, extra buffer storage needs etc.

Some potential use cases for the model in future projects concerning the decommissioning can be identified. Modifications in plant processes also mean that many field automations need modifications, or completely new automation systems are needed. A simulation model offers a good test bench to test and verify how well the different systems needed in process water treatment behave as whole. Also, there is likely a need for rearrangements in the control room design where human-factors engineering plays a role. Simulation model to be used

in ergonomics planning does not need to be physically exact, because the purpose of the model is to simulate the power plant behavior there and results are obtained elsewhere.

Finally, the training aspect should not be forgotten. It is common that operators train the normal operation of the power plant using a training simulator, to ensure that the daily operation will remain safe and efficient. When the decommissioning becomes more topical, operators and plant staff need to prepare for a whole new operational phase and the actions taken then. The treatment of process water during the decommissioning is one of the main issues to be handled, yet also at least partially managed by the operators. Simulation model offers a great way to simulate the inherent complexity that is bound in arranging the process water logistics during the decommissioning. It helps to understand the time spans of different processes: whether it concerns the draining of process water, the logistical issues or the evaporation process. Certainly, there is still a lot of work to do before this simulation model could be implemented on an actual simulator environment, but as a standalone simulator, it already fulfills the training aspect. While it is not necessarily the right tool to analyze how well the water is purified in the treatment, it clearly helps to grow the understanding and the demands process water treatment sets towards the decommissioning.

## **9.2 Further development in Apros physics**

Simulation model has shown its usability in analyzing the evaporation process and growing understanding on the demands in process water treatment. However, some improvement areas were found in Apros physics that would enhance further liquid waste management analyzes. The most interesting new modelling aspect should address the crystallization of boric acid.

The crystallization of boric acid is a real threat considering the process water treatment and should be considered whenever processes and treatment methods are planned. Currently, Apros does not restrict the amount of boric acid to be diluted in a solution. This might give erroneous indications on the reality, taken for example the evaporation process where calculations can easily result in remarkably high concentrations of boric acid in the concentrates. Therefore, it would be beneficial to have the crystallization of boric acid modelled in Apros to be used in process water treatment planning. Other than liquid waste management applications, nuclear safety analyzes would also gain benefits from it. It was noted that it is

possible that in a loss-of-coolant-accident, the concentration of boric acid in the reactor core could increase into a level where boric acid crystallizes, blocks flow paths and in the worst case, leads to a fuel failure. One could also want to predict whether there are risks related to mixing of cold water with a substantially high amount of boric acid, that might happen in some injection lines or in sampling lines.

A base for new Apros physics development should involve at least the temperature dependence in the solubility of boric acid. The influence of pH value and other substances present in water also have an effect into the solubility of boric acid, but these are much more difficult to quantify accurately. Before modifications in the calculation engine and code are needed, a relatively easy way to start tackling this issue would be to inform the modeler whenever the critical concentration of boric acid, dependent on the temperature of the solution, is exceeded. Similarly, known variations in the solubility of boric acid in accordance with different pH values could be tabulated, and monitored based on user input stating the initial conditions of the solution. The latter implementation contains a few challenges, since the temperature dependence in the pH value of the solution should be accounted, but also the changes in pH value of the solution that may occur in different unit operations, as it happens in the evaporation process where water boils away.

To model the crystallization, the conservation equation for boron would need to introduce a mass transfer term. This describes the phase change where either boric acid crystallizes in the solution in supersaturated conditions, or the solid crystals dissolve back into liquid form. As consequence of crystallization, the whole system dynamics changes and this needs to be considered in other conservation equations. For example, the crystallization of boric acid leads to changes in the geometry, decreasing the flow area. Crystallization might also introduce fouling in heat transfer surfaces and decrease the heat conductivity in pipe surfaces. Another development area involves water chemistry and the calculation of the pH value in the solution. pH value is very important parameter to be known in liquid waste management planning, not just to be used for estimating the crystallization of boric acid. In many times, the optimal use of ion exchange resins for radioactive liquid waste treatment requires to have a specific pH value region. With that, processes could be planned further even more accurately, as new tools to be used in process water treatment planning are needed.

## 10 SUMMARY

This thesis was about process water treatment, its planning and simulation during the decommissioning of Loviisa nuclear power plant. The main objective of this thesis was to find out how a process simulation software Apros could be used in the process water treatment planning.

In the beginning of this thesis, sources of process water in Loviisa nuclear power plant were mapped and their characteristics were discussed. A review on the current liquid waste management techniques applied in Loviisa nuclear power plant followed, by going through the liquid waste management chain in Loviisa. It was learnt how the remarkable presence of boric acid in the process waters sets an important constraint for the whole liquid waste treatment chain. This comes from the inherent ability boric acid has; boric acid might crystallize, if its concentration exceeds its solubility limits in an aqueous solution. The crystallization threat can be mitigated by keeping the solution warm or within an appropriate pH region. When process water treatment is planned, crystallization must be accounted, since it can significantly complicate the treatment process.

The utilization of a process simulation software Apros in process water treatment planning was studied in the empirical part of the thesis. Loviisa had noticed anomalies on the drain water evaporation process: drain water evaporator process monitoring system had been noticed to calculate different boric acid concentrations for evaporator concentrates, than measurements taken from the process indicate. Since evaporation is an important method applied for process water treatment during the decommissioning of Loviisa, this issue was investigated more by modelling the evaporation process and the plant's monitoring algorithm with Apros.

Simulations on the drain water evaporation process showed that the process is not operating desirably. Measurements supported the simulation results as well. Simulations showed that drain water evaporation produces concentrates that have less boric acid than desired in the beginning of an evaporation campaign. Towards the end of the campaign, boric acid concentration in the concentrates rises into a level where the crystallization of boric acid becomes highly possible. Based on the simulation results, Loviisa should adjust the plant

monitoring system algorithm, or introduce a new monitoring system to mitigate any risks related to boric acid crystallization prior to plant decommissioning.

These simulations demonstrated that process simulation with Apros is well suitable for analyzing thermohydraulic problems present in the process water treatment chain. Other liquid waste treatment methods, such as the ion exchange process are involving mechanisms that are currently not included in Apros. This limits the analyzability of those processes, as well as analyzing the whole the liquid waste treatment chain efficiency with Apros. Nevertheless, Apros has shown that it can be used to simulate the draining of process systems and process water treatment chain logistics during the decommissioning. This was proved by successfully creating a conceptual representation of the whole process water treatment chain in Loviisa. A simulation model offers a tool to practice and study the process water treatment well before it is done. Many upcoming projects focusing on the decommissioning of Loviisa may find uses for the simulation model in the future, even though it is not yet able to fully analyze the liquid waste treatment chain.

Other findings during this thesis points out that improvements in the physics of the simulation software would be beneficial for liquid waste management planning in the future. Namely, the crystallization of boric acid, as well as the ability to calculate and model water chemistry are possible improvement areas in the future.

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## APPENDIX I. COMPARISON OF TYPICAL AQUEOUS RADIOACTIVE WASTE TREATMENT METHODS

The table is based on the following sources: IAEA 2001, p. 46-47; IAEA 2017, p. 29-30; Ojovan & Lee 2014, p. 173.

Treatment method	Features	Limitations	Secondary waste
Evaporation	<ul style="list-style-type: none"> <li>Well established technology, many different designs available</li> <li>Suitable for large aqueous waste volumes - high VRF</li> <li>High DF, varying from <math>10^4</math> to <math>10^6</math></li> <li>Use for primary coolant cleanup, utility liquid waste in nuclear power plants</li> </ul>	<ul style="list-style-type: none"> <li>Not suitable for the treatment of volatile radionuclides like tritium</li> <li>Process limitations: foaming, corrosion, scaling</li> <li>Condensates may require polishing</li> <li>High energy consumption in the evaporation increases costs</li> </ul>	<ul style="list-style-type: none"> <li>Evaporator concentrates</li> <li>Condensate, requiring further treatment</li> </ul>
Ion exchange	<ul style="list-style-type: none"> <li>DF for organic ion exchangers varies <math>10^1</math>-<math>10^3</math></li> <li>DF for inorganic ion exchangers varies <math>10^1</math>-<math>10^4</math></li> <li>Use as post-treatment of effluents</li> </ul>	<ul style="list-style-type: none"> <li>High amount of suspended solids or salts in the liquid waste undesirable for the process</li> </ul>	<ul style="list-style-type: none"> <li>Spent ion exchange resins</li> </ul>

	<p>after another method (e.g., evaporation)</p> <ul style="list-style-type: none"> <li>• Resins are relatively easy to immobilize</li> </ul>	<ul style="list-style-type: none"> <li>• Possible blockage of ion exchange beds</li> <li>• Resins can be expensive</li> <li>• Non-ionic species are not captured</li> </ul>	
Chemical precipitation	<ul style="list-style-type: none"> <li>• Relatively cheap</li> <li>• Suitable for large waste volumes</li> <li>• DF varies <math>10^1</math>-<math>10^2</math> for <math>\beta</math> &amp; <math>\gamma</math> active nuclides, DF varies <math>10^1</math>-<math>10^3</math> for <math>\alpha</math> active nuclides</li> </ul>	<ul style="list-style-type: none"> <li>• DF not so high as in other processes</li> <li>• Solid and liquid must be separated efficiently after the treatment</li> </ul>	<ul style="list-style-type: none"> <li>• Sludge</li> </ul>
Filtration	<ul style="list-style-type: none"> <li>• Removal of suspended solids and particulates</li> <li>• Use before ion exchange process (or other methods) as a pre-treatment step</li> </ul>	<ul style="list-style-type: none"> <li>• Replacement of filter media needed</li> </ul>	<ul style="list-style-type: none"> <li>• Filter media</li> <li>• Cartridges</li> </ul>

## APPENDIX II. DATA FROM EVAPORATION PLANT EXPERIMENTS IN 2018-2019

Data on the following table was gathered during the evaporation plant experiments in between years 2018-2019 as presented by Mäkinen (2019). Measured boric acid concentration in drain water before evaporation (on first column) was gathered from another Loviisa power plant database (LamDa) and combined with the original data.

During the experiments, the limit value for boric acid concentration (PMS calculated, on the third column) in the auxiliary evaporator was 115 g/l. The time when auxiliary evaporator bottoms samples (on the second column) should have been taken was instructed to be at that point when the drain water volume in the tank under evaporation had reduced to half from the start of the evaporation. However, the exact time when the samples were taken was not documented.

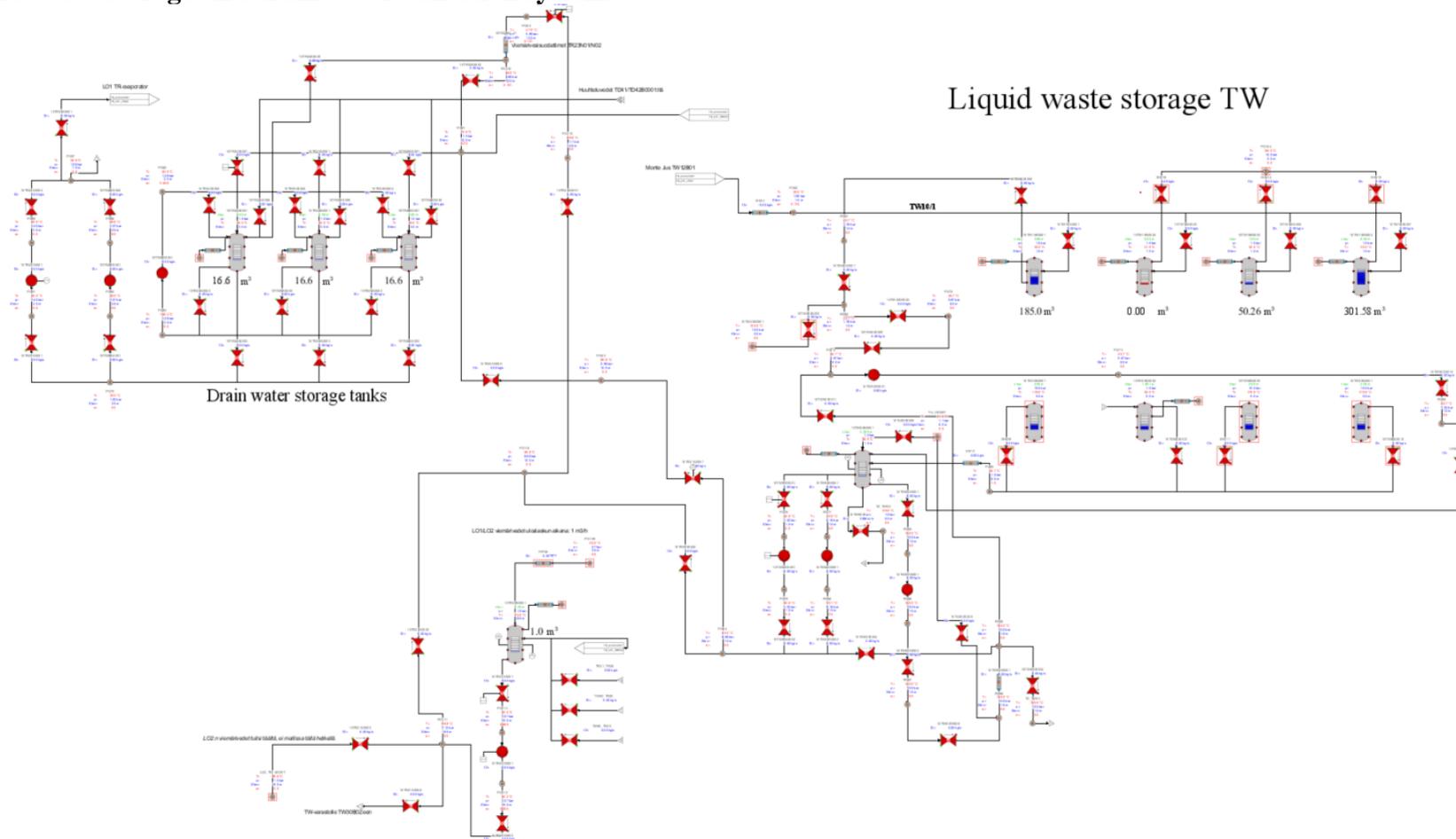
The average value of initial boric acid concentration in drain water is approximately 2.7 g/l and the average value in evaporator bottoms concentrates is approximately 91.8 g/l. On average, measured evaporator bottoms concentrate values were 19 % less than the PMS calculated value.

Measured boric acid concentration in drain water before the evaporation [g/l]	Measured boric acid concentration in auxiliary evaporator bottoms concentrates, after emptying the auxiliary evaporator [g/l]	PMS estimation on the boric acid concentration after evaporation [g/l]
1.16	53.0	116
1.27	106.6	113
1.48	90.6	113
1.48	88.7	112
1.50	72.9	115
1.51	91.6	117
1.59	68.6	112
1.60	138.6	114
1.69	101.7	113
1.71	87.2	113
1.77	64.1	111
1.80	85.8	112

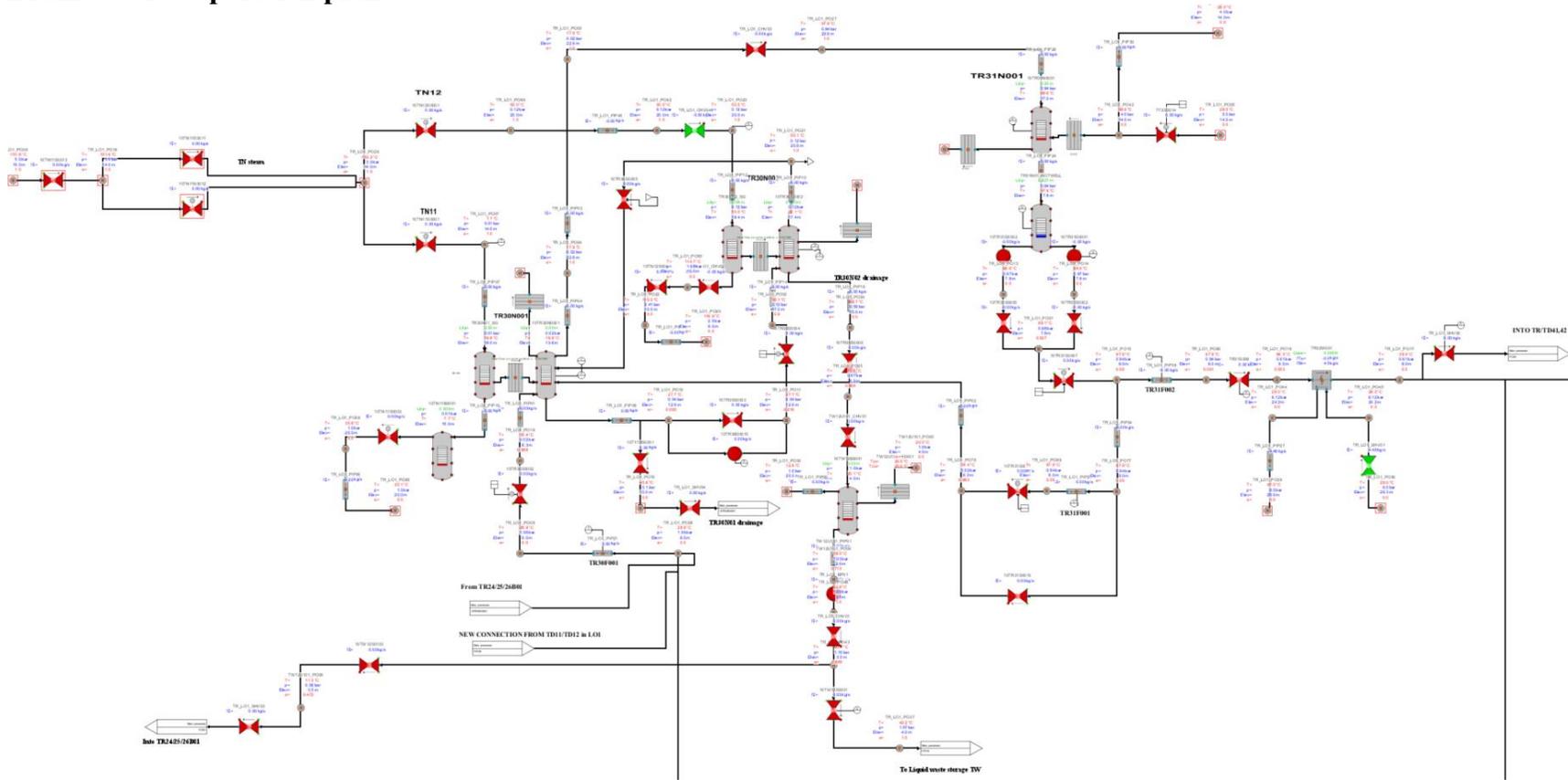
1.98	70.3	117
2.00	110.0	113
2.17	103.1	113
2.26	107.1	113
2.36	93.1	114
2.39	71.6	114
2.40	99.9	114
2.43	90.0	113
2.48	100.5	112
2.57	92.2	110
2.59	87.5	109
2.59	88.3	114
2.83	73.9	114
2.85	71.8	114
2.96	108.7	115
2.96	53.5	116
3.08	92.7	113
3.23	58.1	112
3.28	112.2	115
3.32	104.0	114
3.34	93.5	110
3.35	110.0	111
3.37	112.0	113
3.43	94.9	110
3.43	101.1	115
3.46	93.8	116
3.50	80.3	113
3.53	89.4	112
3.70	77.7	106
3.98	96.2	110
4.09	96.5	110
4.25	105.6	116
4.47	80.2	117
4.54	106.9	108
4.58	107.0	115
4.86	148.4	114
5.62	80.3	120



**Liquid waste storage and drain water collection systems**



Drain water evaporation plant



**PMS routine for TR-evaporator**

