IMPROVING THE SUSTAINABILITY OF ON-LINE PARTICLE SIZE ANALYSER USED IN PRECURSOR CATHODE ACTIVE MATERIAL MANUFACTURING WITH INTERNAL WATER RECYCLING

Lappeenranta–Lahti University of Technology LUT

Master’s Programme in Sustainability Science and Solutions, master's thesis

2024

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ABSTRACT

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LUT School of Energy Systems

Sustainability Science and Solutions

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Improving the sustainability of on-line particle size analyser used in precursor cathode active material manufacturing with internal water recycling.

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88 pages, 42 figures, 18 tables and 5 appendices

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Keywords: Sustainability, pCAM, Water recycling, Battery production, Membranes

Sustainable water use has gained attention in recent years due to increased awareness of sustainability issues and more robust regulations. This forces companies to adopt good water stewardship practices to reduce impacts caused by their own operations. Sustainable water practices will also help mitigate costs associated with water and wastewater treatment and to maintain good public reputations.

Objective of this master's thesis was to find way to recycle water internally in particle size analyser used in pCAM monitoring to improve sustainability of the process. Water that analyser uses must be particle free and for this purpose, potable water has been used. For this reason, analyzer wastewater must be cleaned between utilizations to remove particles that might affect analyzer results.

In the literature part, several different water treatment methods were explored and assessed viability of those to be used for pCAM water treatment. Among these methods, membrane filtration was found to be the most suitable technology for pCAM water treatment. Furthermore, membrane filtration was studied further, and concept filter system was formed based on the literature.

The membrane's ability to clean analyzer wastewater was tested in LUT separation laboratory. It was found out that membrane with 1 µm and smaller pore size could be utilized to achieve water clean enough for internal recycling. Due to limited resources thesis could not test how fouling, one of the main challenges in membrane filtration, affects filtration system.

TIIVISTELMÄ

Lappeenrannan–Lahden teknillinen yliopisto LUT

LUT Energiajärjestelmät

Ympäristötekniikka

Valtteri Parkko

Esiasteisen katodiaktiivisen materiaalin valmistusprosessissa käytettävän jatkuvatoimisen raekokoanalysaattorin kestävyyden parantaminen sisäisellä vedenkierrätyksellä

Maisterintyö

2024

88 sivua, 42 kuvaa, 18 taulukkoa ja 5 liitettä

Tarkastajat: Professori, TkT. Risto Soukka

Laboratorio insinööri, TkL. Simo Hammo

Ohjaaja: DI. Valtteri Torppala

Avainsanat: Kestävyys, pCAM, Veden kierrätys, Akkujen valmistus, Membraanit

Kestävä vedenkäyttö on saanut huomiota viime vuosina kestävyys tietoisuuden lisääntyessä ja tiukentuneiden säännösten myötä. Tämä pakottaa yritykset omaksumaan hyvän vesietiketin mukaisia toiminta tapoja vähentääkseen veden kulutuksesta aiheutuvia ympäristö vaikutuksia. Kestävä veden käyttö myös vähentää veteen ja jäteveden käsittelyyn liittyviä kustannuksia ja auttaa yrityksiä säilyttämään hyvän maineen.

Tämän maisteri työn tavoitteena oli löytää tapa kierrättää vettä sisäisesti raekokoanalysaattorissa, jota käytetään pCAM prosessin seurantaan. Sisäinen kierrätys olisi tapa parantaa prosessin kestävyyttä. Pitää kuitenkin muistaa että, analysaattorin tarvitsema vesi on oltava partikkeli vapaata ja siksi tähän on käytetty juomavettä. Tästä syystä analysaattorin jätevesi on puhdistettava käyttökertojen välillä partikkelien poistamiseksi. Nämä partikkelit voivat vaikuttaa analysaattorin tuloksiin.

Kirjallisuus katsauksessa useita erilaisia vedenpuhdistus menetelmiä tutkittiin ja arvioitiin niiden soveltuvuutta pCAM käyttöön. Tutkituista menetelmistä kalvosuodatus todettiin sopivimmaksi teknologiaksi tähän tarkoitukseen. Minkä jälkeen kalvosuodatusta tutkittiin syvällisemmin ja kirjallisuuteen perustuva konseptisuodatusjärjestelmä esiteltiin.

Kalvon kykyä puhdistaa analysaattorin jätevettä testattiin LUT:in erotusteknologian laboratoriossa. Testissä havaittiin, että 1 µm:n ja sitä pienemmän huokoskoon kalvo pystyy suodattamaan vettä tarpeeksi puhtaaksi sisäistä kierrätystä varten. Rajoitettujen resurssien vuoksi työssä ei pystytty testaamaan, miten saostuminen vaikuttaa suodatinjärjestelmään.

Acknowledgements

This master's thesis was carried out in collaboration with Metso Finland Oy as a part of the effort to find sustainability improvements in analyzer business line.

First, I would like to thank my advisor Valtteri Torppala for supporting me through whole thesis process and always answering my questions. I would also like to thank him for the opportunity to work on this thesis. I also express my sincerest gratitude for my examiners Risto Soukka and Simo Hammo for all the insight they have given me during the thesis.

Finally, I would express my appreciation for all the people in the Metso Finland Oy that have answered my question during the thesis process.

Valtteri Parkko

June 2024, Lappeenranta, Finland

Symbols and abbreviations

Roman characters:

A	Active surface area of membrane
b	Isotherm parameter
c	Concentration
CF	Characterization factor
$D10$	Particle diameter class 10 µm
$D50$	Particle diameter class 50 µm
$D90$	Particle diameter class 90 µm
J	Flux
K	Isotherm parameter
m	Permeate mass
n	Isotherm parameter
ΔP	Transmembrane pressure
P	Pressure
PBP	Payback period
q	Adsorbent loading
q_{m}	Isotherm parameter
Rm	Hydraulic resistance of membrane
$span$	Width of the size distribution
t	Filtration time
w	Water flow
WC	Water consumption of process

WSF	Water Scarcity Footprint

Greek characters:

μ	Solution viscosity

Subscripts:

c_{AWARE}	CF of location and time in calculation
P_1	Pressure at entry of membrane module
P_2	Pressure at exit of membrane module
P_{p}	Pressure of permeate
$w_{\mathrm{c,min}}$	Minimum consumption
$w_{\mathrm{c,max}}$	Maximum consumption
w_{c}	Design water consumption

Superscripts:

Abbreviations:

AC	Activated carbon
AWARE	Available Water Remaining (Water Scarcity Index)
CA	Cellulose asethane
CAM	Cathode active material
CAPEX	Capital expenditure
CCD	Counter Current Decantation
CIP	Cleaning in place

COD	Chemical Oxygen Demand
COP	Cleaning out of place
CSR	Corporate social responsibility
CSRD	Corporate sustainability reporting directive
CtG	Cradle-to-Gate
EFRAG	European financial reporting advisory group
ESG	Environmental, Social, And Governance
ESRS	European sustainability reporting standards
EW	Electro Winning
FS	Fluoro polymer
HPAL	High pressure acid leaching
LCA	Life cycle assessment
MF	Microfiltration
MWCO	Molecular weight cut off
NCM	Nickel-cobalt-manganese
NF	Nanofiltration
NTU	Nephelometric Turbidity Units
OPEX	Operating expenses
P&I	Piping and instrumentation
PAN	Polyacrylonitrile
pCAM	Precursor Active Cathode Material
PES	Polyether sulfone
PS	Polystyrene
PSU	Polysulphone

PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
TDS	Total Dissolved Solids
TMP	Transmembrane pressure
TSS	Total Suspended Solids
RO	Reverse osmosis
RR	Recovery rate
UF	Ultrafiltration
WRF	Water risk filter
WULCA	Water use in life cycle analysis
WWF	World wildlife fund
WWT	Wastewater treatment

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1 Introduction

In the modern world water scarcity is an ever-present problem which will only get worse in the future. Factors such as climate change, overconsumption and pollution contribute to this pressing issue. While efforts to mitigate climate change have long history but that alone cannot solve the water scarcity crisis. Growing and more industrialized population will need more water and without optimization of water use, demand will exceed supply in many countries. (UN WATER n.a.) One promising solution to this problem is wastewater reuse. By reusing water in industry, we will not only reduce water consumption overall but also minimize the need for wastewater treatment (WWT). This approach mitigates the risks associated with releasing untreated wastewater and potential leaks. (World Bank 2019.)

Precursor cathode active materials (pCAM) are integral part of battery manufacturing value chain during and after green transition (CNGR 2024a). However, pCAM manufacturing is not without its own problems. The process consumes water and produces significant amount of wastewater. Even after treatment, released wastewater can pose problems due to its high salinity and nitrogen content. Additionally trace amounts of nickel can be present in the wastewater. (CNGR 2024b.) Solving all issues associated with pCAM manufacturing is out of the scope for thesis work, instead one of the unit processes is taken into closer inspection.

Unit chosen for closer inspection is Metso PSI® 1000 particle size analyzer for pCAM production. The analyzer is used to monitor particle size distribution during pCAM production. Accurate particle size data is important since it allows operators to optimize processes which leads to energy and water savings (Koponen et al 2024). However, the analyzer consumes water at least of 10 l/min with peaks reaching 30 l/min (Metso 2023a). While this water usage may seem insignificant on larger scale, water required by the analyzer must be clean and thus traditionally potable water has been used. However, this practice poses challenges, especially in arid regions where water availability is limited. Using potable water for industrial processes is not sustainable, given the increasing global water scarcity. Therefore, alternative solutions are needed. (Peña and Huijregts 2013).

The main objective of this study is to find technology for recycling water internally in particle size analyzer. Several different technologies for wastewater treatment are explored and most suitable one is chosen among these. Filter system concept is then developed based on the best technology found and feasibility of this system is analysed with tests conducted in LUT separation laboratory with water sample from Metso Research Center pCAM pilot plant.

2 Current water situation on pCAM production

Precursor cathode active materials (pCAM) are transition metals that have been transformed to precursor materials for battery production. These materials are mixed with lithium to produce cathodes for Li-Ion batteries. (Swart et al. 2014.) Simplified life cycle of pCAM can be seen in Fig 1. Focus is precursor manufacturing which contains the pCAM production and particle size analyser.

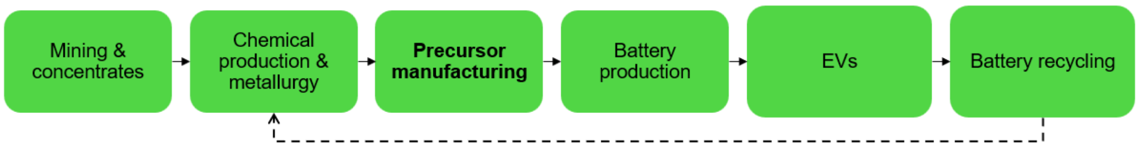

Figure 1. Flow of pCAM materials (Metso 2023b).

There are several different metals which can be used in pCAM production. Study focuses only on nickel, cobalt and manganese, which are used in production of NCM precursor particles. PCAM production utilized these metals in sulfate form that makes it easier to control metal mixing in coprecipitation process. Nickel and cobalt sulphates can be manufactured from either ore or refined metal. (Kelly et al. 2020.) Manganese sulphate is then manufactured from either manganese ore or electrolytic manganese dioxide (EMD) (Singh et al. 2019).

2.1 Precursor manufacturing

Nickel-cobalt-manganese (NCM) is one of the most promising cathode active material (CAM) currently in the market. It has high specific capacity and good cycling performance. NCM can be manufactured with different ratios of metals. This ratio controls properties of NCM and can be optimized to suit specific applications. NCM111 for example contains equal parts of nickel, cobalt and manganese. Ratio is not ideal since cobalt is expensive compared to other raw materials. So, NCM811 and NCM622 have gained popularity in recent years. (Mallick et al. 2023.)

NCM can be produced with multiple routes, but the most common one is hydroxide coprecipitation. In this process metal sulfides are mixed with wanted molar ratios for final product and sodium hydroxide and ammonia solution are added to the mixture. Mixture is then kept chosen reactor temperature to achieve optimal process conditions. Finished product is formed according to reaction equation (1) (Berk et al. 2023). In which M is metals used with stoichiometric ratios.

$$MSO_4 + 2\,NaOH \xrightarrow{NH_3} M(OH)_2 + Na_2SO_4 \qquad (1)$$

Final product from the process is NiCoMn$(OH)_2$ hydroxide (Berk et al. 2023). Coprecipitation process can operate in continuous, semi-batch or batch configuration. Traditionally continuous and semi-batch processes have been dominant in the pCAM production. However, industry has been moving towards semi-batch process since it has more options to control process parameters and product quality. Increased quality control gives an ability to match raising quality requirements for the pCAM. (Koponen et al. 2024.) Metso has OKTOP pCAM reactor Fig 2. which can be used for coprecipitation process.

Figure 2. Metso OKTOP pCAM reactor (Koponen et al. 2024)

Basic flow sheet of stirring reactor used in the coprecipitation process can be seen on Fig 3. Normally after reactor pCAM is separated from the liquid by hydrocyclone. However, Metso uses proprietary filter for separation. Separated sludge is then washed with purified water to remove any impurities left from the process. Purified pCAM is then dried on vacuum overnight. (Nam et al. 2013.) Obtained brown powder is heated to high temperature with lithium to perform lithiation reaction which produces CAM (Mallick et al. 2023).

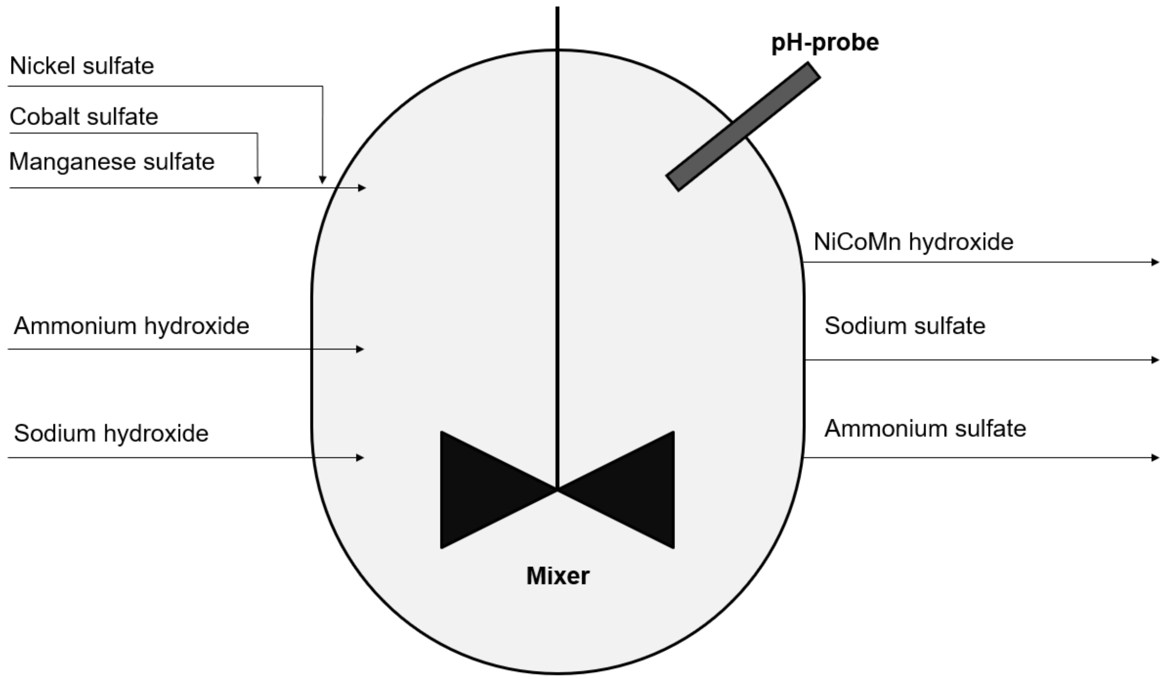

Figure 3. Stirring tank used for coprecipitation (Berk et al. 2023).

Formed precursor particles are measured with particle size analyzer during coprecipitation process. Particle size distribution is one of the main deciding factors for electrochemical performance of the electrodes produced from pCAM. Particle size distribution is usually measured as a span which can be calculated with equation (2) (Malvern Panalytical 2016).

$$Span = \frac{D90 - D10}{D50} \tag{2}$$

in which,

span	width of the size distribution
D90	diameter that contains 90 % of particles
D10	diameter that contains 10 % of particles
D50	diameter that contains 50 % of particles

Other important factors for particles are tap density, morphology and yield (Mallick et al. 2023).

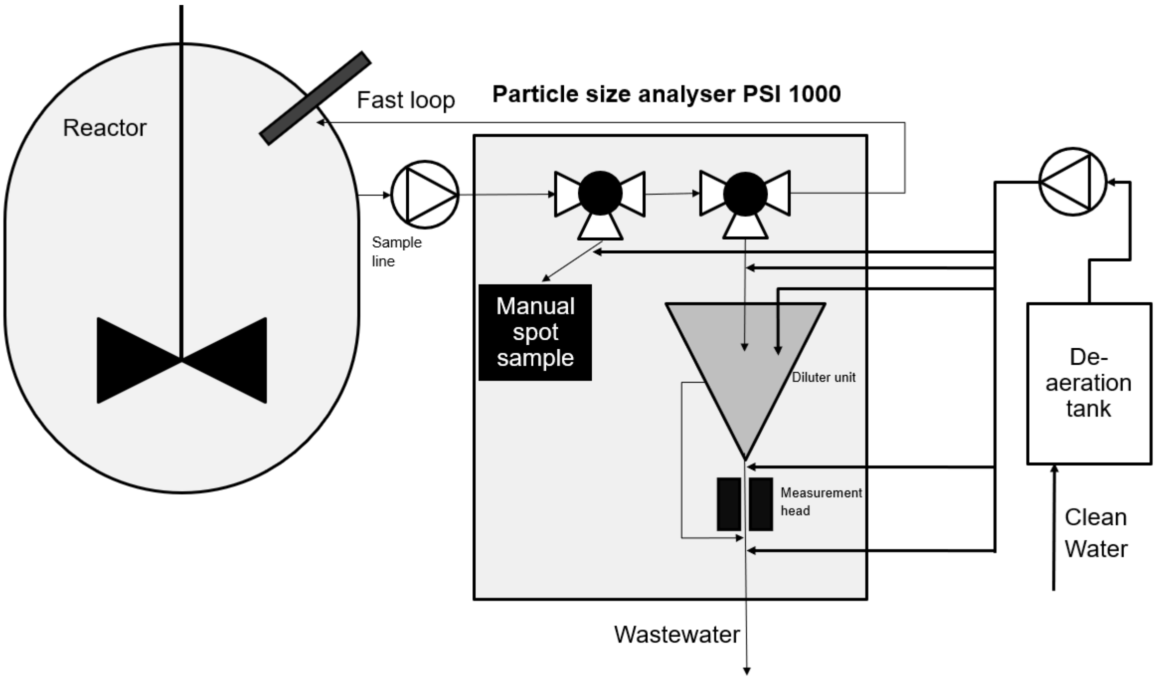

Figure 4. Particle size analyzation flow sheet (METSO 2024a)

Integration of particle size analyzer to the system can be seen on Fig 4. Analyzer in question is Metso PSI 1000 particle size analyzer that can measure in real time during whole precipitation process. Measuring particles will help optimize particle size distribution and span for produced precursor particles. (Metso 2023b.) On-line analysis of particle size distribution can help manufacturers to optimize manufacturing process parameters in real time. Compared to lab analysis which can take hours to get feedback from. Good example why this matter is presented in Fig 5. in which even thou lab measurements gives good overall picture of the process sudden changes in process are not detected early enough and plenty of off-spec material can be produced which is expensive This effect can be even more profound when on-line analysis frequency is increased.

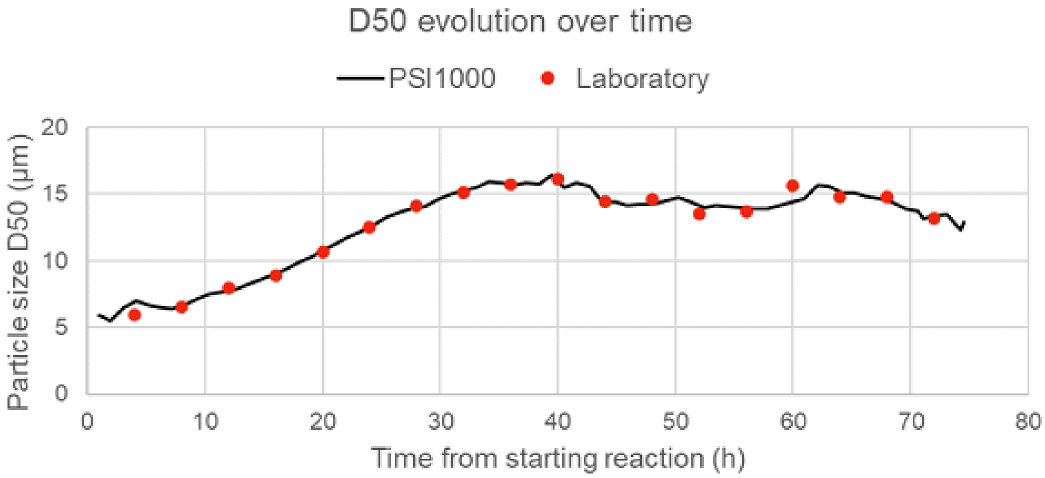

Figure 5. Comparison between on-line analysis and lab analysis (Koponen et al. 2024).

This constant optimization will help reduce waste generated from the process and minimize input flows reducing raw material consumption and wastage of raw materials. (Koponen et al. 2024, Malvern Panalytical 2019.) Currently the particle size analyzer consumes plenty of potable water. Proposed process flow for water recycling in analyzer is shown on Fig 6.

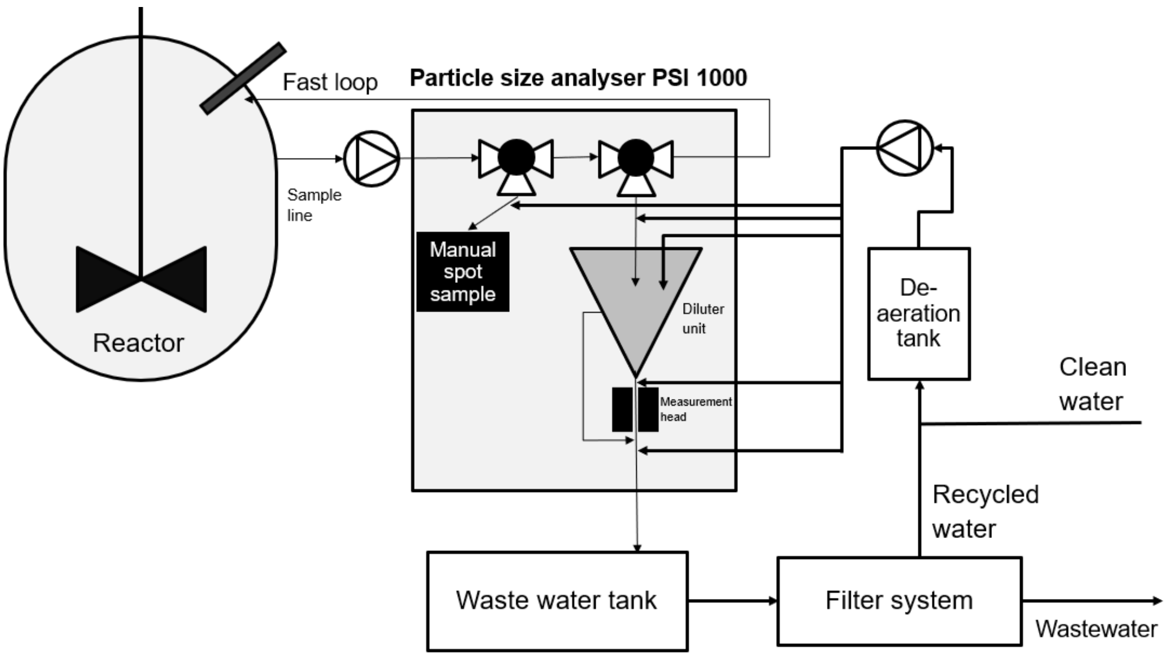

Figure 6. PCAM process flow with filtering system (METSO 2024a).

2.2 Wastewater quality from mining and mineral industry processes

Currently there is no standardized tests to measure process water quality in mining and mineral industry, which makes it challenging to utilize the process water flows. Most of the sampling done for the water is to make sure that effluent meets required environmental standards to be released back to the environment. However, there has been some changes recently since recycling process water in closed loop can be potential option to reduce water consumption of the processes. Still recycling water might affect process efficiency due to accumulating contaminants. This is particularly concern in processes that use chemicals such as flotation processes. (Le et al. 2020.)

Authors of Le et al. 2020 also argues that high quality, frequent analysis of process water and monitoring water flows inside the facilities is mandatory to make it feasible to recycle water back to the process. Analysis should be online or in situ analysis for more real time information about parameters that might affect other processes down the line. They also proposed that mining industry should collaborate and make standards for measurement of process waters in industry.

As can be seen on (Appendix 2.) data for mine process water qualities is lacking in scientific research. This lack of data is due to the absence of industry wide standards for measuring process water quality and the only measurement that exists is measurement of water quality for released water. This lack of data is especially prevalent in pCAM production process since it is still emerging field. Therefore, since there is lack of data about process water qualities. Filtering system is designed based on educated guesses from process parameters and initial raw materials.

2.2.1 PCAM wastewater quality

Example pCAM manufacturing plant is estimated to produce 29 cubic meters of wastewater per ton of product. This wastewater contains sodium, sulfate, nitrogen, and metals used for pCAM production. Wastewater composition can be seen in Table 1.

Table 1. PCAM plant wastewater composition (Aluehallintavirasto 2024).

	Amount [t/a]	**Amount [kg/d]**	**Concentration [mg/l]**	**Concentration in released water [mg/l]**
Flux [m^3]	1560000 m^3/a	4680 m^3/a		
Na	46200	139000	29600	15700
SO_4	96400	289000	61800	30900
Cl^-				1300
NH_4-N	19	57	12	6
Ni	0.3	1	0.2	0.1
Mn	0.11	0.4	0.07	0.035
Co	0.11	0.4	0.07	0.035
Al	22	66	14	7

These concentrations change based on process parameters and manufactured product. Released water is diluted in ratio of 1:1 with seawater before releasing back to the sea. (Aluehallintovirasto 2024.) Since concentrations can vary between sites. Solution must be done case by case.

2.2.2 PCAM process water quality

From process equation it can be seen that process water from coprecipitation contains NiCoMn(OH) particles. These particles are in size range of 1 µm to 30 µm depending on process parameters and time process has been ongoing (Berk et al. 2023). Additionally, chemicals used in the process are still present in sample collected from reactor as sodium sulphate (Na_2SO_4) and ammonium sulphate ($(NH_4)_2SO_4$). If process is not optimized or process has not been running for sufficient time, some of the initial metal sulphates might still be present on the product flow.

Contaminants present in the water will accumulate to the water used for analyzer if water is not filtrated between recycling. Accumulation of NiCoMn(OH) particles on the water will skew results from the particle size analysis. Since particles left over from previous run are still present and get double counted. Accumulation of Na_2SO_4 will increase salinity of the reused water. Increased salinity will impact reflective properties of the water which in turn might impact result of the analysis. However, if accumulation is slow background analysis done by the particle size analyzer should be able to mitigate problems caused by increased salinity. (Metso int.) Additionally, accumulation of $(NH_4)_2SO_4$ might cause problems with oxidation of parts made from bronze, copper, or zinc. This should not be problematic since analyzer is mostly made from corrosion resistant steel. (Metso int.)

2.3 Requirements for water to be recycled

Requirements for water quality and quantity that analyser needs are presented in this chapter. Water quantity target is not essential achieve since water can always be substituted with tap water. But water quality requirements must be met to minimize error in measurements.

2.3.1 Water consumption for analyser

Analyzer operates in continuous basis for 24 hours per day and 7 days per week and it consumes water at the rate of 10 l/min with peaks of 30 l/min (Metso 2023a). This means that in minimum it will consume water per hour.

$$w_{c,min} = 10\frac{l}{min} * 60\frac{min}{h} = 600\frac{l}{h} \tag{3}$$

And at minimum water consumption per day.

$$w_{c,min} = 600\frac{l}{h} * 24\frac{h}{d} = 14400\frac{l}{d} = 14.4\frac{m^3}{d} \tag{4}$$

Assuming minimal downtime for analyser it will operate approximately 8000 hours per year.

$$w_{c,min} = 600\frac{l}{h} * 8000\frac{h}{a} = 4800\frac{m^3}{a} \tag{5}$$

The maximum water consumption of the analyzer per hour is.

$$w_{c,max} = 30\ \frac{l}{min} * 60\ \frac{min}{h} = 1800\frac{l}{h} \tag{6}$$

And maximum water consumption per day.

$$w_{c,max} = 1800\frac{l}{h} * 24\frac{h}{d} = 43200\ \frac{l}{d} = 43.2\ \frac{m^3}{d} \tag{7}$$

Since maximum consumption can be assumed to be only momentary. The water consumption is somewhere between minimum and maximum. System can then be designed to have lower water intake than maximum consumption when buffer tank is utilised. Design water consumption per hour.

$$w_c = 20\frac{l}{min} * 60\frac{min}{h} = 1200\frac{l}{h} \tag{8}$$

Design water consumption per day.

$$w_c = 1200\frac{l}{h} * 24\frac{h}{d} = 28800\frac{l}{d} = 28.8\frac{m^3}{d} \tag{9}$$

The filtration system needs to be designed to be suitable for the calculated design water flow.

2.3.2 Water quality needed for particle size analyzer

In this chapter water quality required for recycled water are presented. Quality is important because if the water is not sufficient in quality, it will affect the analyser results. Water quality requirements for analyser can be found in Table 2. and more information can be found on (Appendix 1.).

Table 2. Water quality requirements for the dilution water of PSI 1000 (Metso int.)

TSS[1]	**Turbidity**[1]	**Particle size**	**Water hardness**	**Permanganate value**	**Ferro content**	**TDS**[2]	**Conductivity**[2]
mg/l	NTU	µm	mg $CaCO_3$/l	mg $KMnO_4$/l	mg/l	mg/l	µS/cm
< 50	< 10	< 50	< 120	< 30	< 1	< 1000	<1500

1. Turbidity can be used if TSS not available.

2. Conductivity can be used if TDS not available

Hardness can be calculated from concentrations of calcium and magnesium with following equation (10) and is usually shown as calcium carbonate (EPA 2008).

$$Hardness = CaCO_3\left(\frac{mg}{l}\right) = 2.497 * \left[Ca\frac{mg}{l}\right] + 4.118 * \left[Mg\frac{mg}{l}\right] \tag{10}$$

If water is going to be recycled back to analyser it must meet the values presented above. If TSS and TDS values are not easily available, they can be replaced with turbidity and conductivity, respectively. Additionally, pH of the water is important parameter to monitor since pH can affect chemistry of the particles in the water (USGS 2019).

3 Sustainability challenges of water use

In 2025 two-thirds of the global population will live in regions with increased water stress and in 2050 half of the population is estimated to live under severe water stress (FAO 2011). This is why United Nations have implemented sustainability goal number 6. "Clean Water and Sanitation". Goal is to ensure safe water and sanitation for all of the humanity and to make sure that water demand for agriculture, industry and energy sectors are met without stressing current environment. (UN 2023.) However, at the moment progress towards this goal is lacklustre and in some areas four times more progress is needed to achieve targets by 2030. Main water consumer globally is agriculture that consumes around 70 % of the freshwater withdrawals followed by domestic consumption 11 %, energy usage 10 % and industrial consumption 9%. (UNESCO 2023.)

Water scarcity, water overexploitation and water pollution occur in specific area at specific times. This means that water issues cannot be measured in global scale. For this reason, water balances should be calculated on basin basis. Generally, 80 % water flows in rivers are needed to maintain ecosystem functions. This means that only 20 % of the flow in river can be utilised for human consumption. This leads to situations where half of the river basins in the world are overexploited. (Hoekstra 2014.)

Lack of useable river or groundwater is called blue water scarcity. Additionally, there are green water scarcity and grey water scarcity. Green water means moisture content in soil from precipitation. This water is consumed by plants in evapotranspiration or incorporated into them. Green water is relevant when product farmed or uses farmed raw materials. Pollution potential of process is measured in grey water footprint. It is the amount of water needed to dilute pollutants released to safe concentration. (Liu et al. 2017.) These are physical measures for water consumption and can tell about physical water scarcity. Economical water scarcity is situation where water would otherwise be available, but communities lack the funds for proper infrastructure to utilise them effectively. (UNESCO 2023.)

3.1 Corporate social responsibility and sustainability

Corporate social responsibility (CSR) is the corporation's ethical responsibility to society and environment. It also includes company's voluntary actions to address operational concerns and relationship building with local communities. However, CSR is still seen more as a public relations tool rather than way to channel resources to help communities. This can be seen in the Table 3. in which UNESCO has listed enhancing brand value to priority for the private sector. (Silva 2024.)

Table 3. Motivation of stakeholder investment for watersheds (UNESCO 2023).

	Public sector	**Private sector**	**Water utility**	**NGO**
1	Environmental co-benefits	Enhance brand value	Mitigation of risk for water resources	Mitigation of risk for water resources
2	Mitigation of risk for water resources	Address physical risks	Compliance with regulations	Environmental co-benefits
3	Social co-benefits	Supply chain resiliency	Reduce operational/Maintenace costs	Social co-benefits
4	Compliance with regulations	Social co-benefits	Reduce capital cost of water services	Improvement of local governance
5	Improvement of local governance	Compliance with regulations	Environmental co-benefits	Reduce risks from climate change

Most CSR initiatives have been shown to fail due to poor management and corruption on local level. To mitigate this, companies need to establish a clear vision and be transparent about operations. This will also help reduce internal and external resistance for initiatives. CSR also needs constant innovation which forces companies to adapt for changing environment. (Silva 2024.)

Ways for companies to utilizing water in sustainable, equitable and economically viable way is referred as water stewardship. Core of this water stewardship is three Rs: reduce, reuse and reserve. First two of these are beneficial to companies even in monetary way since improving water efficiency of the process reduces cost associated with obtaining water. This cost will increase in the future since currently almost 40% of water scarcity is associated with climate change and will increase in the future. Reusing water in the process is thought to be one of the most effective strategies to ensure sustainable water supply for the companies in coming decades. (Silva 2024.)

One of the most noticeable industries for water consumption is mining industry. Unsustainable use of water is long-standing problem, and it has been recognized for decades. However, using water in a sustainable way in the industry is a complex issue since no location is the same as other and water consumption depends about local hydrological variables and process in question. Despite mining and mineral processing not being major consumer of water in global scale, having only around 1-2% of the global water consumption, it can be dominating in local usage. For example, in Antofagasta Chile 65% of local water is consumed by mining operations. (Kinnunen et al. 2020.) This local dominance in water consumption can directly clash with needs of other stakeholders in the area.

For this reason, mining and mineral processing companies should follow good water stewardship in their operations. Losing grace of green consumers can cause reputational damage and even revert companies permit to operate. As environmental concerns of the consumers raise due to raising awareness about environmental issues, share of green consumers will also grow. Thus, need for social and ecological business practices are essential to maintain good reputation with consumer base. (Kostadinova 2016.)

3.2 Corporate sustainability reporting directive

Corporate sustainability reporting directive (CSRD) is European Union new directive that requires large companies and almost all of the small and medium companies to report regularly risk and opportunities on social and environmental issues. This new directive is drafted to improve and ensure that investors and other stakeholders have better understanding on companies' impact on social and environmental issues. (European Commission 2022.) CSRD is extension of previously implemented sustainability reporting initiatives. These however were voluntary and thus quality and reliability of the reports were not on the sufficient level. For this reason, CSRD tries to bring environmental reporting on the same level as financial reporting. (European Union 2022.)

CSRD will affect companies that fulfil two of these three criteria:

- € 50M in net turnover, accounting for the profitability of your business
- € 25M in assets, accounting for the size of your business
- 250 or more employees, accounting for the size and the social impact of your business

Additionally, to these non-EU companies that have subsidiaries or securities in the EU countries with net turnover of over € 150M for last two consecutive fiscal years are also required to comply with CSRD. (Normative 2024.) For affected companies, CSRD will take effect starting on reporting for fiscal year 2024 in large companies with 500 or more employees. Fiscal year 2025 for rest of the large companies and fiscal year 2026 for small and medium companies affected. (European Union 2022.)

CSRD reporting must be conducted according to European Sustainability Reporting Standards (ESRS), which is drafted by European Financial Reporting Advisory Group (EFRAG) (European Commission 2022). ESRS is divided into 12 different standards Table 4. and each of those standards have theme that it focuses on (EFRAG a.). Additionally, to general standards ESRS will have sector specific standards but those standards are still work in progress and due to this not currently available to public (EFRAG b.).

Table 4. ESRS standards (EFRAG a.).

Code	Name
ESRS 1	General requirements
ESRS 2	General disclosures
ESRS E1	Climate change
ESRS E2	Pollution
ESRS E3	Water and marine resources
ESRS E4	Biodiversity and ecosystems
ESRS E5	Resource use and circular economy
ESRS S1	Own workforce
ESRS S2	Workers in the value chain
ESRS S3	Affected Communities
ESRS S4	Consumers and end-users
ESRS G1	Business conduct

From these **ESRS E3** is interesting since it forces companies to report total water consumption with total water recycled and total water discharged. Potential commitment and policies to reduce water consumption on water scarce areas must also be reported with financial calculations about risk caused by water scarcity and financial opportunities to benefit from good water stewardship. (EFRAG 2022a.) When combined with **ESRS S3** and **ESRS E2** reporting regarding water withdraws and pollution affecting local communities will most likely cause reputational damage for the companies if proper mitigation strategy is not implemented alongside it. (EFRAG 2022b.) CSRD is binding EU-directive which forces companies to develop and innovate ways to address and mitigate sustainability issues caused by their operation.

3.3 Ways to measure water stress

Water issues can be studied using several available parameters depending on interest of the study. One of the methods used by life cycle assessment (LCA) scientist is AWARE index which analyse water scarcity in time and location basis. Another commonly utilized one is water risk filter from developed by WWF. This can be used to analyse more unconventional sustainability risks associated with production processes such as reputation or regulatory risk.

3.3.1 Water scarcity footprint

Direct water consumption of process is usually well known. However, when assessing sustainability of water use in the area more factors should be considered as well. For better understanding of impacts caused by water consumption, Water Use in Life Cycle Assessment (WULCA) group mandated by UNEP-SETAC developed AWARE method to assess water scarcity impacts in comparable way. AWARE is midpoint indicator which takes account relative available water remaining in the area after human and ecosystems needs are met. (Boulay et al. 2018.) To make it easier to understand what AWARE is measuring, water equivalents are how much water average location needs to consume to have same environmental effects as are caused by water consumption in target location. Calculating AWARE is done with equation (11).

$$WSF = WC \times CF_{AWARE} \tag{11}$$

in which

WSF	Water Scarcity Footprint
WC	Water consumption of process
CF_{AWARE}	Characterization factor of location and time for operation

Still to get holistic picture of water consumption, impacts on water quality and indirect water consumption mut be assessed simultaneously to the direct water consumption. Northey et al 2014 presents good example why assessing indirect water consumption is necessary for products. They present that production of 1 ton of nickel consumes directly 300 m^3 water, but production of sulfuric acid utilized in nickel extraction process consumes around 1350 m^3 thus making indirect water consumption 4.5 times larger than direct water consumption. Production of sulfuric acid most likely occurs in different location than where nickel is beneficiated. This spatial difference needs to be considered when calculating total water footprint caused by processes.

3.3.2 Water risk filter

Water risk filter is comprehensive risk assessment tool composed by WWF to help companies to identify risks regarding water consumption in operation locations. Tool consists of 32 peer-reviewed datasets that measure different risks regarding water basins. Indicator has values according to table 5. (WWF 2023.)

Table 5. WRF risk categories.

Risk categories and Risk types	
1-1.8	**Very low risk**
1.9-2.6	**Low risk**
2.7-3.4	**Medium risk**
3.5-4.2	**High risk**
4.3-5.0	**Very high risk**
5.1-6.6	**Extreme risk**

Water risk filter is split into three different categories which are measured by several parameters as can be seen on Table 6.

Table 6. Risk categories utilized in Water Risk Filter (WWF 2023).

Basin Physical Risk	**1. Water Scarcity**	**2. Flooding**	**3. Water Quality**	**4. Ecosystem Services Status**
Basin Regulatory Risk	**5. Enabling Environment**	**6. Institutions & Governance**	**7. Management Instruments**	**8. Infrastructure & Finance**
Basin Reputational Risk	**9. Cultural Importance**	**10. Biodiversity Importance**	**11. Media Scrutiny**	**12. Conflict**

Each of these categories is given value based on data and from these holistic sustainability view can be determined. More information about different indicators used for tool can be found on (Appendix 3.).

3.4 Sustainability challenges of pCAM water use

When utilizing AWARE for mining and minerals processes water use estimations watershed level characterisation factors should be used. Utilizing country level data has bias towards agriculture, which can overestimate water use by over 60%. This is due to mining and mineral operations taking place only on limited locations and having relatively low water consumption compared to country level. (Northey et al. 2018.) When utilizing WRF for metals and mining analysis, weighting presented in Table 7. should be utilized. This weighting targets indicators important to this field and gives better overall result. (WWF 2023.)

Table 7. Weighting used for mining and metals (WWF 2023).

Basin Physical Risk	**1. Water Scarcity**	**2. Flooding**	**3. Water Quality**	**4. Ecosystem Services Status**
70 %	60 %	25 %	5 %	10 %
Basin Regulatory Risk	**5. Enabling Environment**	**6. Institutions & Governance**	**7. Management Instruments**	**8. Infrastructure & Finance**
5 %	30 %	30 %	25 %	15 %
Basin Reputational Risk	**9. Cultural Importance**	**10. Biodiversity Importance**	**11. Media Scrutiny**	**12. Conflict**
25 %	5 %	15 %	40 %	40 %

Indirect consumption is majority in pCAM production. Process itself only consumes around 4% of total water footprint for product and rest is indirect consumption from raw material production. As can be seen in Fig 7. most of the pCAM water footprint can be associated with production of nickel sulfate.

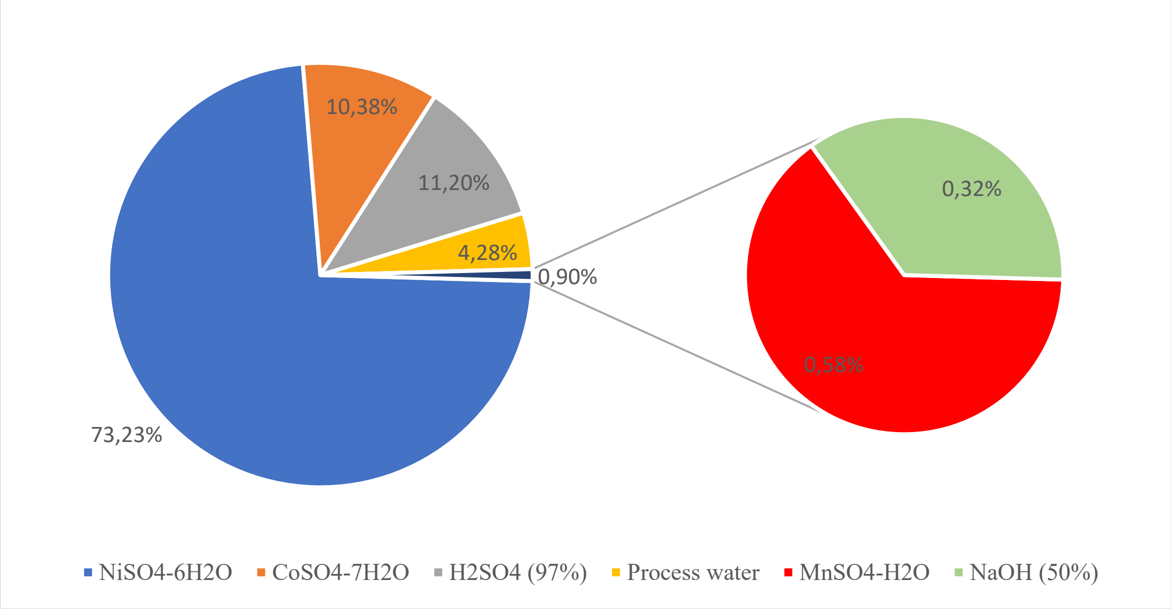

Figure 7. Water consumption of one ton of pCAM (Adopted Aluehallintavirasto 2024, (Appendix 4).).

Grey water footprint associated with pCAM production comes mainly from leftover nickel or sodium sulfate in water. Sodium sulfate concentration can be determining factor since other contaminants are subject to regulations and are mostly removed from water before release. (Aluehallintavirasto 2024.)

3.4.1 Sodium sulfate

Sodium sulfate is not currently in the regularly monitored species list in the environmental quality standard guidelines of EU water framework directive (European commission 2018). However increased sulfate levels have been shown to affect fishes and other marine species. Karjalainen et al. 2020 studied effect of sulfate concentration to European whitefish. Study found that increased sulfate concentration of 2000 mg/L caused statistically significant reduction in survival of early embryo period for the fish. However, fish studied was freshwater fish and data from freshwater is not directly applicable to salt or brackish water.

Salt water contains naturally around 2700 mg/L of sulfate and brackish water such as Baltic Sea around 470 mg/L of sulfate (Karjalainen et al. 2020). These concentrations are not directly comparable due to the toxicity of sulfate decreasing with increasing water hardness. Mechanism as why this happens is not fully know (Elphick et al. 2010). Studies regarding sulfate ecotoxicity are still severely lacking (Karjalainen et al. 2023). For this reason, more studies about sulfate effects on marine life are desperately needed to conclusively decide whether currently used limits for sulfate emission are robust enough to protect environment.

4 Technologies suitable for water purification in pCAM applications

Wastewater from analyser contains small particles in the size range of 1 µm - 30 µm diameter. According to Andoh & Smisson 1996. particles smaller than 10 µm will not settle in reasonable time for industrial usage. For example, particles size of 1 µm will take around 20 h to settle without additional aid (Bratby 2016). This makes at least some of the particles on the water non settleable in industrial usage. For this reason, other methods should be utilized for particle removal.

Common methods used for heavy metal removal from water are chemical precipitation, coagulation-flocculation, adsorption, and filtration (Abdullah et al. 2019). Each of these have their own pros and cons. In this chapter each of these technologies are briefly explored and the most fitting one is chosen.

4.1 Chemical precipitation

Chemical precipitation is process in which dissolved materials in wastewater are transformed into solid particles which are easier to remove. Main use of the chemical precipitation is to remove metal cations from water with counter ions. Addition of counter ions change metallic ions from soluble form to insoluble form, which can then be separated more easily. This is why chemical precipitation must always be followed by physical separation process, usually settling or filtration. (Wang et al. 2005.) Two most used types of chemical precipitation are hydroxide precipitation and sulfide precipitation. Both processes are simple to operate and inexpensive. (Fu & Wang 2010.)

4.1.1 Hydroxide precipitation

Hydroxide precipitation is by far the most common and most metal cations can be precipitated with it. The most used reagents for hydroxide precipitation are either lime or caustic soda. Precipitation reaction follows equation (12),

$$M^{2+} + 2(OH)^{-} = M(OH)_2 \tag{12}$$

Hydroxide precipitation is sensitive to pH chances and every metal cation has optimum pH. These pH values fall between 8-11 and if the solution differs from the pH precipitates might resolubilize back to the solution. (Fu & Wang 2010.) Additionally, complex ions such as ammonia may have detrimental effects on ion removal efficiency. Presence of sulfate ions in water will produce gypsum if lime is used. Gypsum can then scale the pipes and clog filters used for precipitate particle removal. Utilizing caustic soda will increase TDS of the treated water. (Wang et al. 2005.) Hydroxide precipitation will also produce lot of low-density sludge that might need dewatering before disposal (Fu & Wang 2010).

4.1.2 Sulfide precipitation

Sulfide precipitation works in same principle as hydroxide precipitation, and will occur according to reaction equation (13),

$$Na_2S + MSO_4 = MS(precipitate) + Na_2SO_4 \tag{13}$$

Reagents used for this process are soluble hydrogen sulfide, sodium sulfide and insoluble ferrous sulfide. Sulfide processes have better removal of the contaminants than hydroxide precipitation, but it will produce toxic sulfide gas. For this reason, process should be kept between pH 8 and 9.5 to mitigate gas formation. Additionally, it is more expensive process which is why it is only used for contaminants that cannot be removed with hydroxide precipitation. Increased cost is due to disposal of the sludge containing toxic sulfide ions. (Wang et al. 2005) Sulfide precipitation may form colloidal particles with some metals which makes separation of these particles more challenging (Fu & Wang 2010).

4.1.3 Chemical precipitation in pCAM

Main reason, why precipitation is not suitable for this application is that metals in analyzer wastewater are already in the hydroxide form. Water also contains ammonium and sodium sulfate, and as previously mentioned ammonium has negative effect on hydroxide precipitation. Also, chemical precipitation does not have added benefit of sodium sulfate removal since Na_2SO_4 start to precipitate only after concentrations as high as 110 000 mg/L (Pinto et al. 2015). This problem can be addressed by addition of hydrated lime ($Ca(OH)_2$) which will turn sulfate to gypsum which will precipitate more easily. With this method reduction of the sulfate concentration from 8000 mg/l to 250 mg/l can be achieved. (Sadeghalvad et al. 2020.)

4.2 Coagulation-flocculation

Coagulation is processing in which addition of chemicals destabilizes colloidal particles by neutralizing repelling forces between them and disturbing prevailing stability in the suspension. Focus of coagulation process is hydrophobic colloids and suspended solids. Coagulants used for coagulation process have traditionally been aluminium sulfate, polyaluminium chloride, ferrous sulfate, and ferric chloride. (Bratby 2016.)

After addition of the coagulant to water, rapid mixing is conducted. Rapid mixing is the most important stage of the coagulation-flocculation process. Since in this stage destabilization of particles and primary flock formation is happening. Flocculation happens right after rapid mixing. (Bratby 2016.) In flocculation particles destabilized by coagulation are agglomerated together to form larger particles which are easier to separate. This is done by addition of polymers that bind particles together. (Fu & Wang 2010.) There are several configurations for coagulation-flocculation Fig 8. but only necessary steps are coagulant addition and rapid mixing (Bratby 2016).

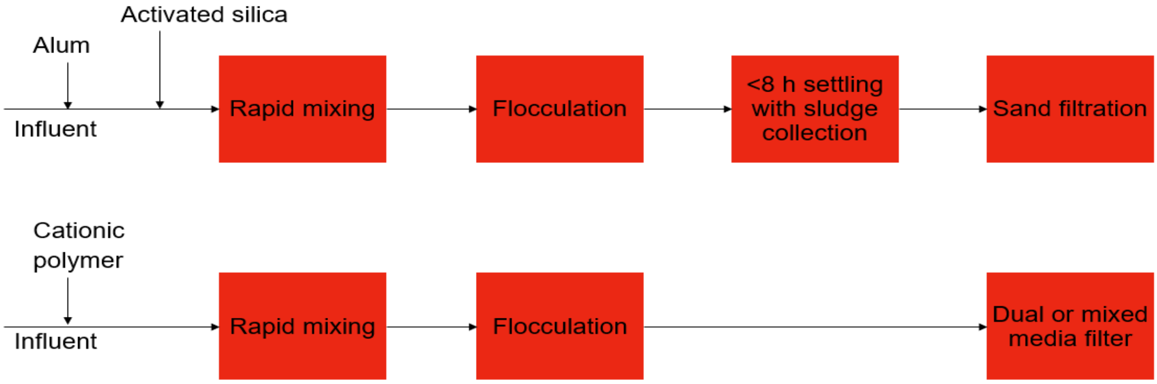

Figure 8. Process flow of two different coagulation-flocculation processes. Top: coagulation-flocculation-sedimentation-filtration. Bottom: Direct filtration after coagulation-flocculation. (Bratby 2016.)

As can be seen on Fig 8. coagulation-flocculation needs multiple unit processes to operate which is not ideal in cramped plant environment. However rapid mixing and coagulant injection can be done inside of the process piping with in-line systems (Bratby 2016). One of the possible ways to do so is shown on Fig 9.

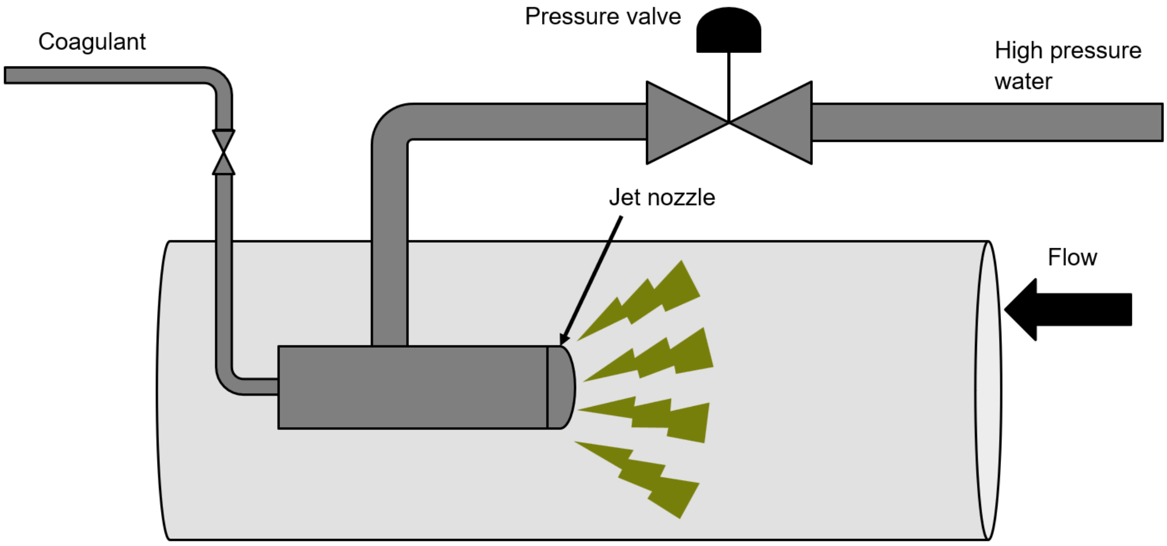

Figure 9. In-line coagulant injection and rapid mixing unit process. (Bratby 2016).

This type of mixing system works since retention time for rapid mixing is between 5-60 seconds and longer retention times have no noticeable impact on performance. Optimum retention time still depends on water type and velocity gradient and needs to be determined by experiments. (Bratby 2016.)

Flocculation process takes longer and regardless of conditions retention times shorter than 2000 seconds are not possible. If flocculation basins are configured in series this time can be reduced to less than half of the original value. Basins are designed to cause velocity gradient with baffled chambers, granular media beds, diffused air, spiral flow, or rotating blades. Simplest and the most used method is baffled basin which can be seen on Fig 10. (Bratby 2016.)

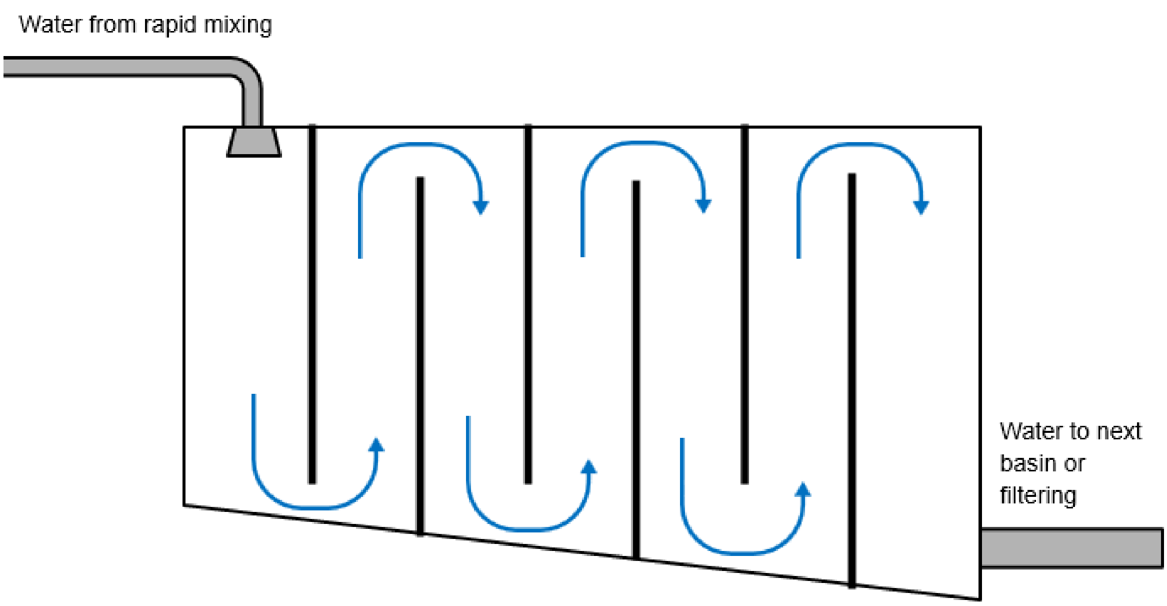

Figure 10. Flocculation in baffled basin (Bratby 2016).

Baffled basins have benefits of being maintenance free, but as a trade-off velocity gradient cannot be controlled effectively since parameter affecting it is flowrate through basin. Turns in the flow are used cause velocity gradient increasement which will make particles collide more and form agglomerates. (Bratby 2016.) This type of unit process requires lot of space, which makes it not ideal in cramped plants. Other readily available methods are blade flocculators. Blades used can be vertical or horizontal. Horizontal models have entire shaft under water which increases need for maintenance since bearings etc. are in contact with water. In comparison in vertical blade system only blade is underwater. Also, in vertical blade system basin is usually baffled to promote mixing and speed up the flocculation process. Blade flocculator Fig 11. takes less space but needs mechanical maintenance. (Bratby 2016.)

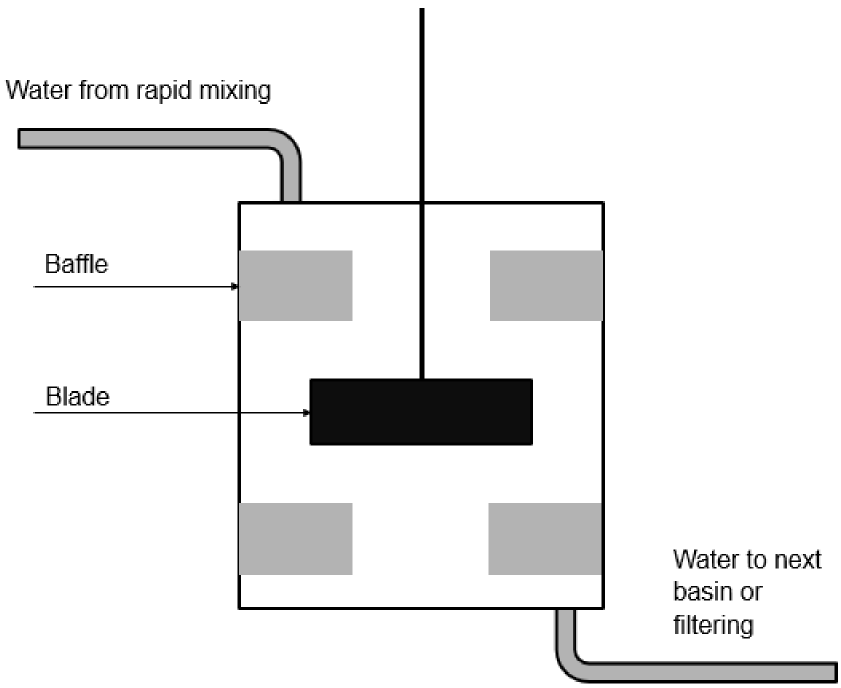

Figure 11. Vertical blade flocculator (Bratby 2016).

No matter which configuration of coagulation-flocculation retention time and velocity gradient are deciding factors when modelling new process. Both factors depend on initial conditions of the treated water, chosen coagulant and additional chemicals. (Bratby 2016.)

4.2.1 Coagulation-flocculation in pCAM wastewater treatment

Coagulation-flocculation has poor efficiency when treating heavy metals in the water and for this reason other treatment methods must be used simultaneously with it (FU & Wang

2010). This limits the attractiveness of coagulation-flocculation in pCAM wastewater treatment since multiple unit processes will be required to achieve sufficient removal. Multiple processes will increase the complexity and maintenance needs for the system. Additionally, removal efficiency of turbidity decreases as pH of the water increases (Fu & Wang 2010). Turbidity is one of the main parameters targeted in this study. And as pCAM wastewater has basic pH, this means coagulation-flocculation might not achieve sufficient removal of the metal hydroxide particles. And as was the case with precipitation coagulation-flocculation needs physical separation process to finally remove agglomerated particles. Some of the chemicals used as coagulants and flocculants are corrosive and hazardous. (Bratby 2016.) Corrosive chemicals will increase handling cost of the chemicals and disposal cost of sludge generated.

4.3 Adsorption

Adsorption is phase transfer process in which chemical species are collected on the surface of solid or liquid due to surface characteristics of adsorbent Fig 12. (Worch 2021).

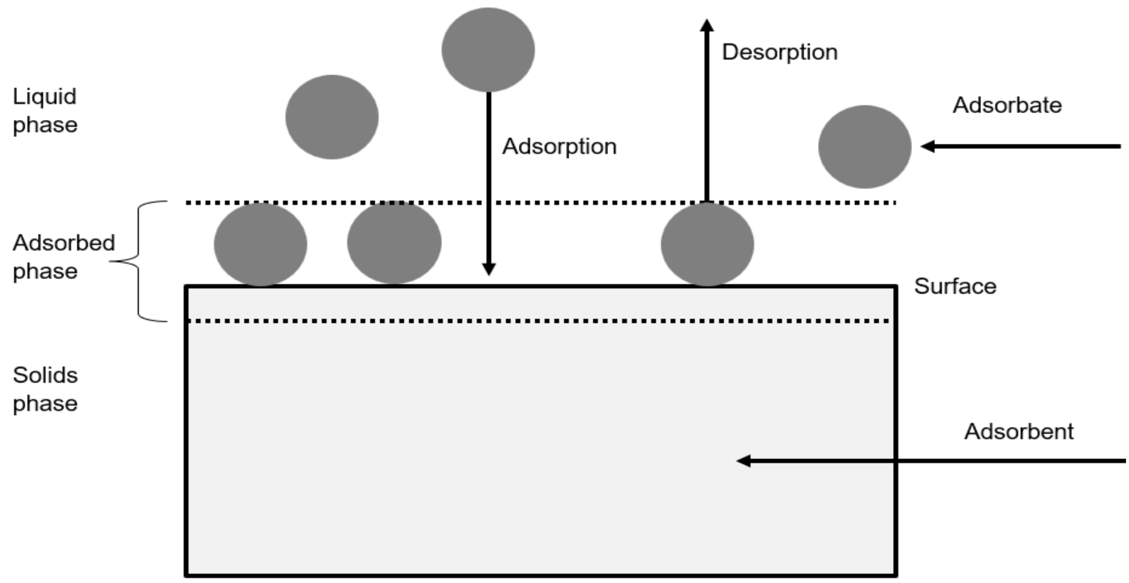

Figure 12. Basic principle of adsorption process (Worch 2021).

Since adsorption is surface phenomena surface area is key factor when deciding adsorbents to utilize. Adsorbents are porous materials with huge internal surface area relative to external surface area. They are usually measured in m^2/g with magnitudes between 100 - 1000 m^2/g. The most used adsorption material is activated carbon (AC) which has internal surface area of 600 - 1200 m^2/g. (Worch 2021.) AC is the cheapest option to use as an adsorbent due to being made from carbon rich raw materials such as coconut husks and wood. Nevertheless, AC is not commonly used for removal of metal cations due to poor surface affinity. Main purpose of AC is then removing negatively charged and non-polar particles such as organic compounds from water. (Pinto et al. 2015.)

Zeolites have better affinity for inorganic cationic compounds and thus it can be utilized for metal ion removal from water. Zeolites are three dimensional crystalline, hydrated aluminosilicates consisting of silica $[SiO_4]^{4-}$ and alumina $[AlO_4]^5$. There are natural and synthetic zeolites which both can be used for adsorption process. Natural zeolites are cheaper option but contains impurities that might affect the performance of adsorbate. Thus, synthetic zeolites have gained attention in the industrial usage. Zeolite A Fig 13. is one of the most used zeolites as an adsorbent. In Zeolite A sodalite cage is constructed from silica and alumina particles. Adsorbate particles are trapped in the α-cage structures between sodalite cages. (Tamiru & Bekele 2020.)

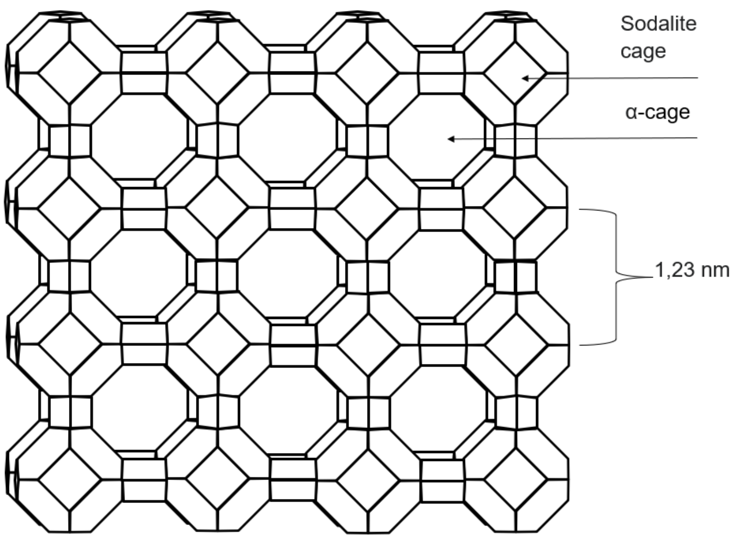

Figure 13. Structure of zeolite A (Wakihara et al. 2005).

Several parameters affect adsorption efficiency. At least pH, adsorbent dose, temperature, and composition of water can affect adsorption process (Mortula & Shabani 2012). For this reason, isotherm equations are used for adsorption process modelling. With these equations equilibrium of adsorption process can be determined. Most used isotherm equations are Langmuir and Freundlich. Langmuir isotherm assumes monolayer adsorption and homogenous adsorption sites. These assumptions make system in a way idealized. Langmuir isotherm equation (14) (Worch 2021).

$$q = \frac{q_m bc}{1+bc} \tag{14}$$

In which,

q	adsorbent loading
q_m	isotherm parameter
b	isotherm parameter
c	concentration

Langmuir isotherm is used since general applicability has been shown on studies. This general applicability makes it good starting point for adsorption analysis. (Sadeghalvad et al. 2020.) and Freundlich isotherm equation (15)

$$q = Kc^n \tag{15}$$

in which,

q	adsorbent loading
K	isotherm parameter

n	isotherm parameter
c	concentration

Freundlich isotherm is used in multi solute adsorption modelling (Worch 2021).

4.3.1 Adsorption in pCAM

Since pCAM contains metal hydroxide particles, adsorption is not efficient option for water treatment. In adsorption metal hydroxides are used as an adsorbent and thus adsorption does not remove them from water (Li et al. 2016). Regardless adsorption can be utilized for metals that have been left over from coprecipitation process. For this, inorganic adsorbents should be utilized since they have higher surface affinity to metal contaminants (Pinto et al. 2015). Tamiru & Bekele 2020. investigated different adsorbents for heavy metal removal from water and found that zeolites and metal oxide nanoparticles can remove over 90% of the metal ions from the water. Similarly, Sadeghalvad et al. 2020 found that sulfite ions can be removed efficiently with zirconium modified zeolites or organic polymer-based adsorbents such as chitosan or cellulose. From these, modified, zeolite was the most efficient option since it has good recoverability and stability in the process.

4.4 Filtration

Filtration is process separating two different phases with different physical properties between phases. Most commonly particle size, density or electric charge of the particles. Filtration usually uses particle size to separate phases using filter media which has certain sized passages. Particles smaller than passages in filter media will flow through filter and larger particles will get stuck on the filter separating them from solution. (Sutherland 2008.)

Most of the filter media is porous in nature. This type of media has three ways to stop particles from passing through. These are presented in Fig 14. Way A is direct interception which occurs when particle is less than half of its diameter from filter grain during flow around it. This gives weak van der Waals forces opportunity to trap particles on to the surface of grain. B is inertial interception in which particles due to inertia are unable to flow around grain and thus particles will hit with top of the grain. C is diffusion in which small particles are not affected by flow patterns but rather are moved around by Brownian motion of carrier fluid. This will dislodge particles near grain surface, and they will be trapped by van der Waals forces. (Sutherland 2008.)

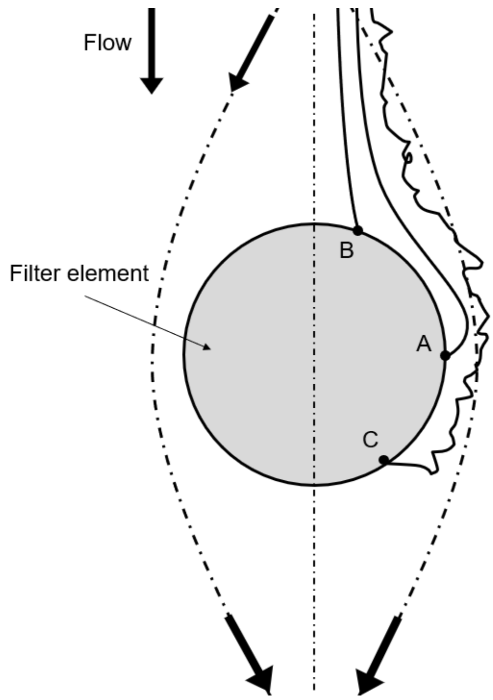

Figure 14. Working principle of filtration (Yao et al. 1971 & Sutherland 2008).

These mechanism makes it possible to filter out particles smaller than flow channels in the filter media. However, even thou this property of filter elements is important for performance it makes so that media cannot be chosen purely based on literature. (Sutherland 2008.) There are two operation principles utilized in filtration. Surface filtration and depth filtration which can be seen on Fig 15. In surface filtration particles are retained on top of the filter media where they will form cake. This cake can be formed when particles are over one third of the diameter of median pore size. Cake can then act as additional filter layer which can remove even smaller particles. When filter is clogged it can be cleaned by scraping cake of the filter or backwashing. (Tien 2012.)

In depth filtration particles are penetrating inside of the filer media. Where they are trapped by either wandering to smaller pore than particle size or mechanism mentioned above. Depth filtration is more suitable for fluids that have low particle concentrations. For example, traditional sand filters should not be used for fluids that have more than 100 mg/l particles. When depth filter is clogged it is cleaned by backwashing with enough flow that bed media starts floating. (Tien 2012.)

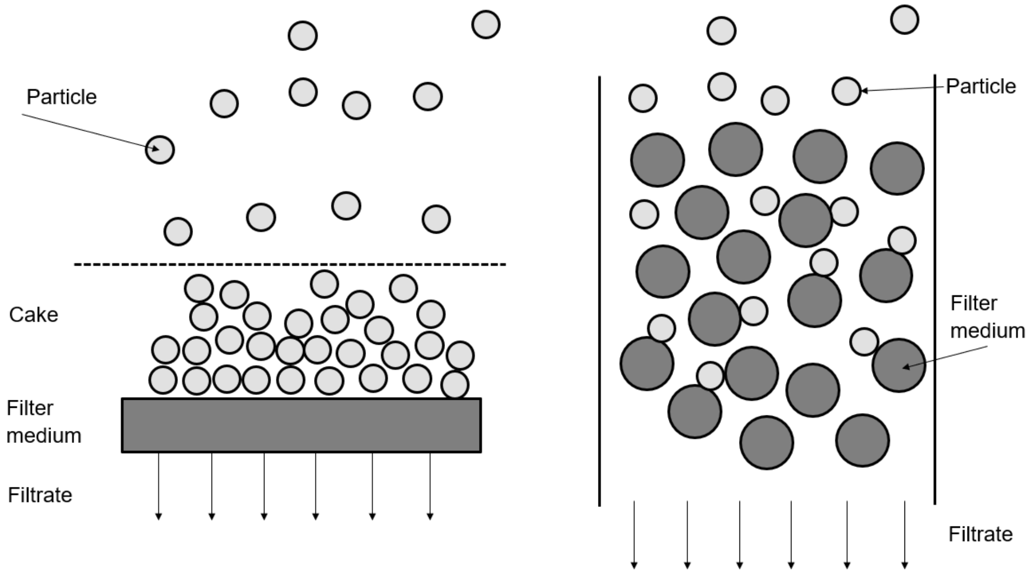

Figure 15. Surface filtration (left) and depth filtration (right) (Tien 2012).

There are two options for filtration mode dead-end and crossflow filtration Fig 16. (Tien 2012). In dead-end filtration all of the feed flow will go perpendicularly through of the filter media and particles form cake on top the surface. This will clog the filter and reduce flux. In crossflow filtration feed flow is parallel to filter surface which will generate shear force that removes particles from filter media surface. (Hakami et al. 2020.)

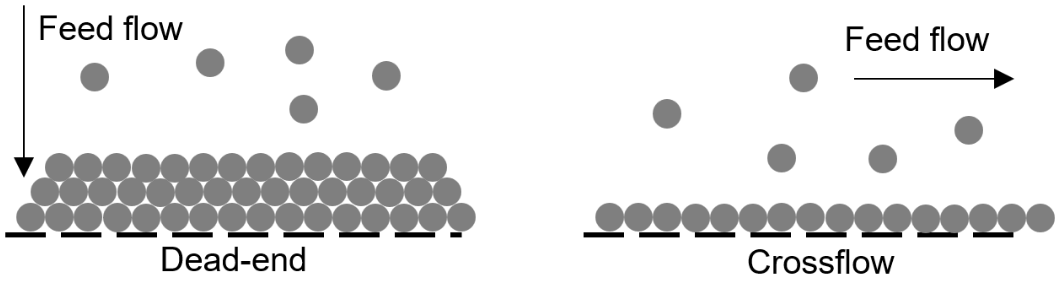

Figure 16. Dead-end and crossflow modes (Hakami et al. 2020).

Dead-end filtration is used only for low concentration low volume applications such as lab scale testing (Hakami et al. 2020). Cartridge filters use dead-end mode thus this type of filter can only be used for flows that have contaminant concentration under 100 mg/l. (Sutherland 2008). Sutherland 2008 presents comparison of different filter media Table 8.

Table 8. Comparison of filter media (Sutherland 2008).

Media	Filter action	Minimum cut-off µm	Advantages	Disadvantages
Paper (untreated)	Surface adsorbent	10-20	Low cost	Low strength
Paper (treated)	Surface	5-20	Low cost	Low strength, subject to element migration
Paper discs	Edge (depth)	1	Low cost, adjustable	Not cleanable
Fabrics	Surface	5	Sustains high pressures	Need support mesh
Felts	Depths	10	Good control on mechanical properties	Need support mesh
Woven wire	Surface	6	High strength	More expensive than paper
Mineral wools	Depth	0.1	High permeability, ultra-fine filtering	Not suitable for liquids
Glass fibre	Depth	1	Suitable for high temperatures	
Diatomaceou s earth	Depth		Very good fine filtering, low resistance	Only used as precoat
Perlite	Depth		Low density, low resistance	Only used as precoat, thick layer
Activated carbon	Adsorbent		Removes vapours, odours	Need housing
Carbon cloth	Adsorbent		Strong, flexible, high adsorption capacity	High cost

Activated clay	Adsorbent			Need container, worse than AC
Anthracite	Depth		High flow rates	Need hardness control
Sintered metal	Depth	2	High strength, suitable for high temperatures	Element migration, high cost, not cleanable
Ceramic	Depth	1	Suitable for corrosive environment, suitable for high temperatures	High cost, not cleanable
Membranes	Surface	0.005	Multiple materials	Requires pressure difference, low flowrate

They also present optimum particle size ranges for different filter medias to aid picking optimal solution Table 9.

Table 9. Optimum particle sizes for different filter elements (Sutherland 2008).

	Submicrometer	**Ultra-fine**	**Very fine**	**Fine**	**Fine/medium**	**Medium**	**Coarse**
Element	**< 1µm**	**1-2.5 µm**	**2.5-5 µm**	**5-10µm**	**10-20µm**	**20-40µm**	**>50 µm**
Perforated metal							X
Wire mesh							X
Wire gauze						X	X
Pleated paper					X	X	
Pleated fabric						X	
Wire wound					X	X	
Wire cloth				X	X	X	X
Sintered wire cloth				X	X		
Felt						X	
Metallic felt			X	X	X		
Edge type, paper	X	X	X	X			
Edge type, ribbon						X	X
Edge type, metal					X	X	X
Edge type, nylon				X	X	X	X
Microglass	X	X	X				
Mineral wool							
Ceramic	X	X	X	X			
Filter cloths				X	X	X	X
Membrane	X	X	X				
Sintered metal		X	X	X	X	X	
Sintered PTFE				X	X		
Sintered polyethene						X	X

Utilizing tables 8. and 9. it can be seen that, paper disc (edge), micro glass fiber, ceramics, membranes, and sintered metals have small enough cut-off to be utilized in pCAM wastewater treatment. Sintered metals have low dirt holding capacity and they are not cleanable, so replacement elements are needed frequently. This is not ideal since sintered metals are on the more expensive side of the filter media. Micro glass fibers are used mostly for air purification, and they have problem of elemental migration, which is not ideal since glass fibers might affect analyzer results. (Sutherland 2008.) Paper disc edge filter is only suitable for oils without waxes (Polytech filtration 2015). Thus, it cannot be utilized for pCAM wastewater treatment. This only leaves membranes and ceramics to available options for filter media.

4.5 Membrane filtration as a solution

Filtration with membranes offer small energy consumption, low footprint, and low maintenance requirements. These traits make them attractive option to replace traditional water purifying technologies such as adsorption, and chemical precipitation. (Gitis & Rothenberg 2016.) Membranes are mature technology that can be used to remove particles as small as 0.5 nm from water. However, 100 nm should be enough to remove all solid particles from analyzer wastewater. Membrane filtration can be separated to four categories Fig 17. microfiltration MF (0.1 µm – 10 µm), ultrafiltration UF (2 nm – 100 nm), nanofiltration NF (1 nm – 2 nm) and reverse osmosis RO (<1 nm) which will remove dissolved ions from the water. (Hakami et al. 2020.)

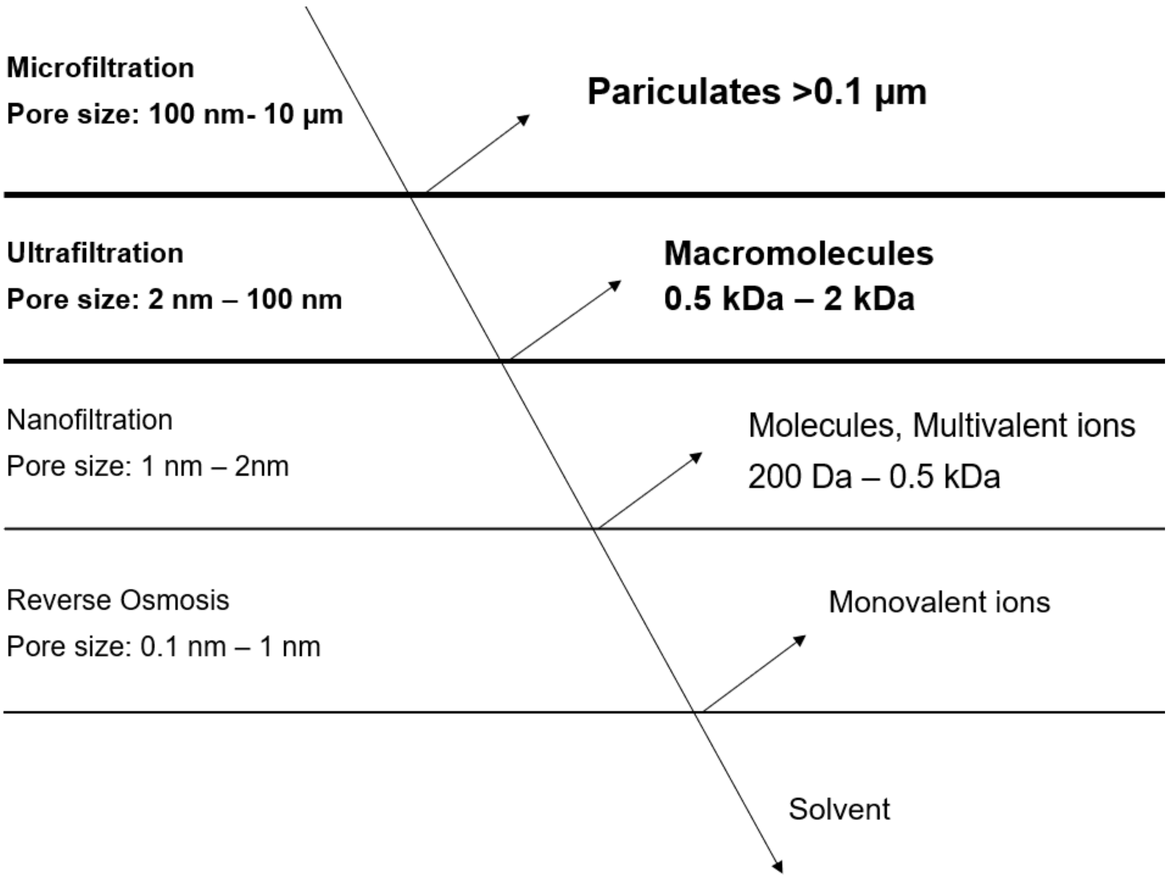

Figure 17. Removal of different particles by distinct types of membranes (Hakami et al. 2020 and Nupehewa 2021).

Dalton (Da) is molecular weight measurement. 1 Dalton is equal of 1/12 of carbon-12 atom mass (Sizes 2024).

4.5.1 Membrane type

Finding right membrane from the several commercially available ones is challenging. There are several factors that affect membrane performance and each of those needs to be chosen case by case. Membrane material for example can be polymer such as polysulfone or polyethylene or from inorganic materials such as metals or ceramics. (Hakami et al. 2020.) In general, ceramic membranes are more resistant to thermal and chemical conditions and they have better flux. However ceramic membranes cost about three times as much as polymeric ones. For this reason, polymeric membranes are dominant in the membrane market currently. Still ceramic membranes are breaking into the market for harsher and niche applications. (Gitis & Rothenberg 2016.) Comparison of some common membrane materials can be seen on Table 10.

Table 10. Comparison of common membrane materials (Shi et al. 2014).

	CA	PAN	PES	PS	PVDF	Ceramics
Mechanical strength	Good	Good	Good	Good	Good	Excellent
Thermal limit (°C)	30	40	80	75	40	High
pH	4-8	2-10	2-12	1-13	2-10.5	Superior
Oxidant tolerance	Moderate	Moderate	Good	Good	Excellent	Superior
Ultrasonic irradiation	Moderate	Moderate	Poor	Good	Good	Excellent

Based on this, ceramic membranes are chosen for its ability withstand chemically harsh conditions and ability to be flushed with high flows due to mechanical strength. Furthermore, ceramic material can resist harsh chemical cleaning agents which makes it easier to remove fouling (Samaei et al. 2007). Additionally, to these positive traits it has been reported that ceramic membrane has lifespan of at least a decade (Gitis & Rothenberg 2016). This long lifespan and low maintenance need, make ceramic membranes ideal for mining industry since utilization location might be in remote areas. Analyzer also need to operate 24/7 and replacing and cleaning membrane elements will reduce recycling efficiency.

4.5.2 Pore size

Pores size and feed flow channel size are the most deciding factors affecting separation efficiency. For channel size industry standard is at least 10 times the size of the largest particle that can enter the membrane. (Gitis & Rothenberg 2016.) Depending on the wastewater minimum channel size should be 0.3 mm. For commercially available membranes minimum channel size is >2 mm (Atech na.). Since MF and UF use sieving as a main separation method pore size should be chosen to be smaller than smallest separatable particle that can enter the membrane (Hakami et al. 2020). In UF especially pores size should be order of magnitude smaller than smallest separatable particle (Singh 2015). Suspended solids in pCAM wastewater have smallest separatable particle in around 200 nm – 300 nm however majority of the particles are 1 µm and higher (Koponen 2024). Since studies have shown that removal of divalent ions from water with UF is not yet efficient. For example, Nupehewa 2021. found that using 5 kDa – 20 kDa UF membrane removed only around 15% sulphate ions from water. If dissolved solid needs to be removed NF can be utilized. However, since NF has molecular weight cut of 200 Da – 0.5 kDa pressure needs to be increase significantly compared to MF or UF (Hakami et al. 2020). If salinity becomes problematic other unit processes presented above should be utilized to boost ion removal efficiency.

4.5.3 Ceramic membrane materials

Choosing right ceramic for membrane is important since different materials have different properties and might not be suitable for all applications. Material also determines manufacturing costs and packing density for the membrane, which determines the unit's physical size. Here properties for different materials commonly used in MF and UF membranes are presented.

Aluminum oxide (Al_2O_3) is the most common material used in ceramic membranes. Since aluminum is abundant, raw materials for the membranes are cheap and easily available. Which makes alumina membranes cheap in ceramic membranes. Despite to this alumina membranes have good chemical and thermal stability, which makes utilizing them in harsh operation conditions possible. Alumina can also be used as a support material for composite membranes to bring rigidity to them. Alumina has two allotropes that are commercially utilized for membranes α- and γ-alumina. Pure α-alumina can have pore size down to 20 nm -100 nm, and membranes coated by γ-alumina can have pore diameter down to single nano meter. (Gitis & Rothenberg 2016.)

Silicon dioxide (SiO_2) also known as pure silica has one of the smallest pore sizes from the membranes available today. Pore size as small as 0.3 nm – 2 nm can be achieved. However, pure silica membranes have poor hydrothermal properties. Due to this, it can only be feasible utilized in temperatures under <100 °C. Poor hydrothermal properties also make that pure silica membranes can be utilized only on water free conditions, and thus main use case for these types of membranes are in gas separation. Hydrothermal properties of silica can be improved by combining silica with carbon to form hybrid silica membrane silicon carbide (SiC). (Gitis & Rothenberg 2016.)

Silicon carbide (SiC) is hybrid material consisting of silica and carbon atom backbone. This backbone makes it that SiC membranes are chemically stable in 0-14 pH and can withstand temperatures up to 800 °C. (Liqtech 2024.) Silica carbon backbone also makes SiC membranes durable and hard which makes installation process easier. Manufacturing cost for SiC are high which might reduce the attractiveness of the material. (Eray et al. 2020.)

Titanium dioxide (TiO_2) has excellent chemical resistance in both acidic and alkali conditions. For this reason, titania is desirable material for applications where other materials cannot function properly. Titania can be utilized as self-standing membrane which contain only titania or as coating layer for composite membranes. Since pure titania membranes have poor structural stability that limits their utilization potential. Titania is usually used as a coating material to achieve good chemical stability without compromising structural integrity of the membrane. Titanium is rare metal which makes production of titania coated membranes costly. This means that they should be utilized only when chemical conditions are so harsh that other materials cannot withstand it. Coating with titania happens in 300-400 °C with sol-gel deposition and with this method pore sizes of below 2 nm can be achieved. (Gitis & Rothenberg 2016.)

Zirconium dioxide (ZrO_2) is popular ceramic coating since it has excellent chemical stability in alkaline conditions. Raw materials for zirconia are rare which makes this membrane more costly option. Zirconia can be doped with yttrium to make manufacturing process easier. This will make production of these membranes even more expensive and thus yttria doped zirconia membranes are used mainly on high-temperature fuel cells. (Gitis & Rothenberg 2016.)

Zeolites are material group of crystalline hydrated alumino-silicates. There are over 200 different families of zeolite frameworks, but only few of them are suitable for membrane utilization. These suitable options pose good thermal and chemical stability and pore size in the nanometre scale. Self-standing zeolite membranes are still not commercially practical since producing membranes larger than few square centimetres is not yet technically viable. For this reason, composite membranes that have zeolite as a top layer are more popular. These however have problem of contaminants adsorption into the pores which makes cleaning membrane harder. Still zeolite composite membranes have high flux, high selectivity and can withstand temperatures around 400-500 °C. Additionally they have great resistivity to organic solvents. (Gitis & Rothenberg 2016.)

4.5.4 Comparison of materials

For these materials Nupehewa 2021. presents comparison matrix that will help choosing the right material for membrane application. This is presented in Table 11. “**+**” means comparatively better than other materials “**–**” then means worse compared to other materials and “**0**” no noticeable difference in comparison.

Table 11. Comparison of different membrane materials (Nupehewa 2021).

Material	**Alumina**	**Silica**	**SiC**	**Titania**	**Zirconia**	**Zeolites**
Chemical resistance	0	-	+	+	0	0
Thermal stability	0	0	+	-	0	0
Hydrothermal stability	0	-	+	0	0	0
Cost	+	+	-	-	-	+
Pore size availability	+	0	0	+	+	-
Scale-up possibility	+	+	-	+	+	0
Total	3	0	1	1	1	0

From the Table 11. it can be seen that alumina membranes should be utilized whenever possible.

4.5.5 Ceramic membrane flow and configuration

In chapter 3.4 different flow configurations are presented and most commercially available membranes use crossflow filtration. In industrial applications cylindrical membranes with multi-channel tubes are more desirable since they can be sealed easier, have higher mechanical stability and larger flux capacity compared to flat models (Samaei et al. 2007). Flow of tubular model can be seen in Fig. 18. and cross section of tubular membrane can be seen on Fig. 19.

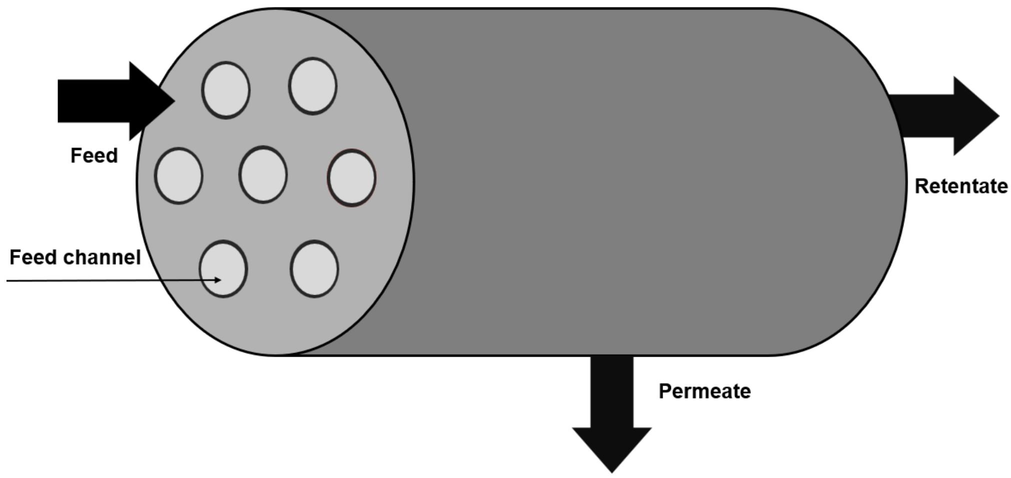

Figure 18. Tubular membrane flow (Samaei et al. 2007).

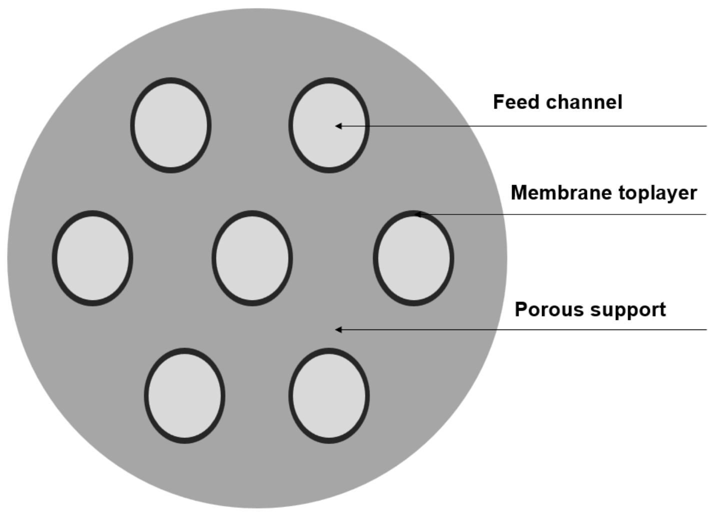

Figure 19. Cross section of tubular membrane (Samaei et al. 2007).

Ceramic membrane filtration is simple process. Basic flow sheet for this process is presented in Fig. 20. This configuration can be used to pilot filtration system, but it does not address the biggest problem regarding membrane filtration **fouling**.

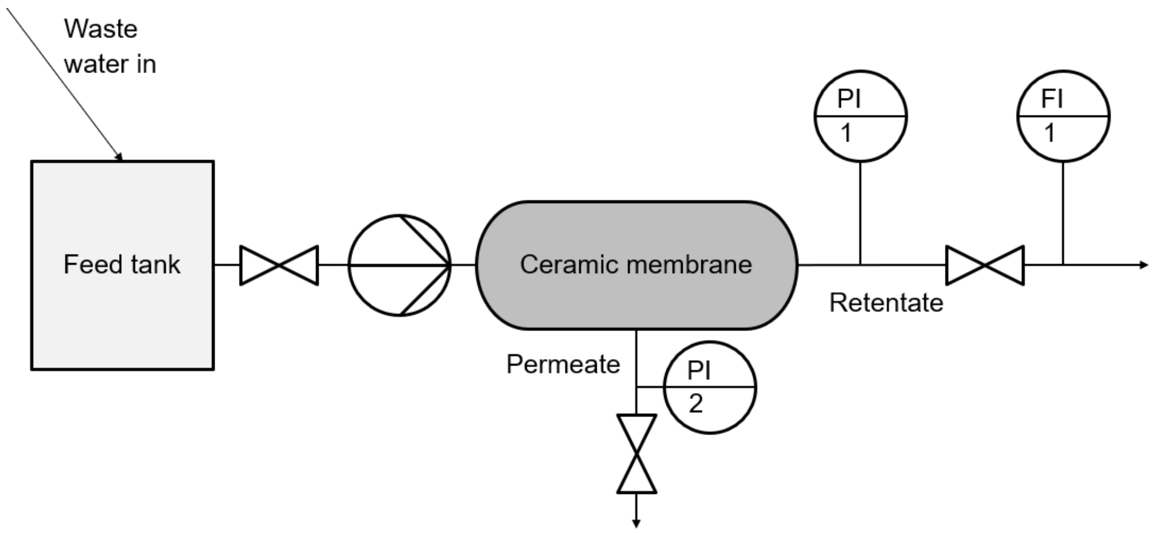

Figure 20. Basic flow sheet of ceramic membrane filtering system.

For this design ways to prevent and reverse fouling and promote ease of cleaning is explored.

4.5.6 Membrane fouling

Fouling of membrane is defined as "The process resulting in loss of performance of a membrane due to the deposition of suspended or dissolved substances on its external surfaces, at its pore openings, or within its pores" (Gitis & Rothenberg 2016). Decrease of performance can usually be seen as reduction in the flux. This reduction of flux is not ideal and thus fouling needs to be cleaned which increases maintenance costs of filter. Controlling the fouling is then one of the most important challenges in membrane operations. (Mohammad et al. 2012.)

Fouling is usually caused by dissolved or suspended particles from the feed water. Contaminants in the water can then interact with membrane surface or fouling layer on top of the membrane surface and get stuck on it. Fouling can be classified as reversible or irreversible depending on difficulty of cleaning membrane. (Hakami et al. 2020.) Example of reversible fouling is particles accumulation on top of the membrane surface. Accumulation is caused by concentration polarisation phenomena, which causes particles move towards membrane surface by convection. These particles are not stuck on the membrane and can diffuse back to the solute however back-diffusion is slower than convection and thus particles are concentrated near the membrane surface. (Singh 2015.) Irreversible fouling is adsorption of the contaminants to the membrane or contaminants getting stuck on the pores (Hakami et al. 2020).

Fouling can also be divided into four types depending on material causing it. These categories are inorganic fouling/scaling, particle/colloid fouling, microbial fouling, and organic fouling. (liu et al. 2005.) For pCAM application only first two are considered since wastewater that comes from analyzer should not contain any microbial activity or organic matter.

4.5.7 Membrane cleaning

Membrane cleaning can be categorized either physical or chemical cleaning. Type of cleaning is chosen based of the type of fouling. Reversible fouling can be removed by physical cleaning. However usually this is not enough, and chemicals are needed to achieve proper cleaning. When planning the cleaning following criteria should be followed. (Shi et al. 2014.)

- Cleaning should restore initial flow through pristine membrane without changing its surface properties.

- Dislodged foulants should be kept in dispersion to remove re-fouling potential.

- Be compatible with membrane and other system components. Cleaning solution should not be corrosive to any components etc.

- Be compatible with water.

- Cleaning solution should have good buffering capacity and stability during cleaning process.

- Promote disinfection of wet surfaces.

- Utilize available and cost-effective methods and chemicals.

Physical cleaning alters the hydrodynamics of the membrane system. Altered hydrodynamic conditions remove foulants thanks to the kinetic forces. However, only foulants that are not reacted with the membrane surface will be removed by this. Chemical cleaning then alters chemistry of the membrane system which chances repulsion forces between particles and membrane surface. Additionally, chemicals can decompose particles and cleave their bonds with membrane surface. This will increase particle solubility back to the liquid. Nowadays these methods are usually used together to optimize cleaning process. (Shi et al. 2014.)

Particulate/colloid fouling can in most cases be cleaned with physical cleaning since particulates rarely enter inside of the membrane's pores. These particles stay in gel-layer on top of the membrane due to concentration polarisation phenomena. Simply chance in hydrological conditions during the cleaning will disperse this gel-layer. (Liu et al. 2005.) Simplest form of physical cleaning is membrane relaxation. It is done by operating membrane in non-continuous way alternating between normal operation and slow flow mode, which allows particles to diffuse from membrane surface back to the bulk solution due to concentration gradient. With membrane relaxation some reversible fouling can be removed but usually time constrains make it that complete cleaning is not feasible achieved. (Shi et al. 2014.)

Backwashing is method in which cleaning liquid is pushed through membrane from permeate side Fig 21. This removes contaminants that are deposited inside of the membrane pores. It also disrupts the fouling cake layer on top of the membrane which makes it possible to remove it with flushing. Backwashing is conducted utilizing two times the normal operation flux for the membrane to ensure proper removal of the deposited particles. Higher flux can damage membrane and for this membrane material should be chosen that it can withstand the increased flux and pressure. Backwashing is fully automated process, and it starts when critical transmembrane pressure (TMP) is reached for the system. Frequency of the backwashing can be from few minutes to several hours. (Shi et al. 2014.) TMP is measured as a pressure difference between inlet and permeate flow and can be calculated with equation (16) (Singh 2015).

$$\Delta P = \frac{P_1 + P_2}{2} - P_p \tag{16}$$

in which,

ΔP	Transmembrane pressure [bar]
P_1	Pressure at entry of membrane module [bar]
P_2	Pressure at exit of membrane module [bar]
P_p	Pressure of permeate [bar]

If system is on steady state operation Darcy's law (17) can be utilized to relate flux, TMP, and membrane resistance (Singh 2015).

$$J = \frac{\Delta P}{\mu R_m} \tag{17}$$

in which,

J	Flux [l*m*h]
ΔP	Transmembrane pressure [bar]
μ	Solution viscosity [cP]

R_m Hydraulic resistance of membrane [bar/l*m*h*cP]

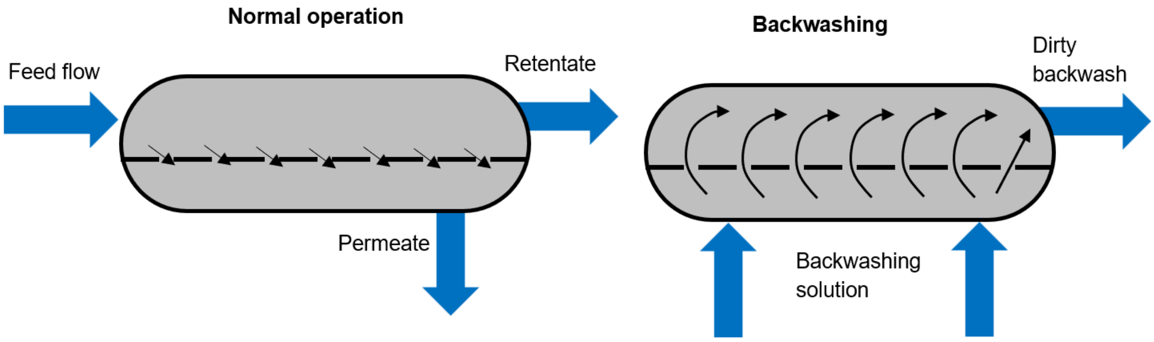

Figure 21. Normal operation and backwashing flows (Shi et al. 2014, Jepsen et al. 2019).

Backwashing process will remove most of the hydraulically reversible fouling. From the process equations (1) if the process is not complete some metal hydroxides can be present in the wastewater. These metal hydroxides might react with other ions and foul membrane irreversible and chemical cleaning is then needed to remove this inorganic fouling. However, this type of fouling should not be prevalent for UF and MF. (Liu et al. 2005.) Still tests will be needed to confirm if chemical cleaning is required and to determine frequency of cleaning.

Chemical cleaning is used for fouling that cannot be removed with physical cleaning. It can be conducted in situ as cleaning-in-place (CIP) where chemicals are injected into the membrane system without disassembling the system or ex situ as cleaning out of place (COP) in separate chemical baths. COP is usually the last option since removing membrane from the casing is time consuming and labour-intensive process which stops whole operation. (Shi et al. 2014.)

Chemical reactions can displace foulants with dissolving and modifying them which causes them to transport back to the bulk solution. There are six cleaning agents that can be used for cleaning: acids, alkalis, oxidants, surfactants, chelants and enzymes. Type of cleaning agent must be chosen based on the fouling affecting membrane and membrane material. Also, chemicals used must be chemically compatible with membrane otherwise membrane deterioration can cause more fouling and reduce membrane flux. (Shi et al. 2014.) In table 12. examples of common chemicals used in cleaning is presented.

Table 12. Cleaning chemicals used in cleaning of membranes (Shi et al. 2014).

	Chemical	**Function in cleaning**
Acids	HCl, HNO_3, H_3PO_4, Citric acid	pH regulation, dissolution of inorganic precipitates, acidic hydrolysis
Alkalis	NaOH, KOH, Na_2CO_3	pH regulation, alteration of surface charges, alkaline hydrolysis of proteins, catalyzing saponification of fats
Oxidants	NaClO, H_2O_2	Oxidation of organics, disinfection
Surfactants	SDS, CTAB, Tween 20	Dispersion of deposits
Chelants	EDTA	Complexation of metals, removal of mineral scaling
Enzymes	Protease, Lipase	Catalysis

Membrane manufacturers usually recommend cleaning products that should be utilized in their membrane cleaning (Liu et al. 2005).

4.5.8 Proposed P&I for membrane system

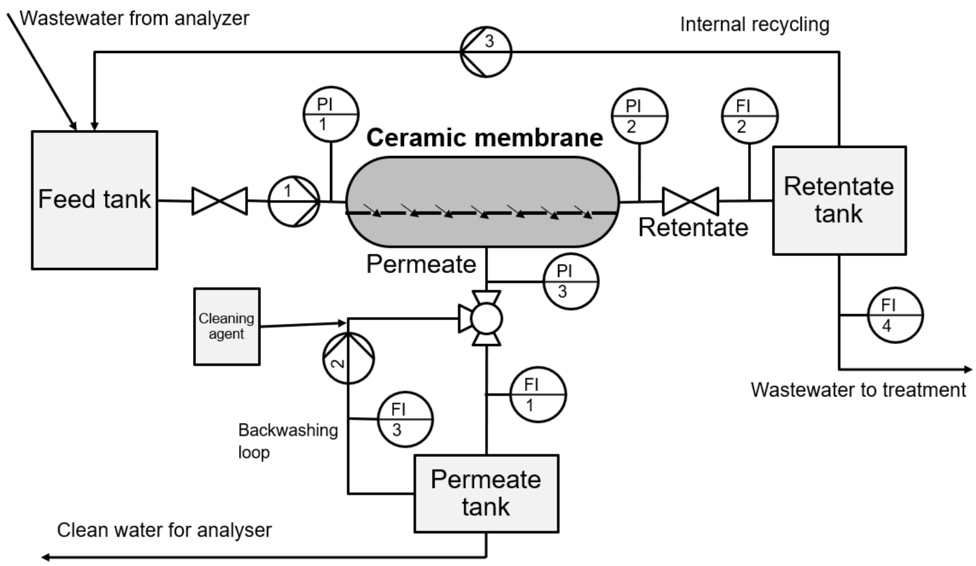

Figure 22 filtration system with backwash to be integrated to the analyzer system (Modified Jepsen et al. 2019).

Membrane system proposed is shown in figure 22. In normal operation centrifugal pump 1. feeds water to membrane with chosen crossflow velocity and TMP. Permeate is collected to tank and part of it is saved for cleaning. Rest of the permeate goes back to the analyser and is utilised for diluting samples. Retentate is recycled back to the feed tank for new filtration. Recycling retentate is done because permeate flow rate for membranes are usually 10-15% of the crossflow rate of the membrane system in 3-4 bar trans membrane pressure (TMP). Tubular membranes can handle solids load of 5%. This means with recycling water internally in the membrane system up to 95% recovery rate (RR) for the water can be achieved. (Singh 2015.) This number is optimistic upper limit and piloting needs to be done to find real recycling rate. Integration of filter system to analyser can be seen on Fig 23.

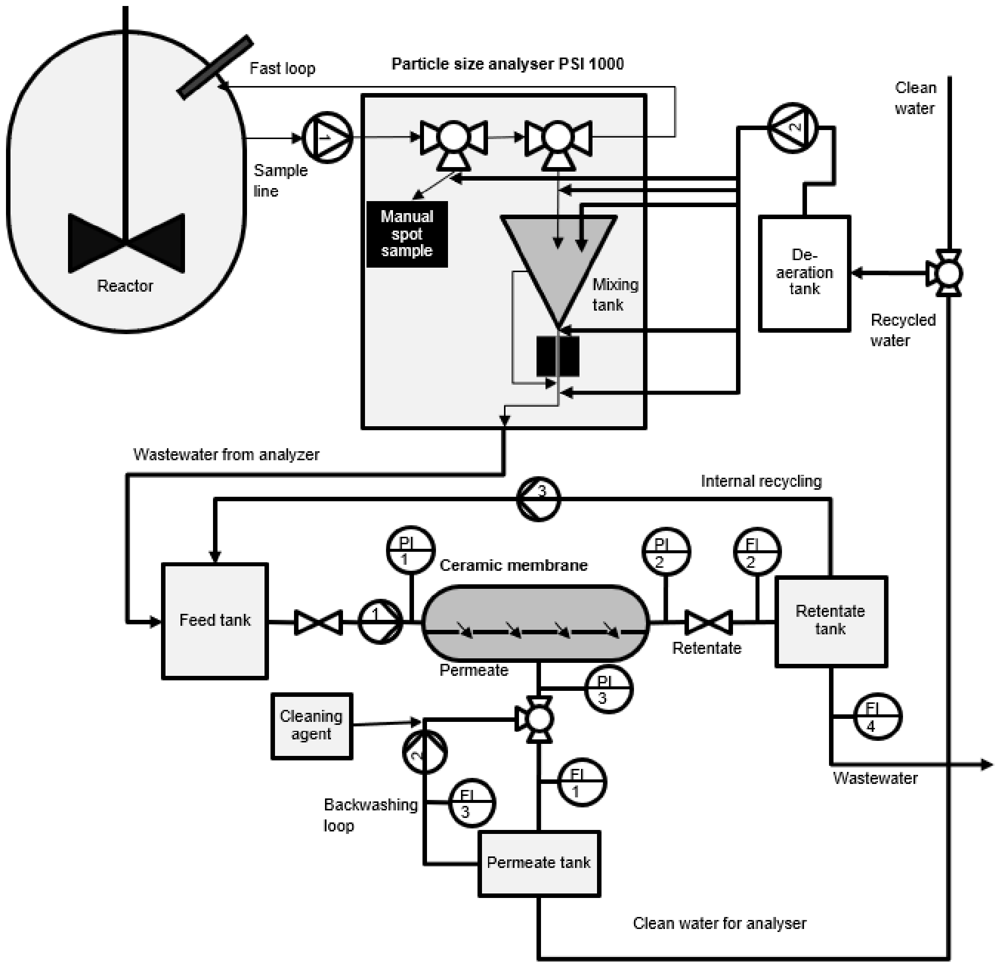

Figure 23. Filter system integrated to the whole analyzer system.

5 Case Metso Research Center pCAM pilot plant

Case study in Metso Research Center pCAM pilot plant in Pori gives an opportunity to see which parameters should be studied for process water recycling. Using information from previous chapters filtering system for pilot plant is partly tested in laboratory environment. Results are analysed and feasibility of the filtering system is assessed with environmental and economic analysis.

5.1 Microfiltration membrane analysis

Microfiltration membranes are analysed with Amicon® stirred cell. This cell uses nitrogen gas to generate TMP. Analysis conducted will estimate the fluxes through membranes and pCAM particle removal potential. Equipment used in analysis can be found in the Table 13. and picture of analysis setup can be found in Fig 25.

Table 13. Equipment used in analysis.

Equipment	Model	Manufacturer
Stirring cell	XFUF04701	Millipore
Magnetic stirrer	MR Hei-end	Heidolph
Digital balance	2200C	Precisa
pH meter	744	Metrohm
Turbimeter	2100 AN IS	Hach

Three sample membranes with active area of 15 cm^2 are cut. Membrane samples are then washed with 20% ethanol solution and rinsed with deionised water to remove preservative chemicals. More information of membrane samples is available on Table 14.

Table 14. Membranes used.

	Type	Manufacturer	Cut off	Material	pH
1.	1FPH	3M	1 µm	PES	1-11
2.	MFP5	Alfa Laval	0.5 µm	FP/PP	1-11
3.	MFG1	Alfa Laval	0.1 µm	PSU/PP	1.5-12

Washed membranes are kept in DI water to keep them wet during analysis process. Membrane 1. is installed on stirring cell Fig 24. Cell is operated at constant 21 °C temperature and 300 rpm rotation speed with magnetic mixer. Pressure is created with nitrogen gas from tanks and controlled with manual valve. Permeate amount is measured with digital balance.

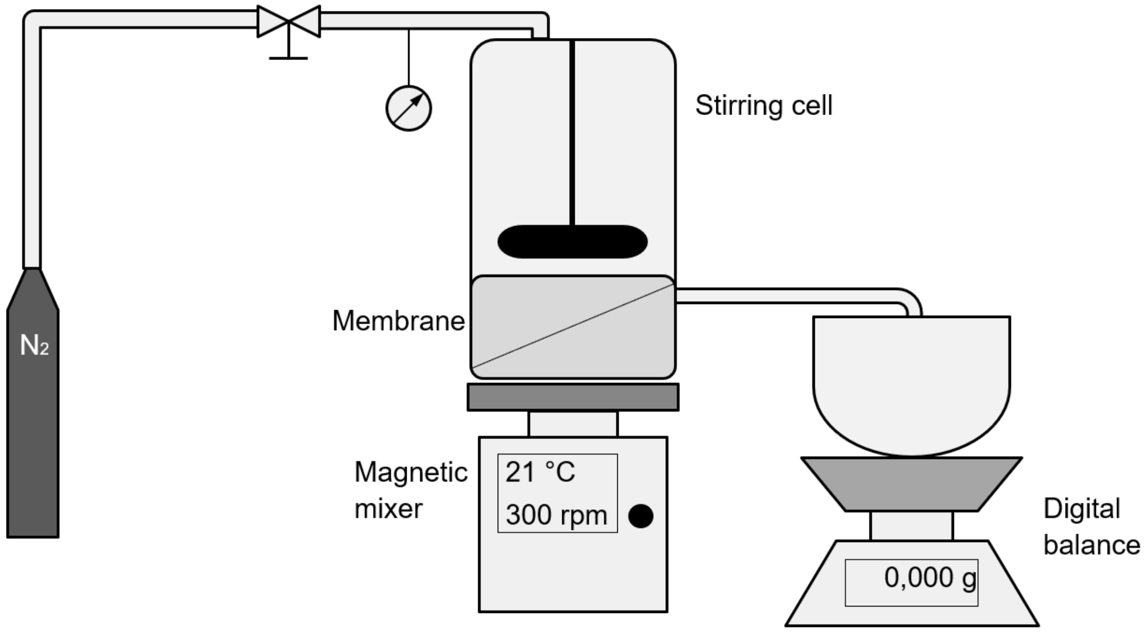

Figure 24. Amicon® used for membrane testing.

Installed membrane is pressurised for 15 minutes. This pressurisation is done by running DI water through the system with pressure of 0.25 bar for first membrane. After pressurisation stirring cell is filled with 400 ml of DI water to measure mass flux trough pristine membrane. System is run at constant 0.21 bar pressure and mass of the permeate is read every 10 seconds. This is continued until the system is empty. System is then emptied, and 200 ml of PSI wastewater is poured into the stirring cell. Before collecting sample from PSI wastewater container should be shaken until fully mixed, otherwise sample might not be representative. Same process is repeated for wastewater, but this time system is run only until edge of the water hits 100 ml mark on stirring cell. Permeate and retentate from the analysis is collected for later analysis. System is cleaned and same process is conducted for second and third membrane. Second membrane is pressurised in 0.3 bar and test is run in 0.23 bar. Third membrane is pressurised in 0.5 bar and test is run in 0.44 bar.

PSI wastewater sample is taken with following protocol. From one of the analysis 30 l of wastewater is taken into the container straight from the wastewater pipe. Container is then shaken until solution is fully mixed. Immediately after shaking 2 l of sample is taken to further analysis. Volume of the sample and solids content is measured from this sample. Additionally, pH is measured before and after the analyzer. With this protocol samples used in Amicon® analysis are also taken. However, due to the circumstance's month passed between obtaining sample and Amicon® analysis. In this period sample did sediment to the bottom of the container which might have caused some of the particles agglomerate and form larger particles. Even after thorough mixing some of the agglomerates might not been broken down to original size. This leads to particle matrix being slightly different than fresh sample.

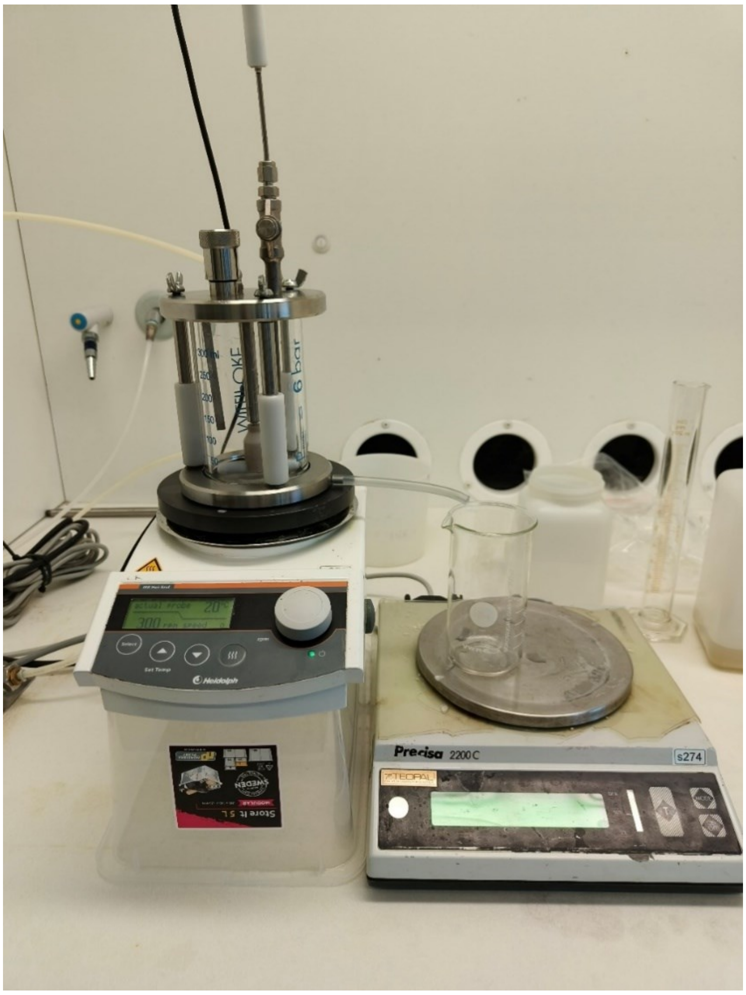

Figure 25. Amicon® analyser equipment.

From these measurements fluxes can be calculated. If process is in constant pressure and temperature flux is calculated with equation

$$J = \frac{m}{At} \tag{18}$$

In which,

J	permeate mass flux
m	permeate mass
A	active surface area of membrane
t	filtration time

With equation (18) fluxes for pristine membranes Fig 26. and PSI wastewaters Fig 27. can be calculated.

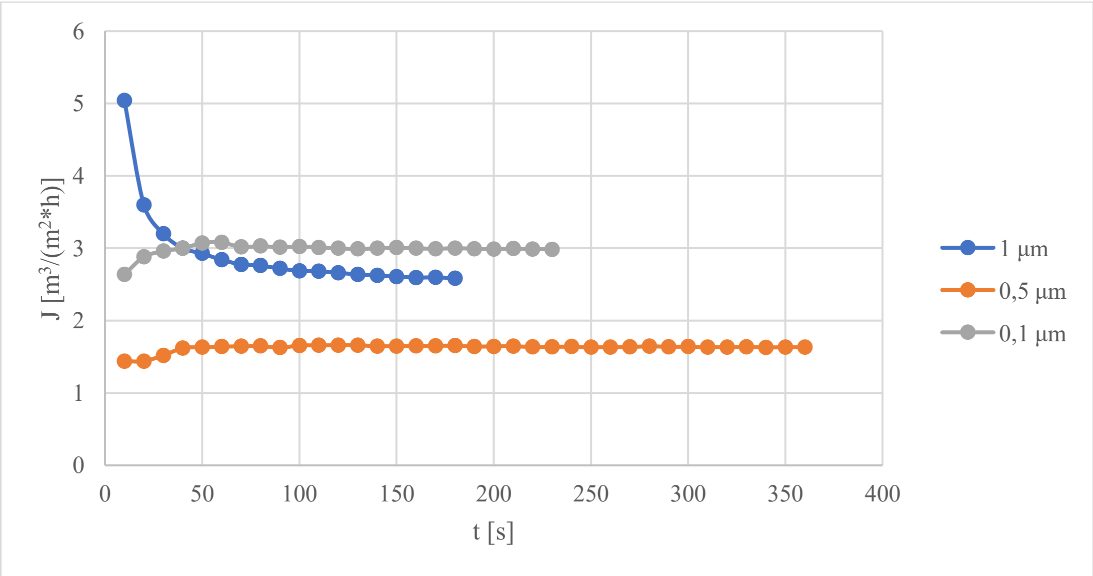

Figure 26. Water flux through membrane.

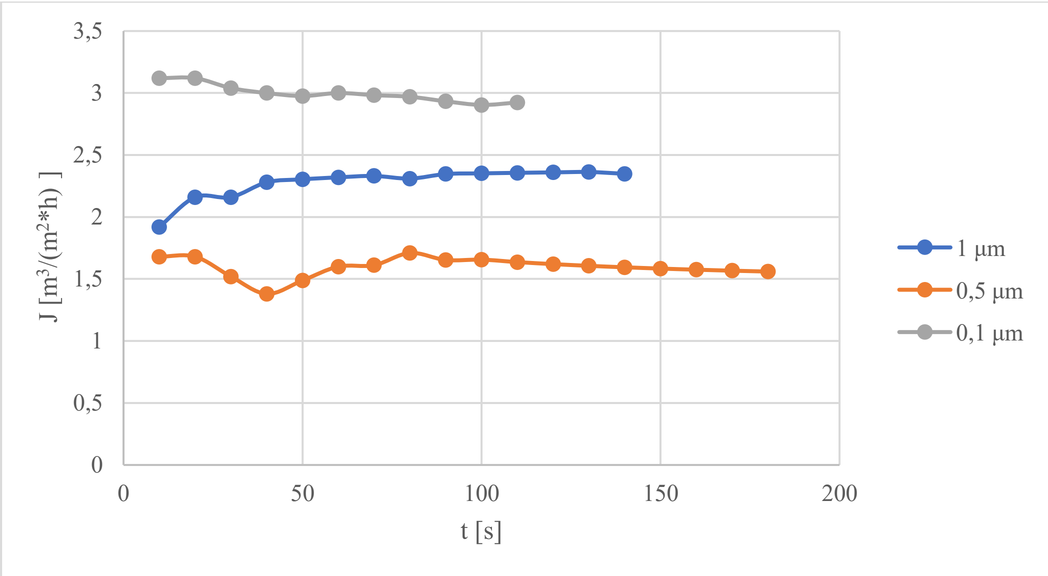

Figure 27. PSI wastewater flux trough membrane.

Pictures of membranes after analysis can be seen in Fig 28. Solid matter can be seen accumulating onto the membrane surface. This accumulation did only have minor effect on the flux since filtration times were low in this test. Longer tests are needed to analyse flux reduction caused by solids accumulation.

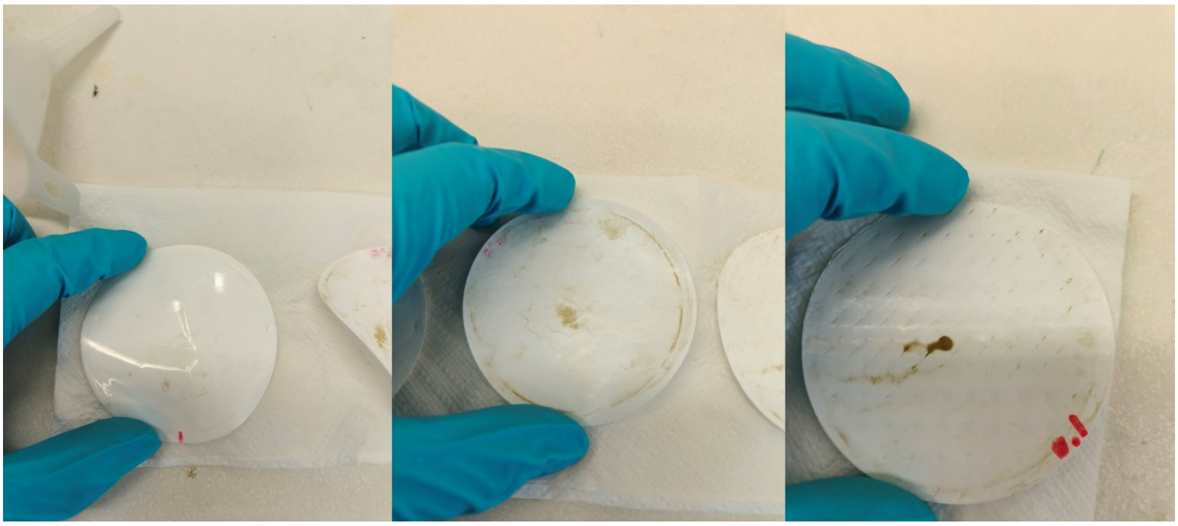

Figure 28. Membranes after filtration. 1µm left, 0.5 µm middle and 0.1 µm right.

These results in isolation are not useful since they do not address permeate quality. To measure this turbidity is measured for permeate and retentate samples. Turbidity is measured by pouring sample into the testing flask which is then inserted to turbimeter for analysis. Before pouring to the test flask samples were shaken until fully mixed. Test flask was cleaned between samples. Since turbidity is time sensitive all samples were measured twice, and average of those measurements is presented in Table 15. Time sensitivity also means that samples should be kept in turbimeter until value is not raising anymore and measured peak value should be used as a result.

Table 15. Turbidity of the samples in NTU (Nephelometric Turbidity Unit).

Deionized water	0.201		
PSI sample	125		
	1 µm	**0.5 µm**	**0.1 µm**
Permeate	1.775	1.605	1.18
Retentate	45.9	240	240

PSI sample has 125 NTU of turbidity. For this reason, in 1 µm test sample was not representative and retentate turbidity should be in low 200 NTU. Regardless, 1 µm still removed most of the contaminants present in the water with permeate having only 1.8 NTU of turbidity. If water is to be recycled turbidity should not be over 10 NTU and from Table 15. it can be seen that all tested membranes passed this qualification. Due to long time passing between sample taking and analysis these results cannot be used as a sole reason for membrane selection. Still Amicon® analysis gives promising results for future experiments.

5.2 Process water quality in Metso pCAM pilot plant

Composition of water from analyser was measured several times during several test runs. Sample was taken with previously mentioned protocol and analysation was conducted in house. Only chemical oxygen demand (COD) and permanganate were analysed by third party. These results were analysed and compared to limit values acceptable for dilution water. Analysed results can be seen on Table 16. in which green means well below limit likely not concern, yellow slightly below limit might need monitoring, and red over the limit will need immediate action.

Table 16. Measured values compared to limit values in Metso pCAM pilot plant.

Na (mg/l)	Mg (mg/l)	Ca (mg/l)	S (mg/l)	Mn (mg/l)	Fe (mg/l)	Co (mg/l)
Ni (mg/l)	COD (mg/l O2)	Permanganate (mg KMnO4/l)	Hardness (CaCO3 mg/l)	pH	TSS (mg/l)	TDS (mg/l)

In Table 17. more information about the suspended solids found in water is presented.

Table 17. Size distribution and chemical concentrations of different pCAM (Koponen et al. 2024).

Chemistry		**NCM 8:1:1**	**NCM 85:5:10**	**NCM 90:5:5**
Morphology		Spherical	Spherical	Spherical
D50, coarse	µm	10 - 13	10 - 18	10 - 18
D50, fine	µm	< 8	< 5	< 5
Span		< 0.7/1.1-1.4	< 0.7	< 0.9
Tap density	g/cm^3	> 2.0	> 2.0	> 2.0

With this and Fig 29. particle size can be determined to be between 4 – 20 µm. These particles are also spherical which makes determining pore size easier.

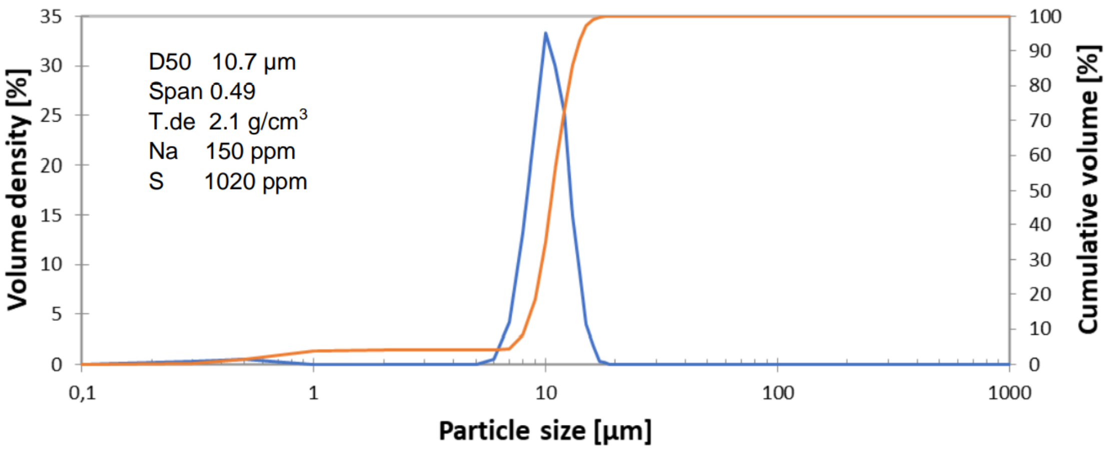

Figure 29. Particle size distribution in Pori (Koponen et al. 2024).

5.3 Economic analysis

Analyzer consumes 10 l water per minute and operates around 8000 hours per year. If regular water (1.51 €/m^3) and wastewater treatment (2.26 €/m^3) fees in Pori are used (Porin vesi 2015). Filter system will save values seen in Fig 30. per year of operation.

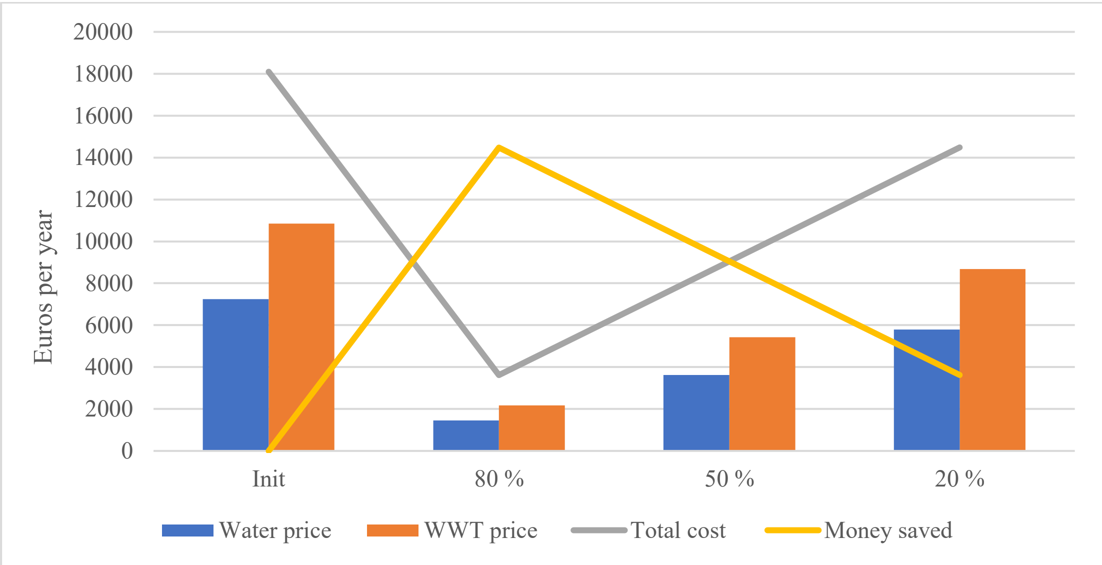

Figure 30. Water and WWT fees per year for different recovery rates.

When making investments calculating payback period is essential to find out when and if investment will be beneficial. Payback period can be calculated with equation (19) (Gitis & Rothenberg 2016).

$$PBP = \frac{CAPEX}{P_{annual}} \tag{19}$$

in which,

PBP Payback period in years

CAPEX Cost of investment

P_{annual} Profit from the investment – operating cost (OPEX)

In literature values for OPEX were found between 0.1 – 3.2 €/m^3 and for the CAPEX between 5000 – 30000 € for system this size (Gitis & Rothenberg 2016, Singh 2014). Using equation (19) PBP were calculated for different options which are presented in Table 18. Highlighted with red are combinations that will never pay back investment and in yellow combinations that will take too long to payback since membranes have lifespan of around 10 years (Gitis & Rothenberg 2016).

Table 18. PBP in years for system with different recovery rates (RR).

CAPEX [€]	**5000**	**10000**	**20000**	**30000**
OPEX [€/m^3]	**80% RR**			
0.1	0.4	0.7	1.4	2.1
0.5	0.4	0.8	1.7	2.5
1	0.5	1.0	2.1	3.1
2	1.0	2.1	4.1	6.2
3	65.1	130.2	260.4	390.6
	50% RR			
0.1	0.6	1.2	2.3	3.5
0.5	0.8	1.5	3.0	4.5
1	1.2	2.4	4.7	7.1
2	-9.1	-18.1	-36.2	-54.3
3	-0.9	-1.9	-3.7	-5.6
	20% RR			
0.1	1.6	3.2	6.4	9.6
0.5	4.1	8.2	16.4	24.6
1	-4.2	-8.5	-16.9	-25.4
2	-0.8	-1.7	-3.3	-50.0
3	-0.5	-0.9	-1.9	-2.8

These values are heavily dependent on water and WWT fees, but calculations show promising results for system that has over 50 % recovery rate. System will never be viable if OPEX is more than WWT fee. Since values used for this are municipal WWT fees, real fees will be higher due to industrial water needing more robust treatment. For example, Metso pCAM pilot plant has industrial wastewater requirements and WWT fees are 2000 €/m^3 (Metso int.). Normal operation of analyzer will cost 1200 euros per hour. Savings that can be achieved with filter system are presented in Fig 31.

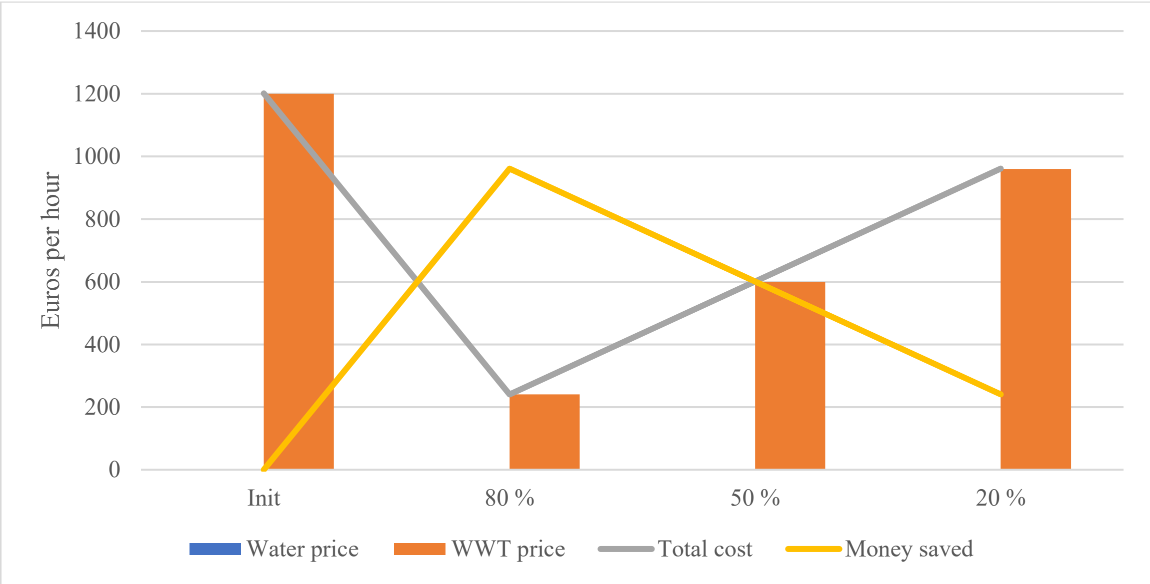

Figure 31. Metso pCAM pilot plant analyzer costs per hour.

High WWT fees leads to situations where filter will payback in just a few hours of operation. In Fig 32. system with 20000 € CAPEX and high 100 €/m^3 OPEX is presented.

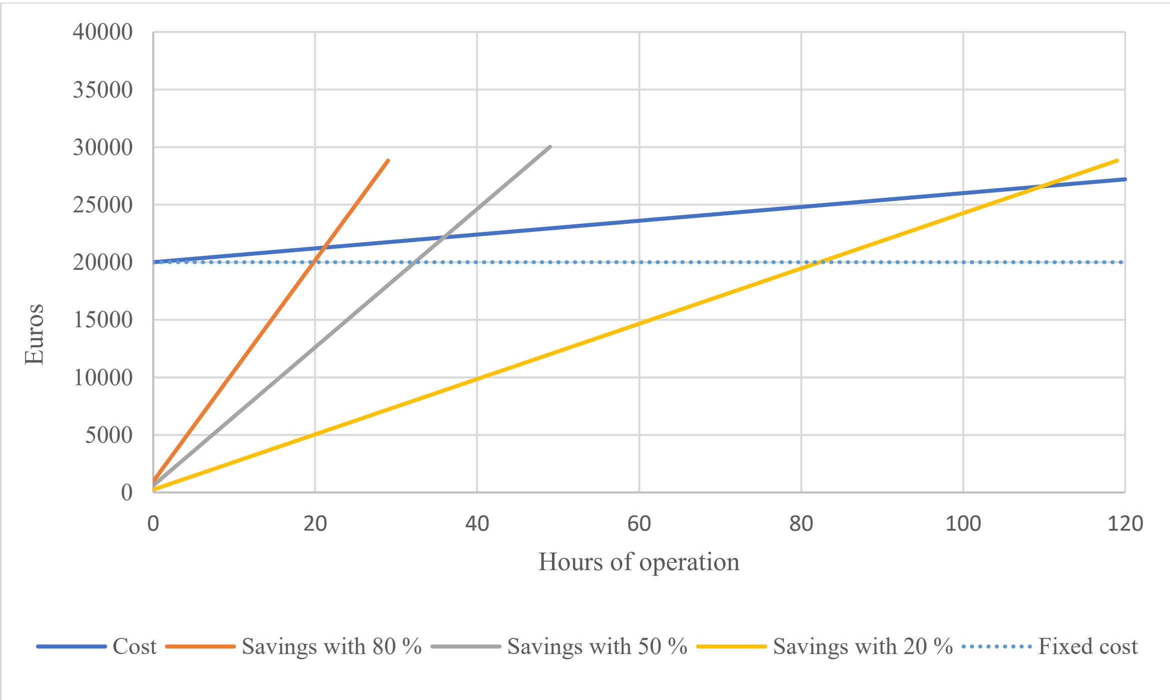

Figure 32. Metso pCAM pilot plant filter system PBP.

Even 20 % RR will pay back the investment in just under 110 hours of full operation if WWT fees are as high as 2000 €/m^3. Places like Metso pCAM pilot plant which have high WWT fees are prime candidate as a customer since they will have almost immediate financial benefit.

5.4 Water handprint

Metso offers **Planet Positive** products which promises significant reduction on some environmental concern compared to industry benchmark levels or previous iteration of product. For water this must be at least -20 % reduction in water consumption comparatively. However, this planet positive performance claims have received limited third-party validation. (Metso 2024b.) PSI 1000 already has this planet positive status, but filter system can be utilized to reduce water consumption even further. In Fig 33. simplified example for water consumption for the analyzer is presented. Analyzer consumes 10 l/min average and is operating 24 hours a day in a seven days per week around the year.

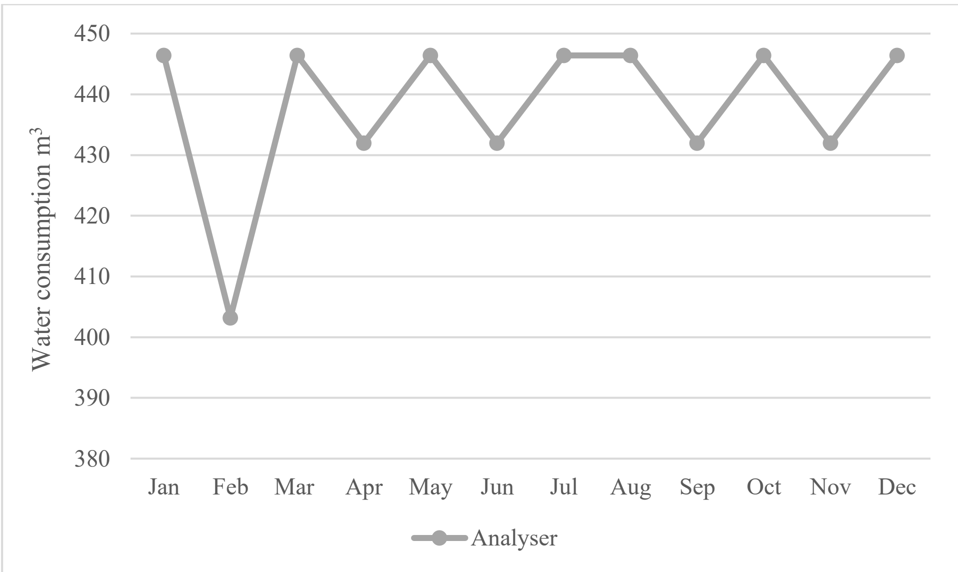

Figure 33. Real water consumption for each month.

With AWARE values for Western Finland (Appendix 5.) and equation (11) consumption is transformed to water equivalents Fig 34.

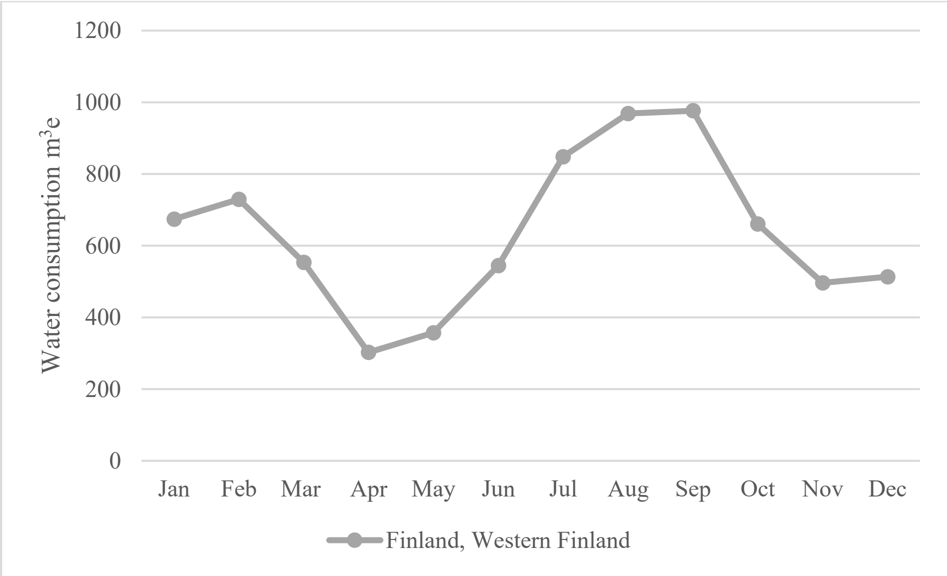

Figure 34. Water equivalents for plant operating in Metso pCAM pilot plant (WULCA 2019, Appendix 5.).

In theory 95% recovery rate (RR) is achievable with membrane filtering system. However, more realistic upper limit is 80% recovery rate when taking account water needed for backwashing and cleaning. Water consumption for several recovery rates were calculated using previous method Fig 35.

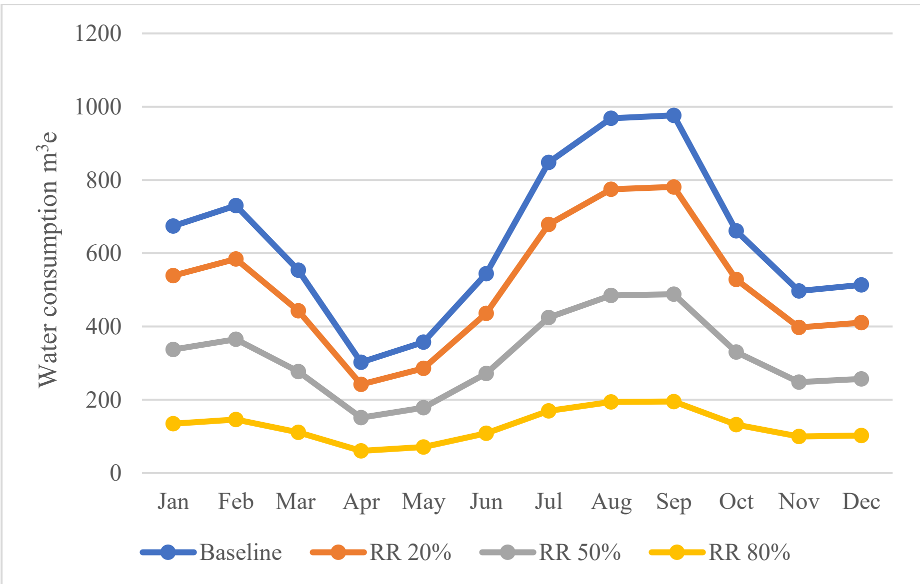

Figure 35. Analyser water consumption with filter system in Metso pCAM pilot plant.

So, with filter system on average 350 m^3 and 500 m^3e of water could be saved per month. In Finland water is usually not concern but if analyser was located in some other place savings would be higher. Two major lithium production location were chosen for comparison Fig 36. Greenbush mine in Western Australia which is largest spodumene ore producer (Geoscience Australia 2023). and Salar the Atacama where two top lithium producers in the world are operating (Bogossian 2021). Locations were chosen by assumption that pCAM production is placed close to lithium production to minimize transport distance of lithium used for CAM production.

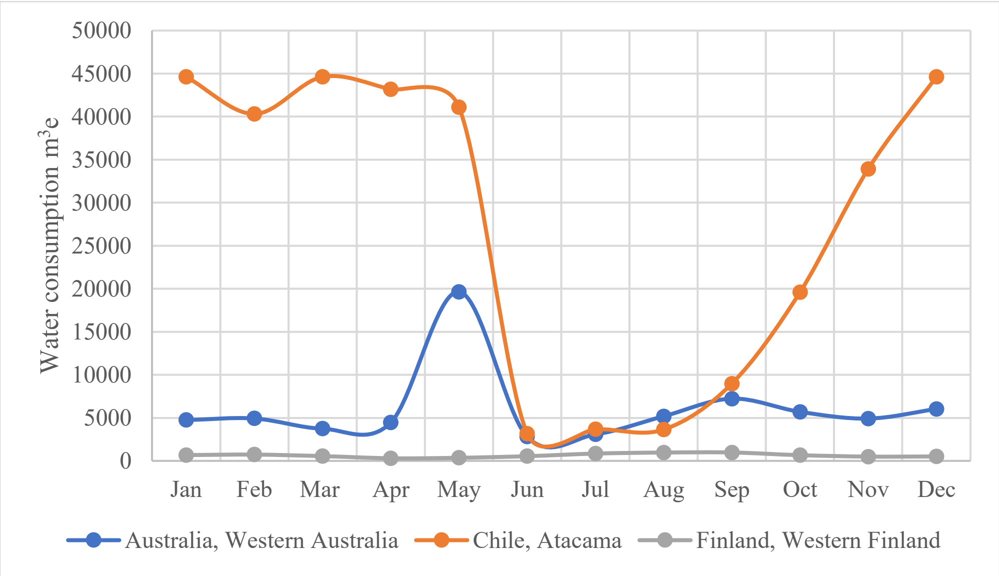

Figure 36. Water consumption equivalents for chosen locations (WULCA 2019).

Filter system with 80% recovery rate Fig 37. could save 4800 m^3e per month in Australia and 22000 m^3e per month in Chile. Additionally, since Chile has lot of variability during the year in the worst month filter system could save 35000 m^3e of water.

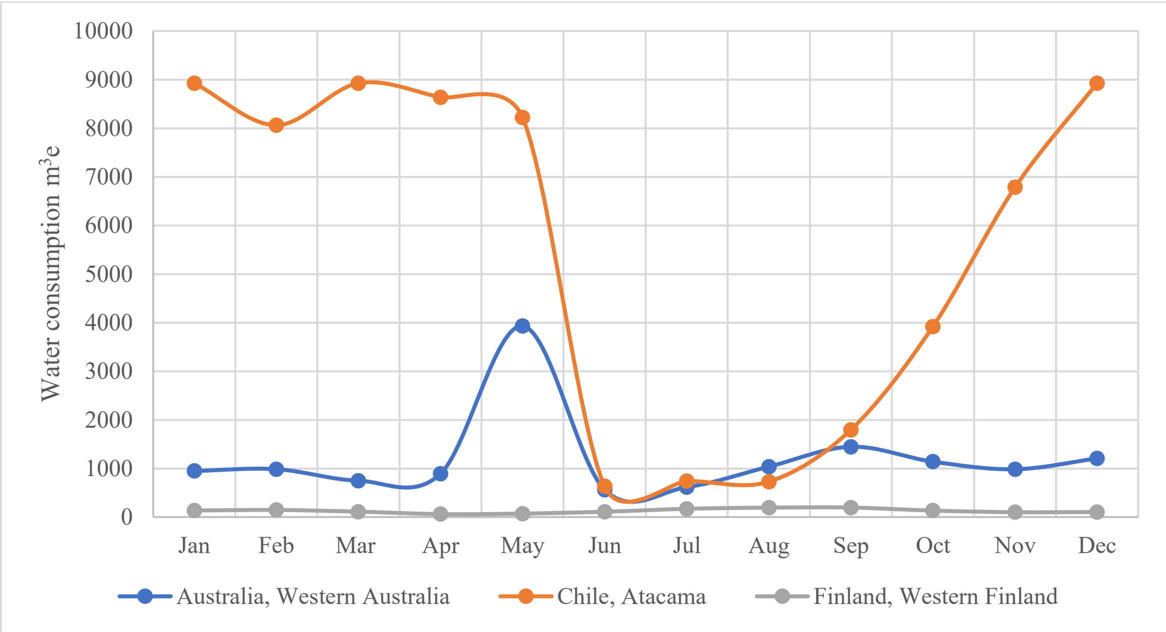

Figure 37. Water consumption equivalents for chosen locations with 80% recovery rate (WULCA 2019).

With these yearly water footprint Fig 38. reduction can be calculated.

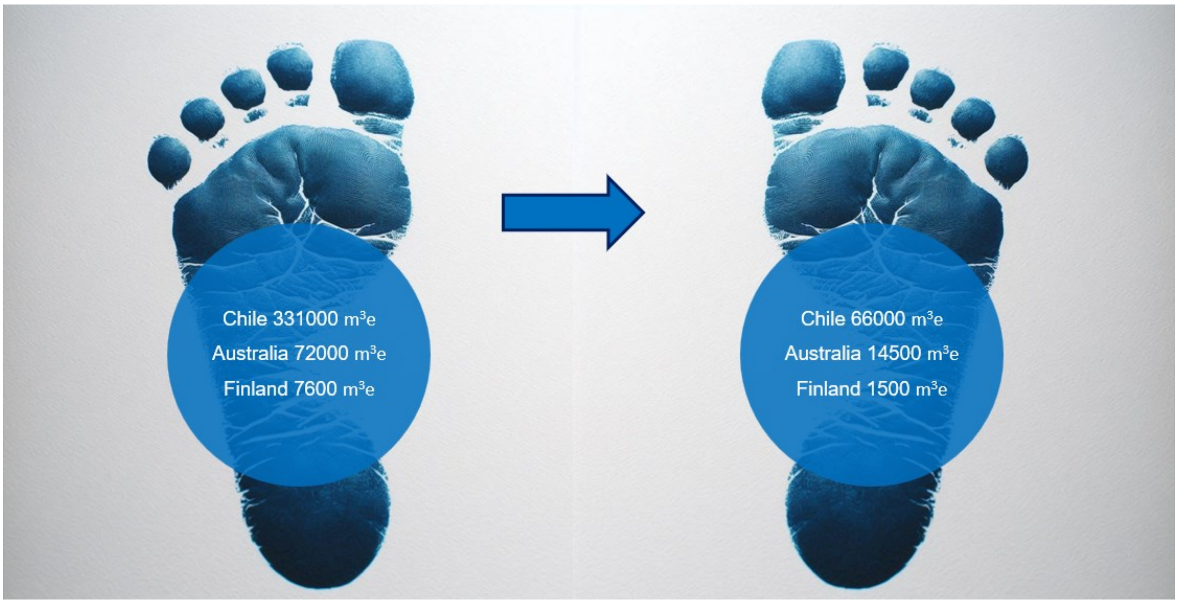

Figure 38. Yearly water consumption before and after filter system (Generated with AI · May 16, 2024, at 2:49 PM).

Water saved with filter on monthly basis can be seen on Fig 39.

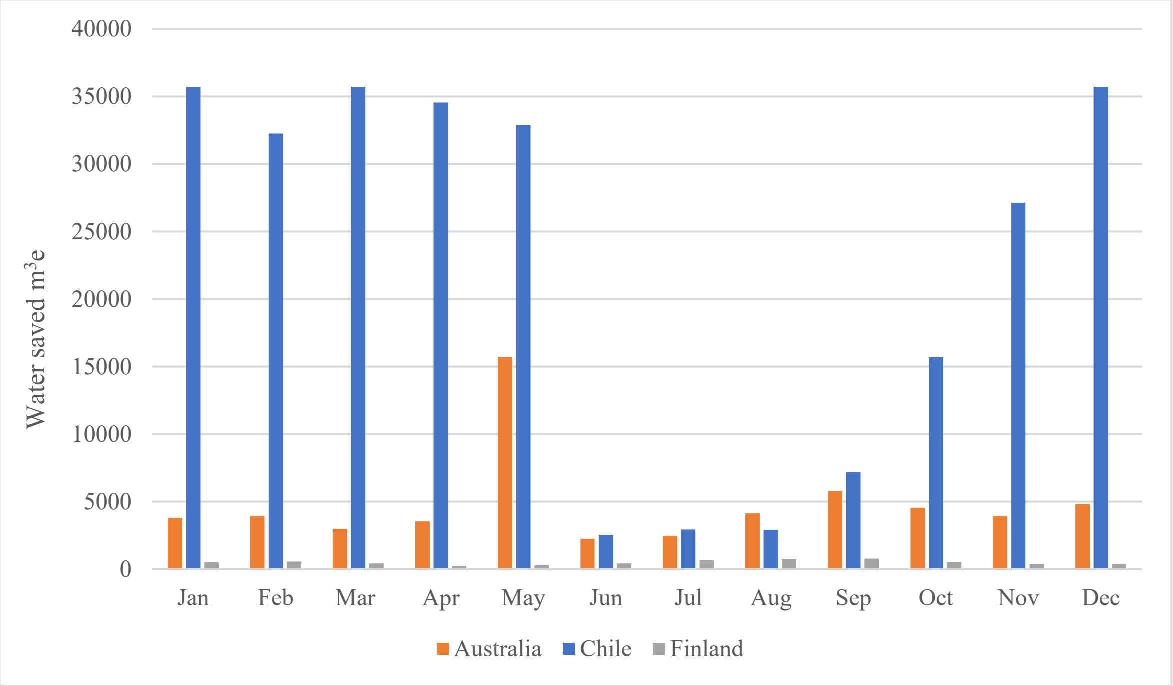

Figure 39. Water saved with 80% recovery rate.

Reduction of water footprint can also be indicated as a handprint. Handprint is measurement of positive impact caused by products or services (Sarni 2023). With these savings water handprint for filter system Fig 40. is calculated.

Figure 40. Water handprint for filter system with 80% RR per year.

5.4.1 Market specific marketing

With WWF water risk filter non-conventional aspects of water consumption can be assessed. Values for example locations are found and presented in Fig 41.

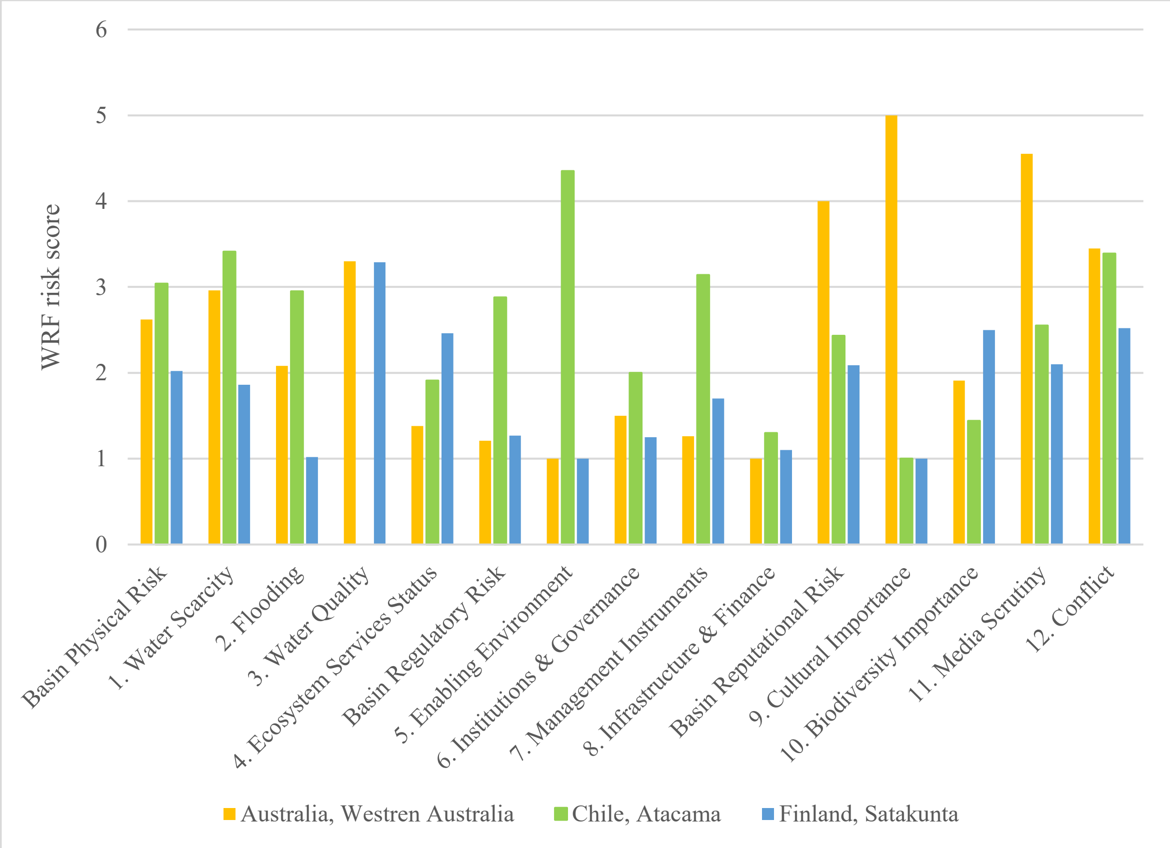

Figure 41. WRF values for example locations (WWF 2023, Appendix 5).

Above values are weighted with metal and mining weighting values from Table 7. From these risk scores various aspects affecting market can be found.

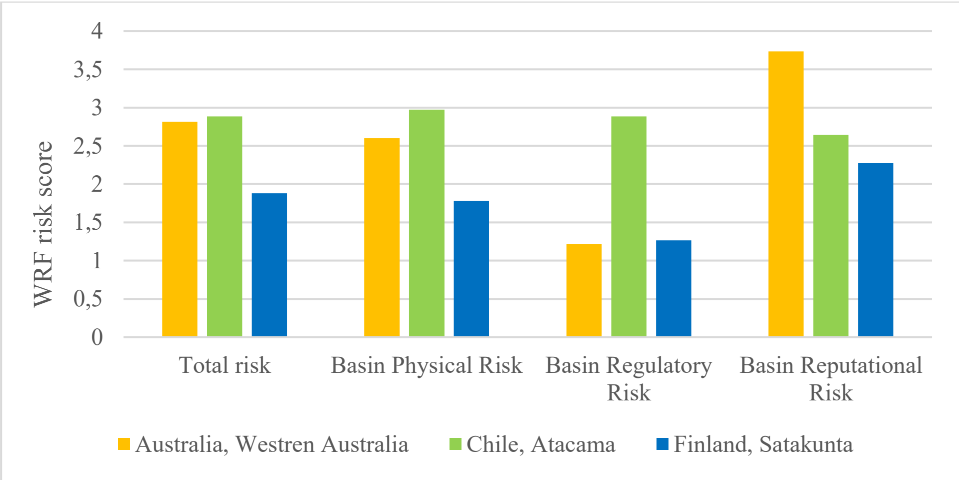

Figure 42. Risk scores calculated using metals and mining weighting in Table 7.

From Fig 42. even thou total risk scores for Australia and Chile are close to each other, cause for score is quite different. When operating in Australia good water stewardship is essential to preserve cultural heritage and reduce risk of media scrutiny. Failing to do so will cause reputational damage for company. In Chile other hand enabling environment and having good reporting and management tools in place is necessary. Failure to do so will result in friction on regulation side and losing the right to operate is real risk.

6 Conclusions

The primary objective of this study was to find suitable technology for internally recycling water in particle size analyzer used in pCAM manufacturing. Through a comprehensive analysis of various water treatment technologies, membrane filtration was identified as the most suitable method for recycling water within the system. To determine the appropriate membrane for the filter, thesis compared different materials and flow configurations. Ultimately, selected membrane was tubular membrane with multiple flow channels made from either aluminium oxide or silicon carbide, depending on the harshness of the conditions. While aluminium oxide is more affordable option, it is not as durable as silicon carbide.

The feasibility of proposed system was validated through experimental tests conducted at the LUT separation laboratory using samples from the Metso Research Center pCAM pilot plant. But due to time constrains and limited availability of analyser wastewater samples only rudimentary tests were performed to assess viability of membranes. It was found out that 1 μm and smaller pore size can remove enough particles from the wastewater rendering it suitable for reusing.

In the subsequent testing phase, longer runs should be conducted for membranes to test flow reduction caused by fouling and determine optimal backwashing frequency to restore pristine flow. Once ideal backwashing frequency is found system can be moved to pilot phase. During which monitoring long term cleanliness of recycled water is conducted. Given the propensity of membranes to foul, operating the system using crossflow configurations with regular backwashing is recommended.

Findings in this thesis indicate that implementing the proposed system could lead to substantial water savings over 80 % in an ideal scenario. Moreover, the system is likely to pay back its investment within a few years of normal operation. This reduction in water consumption is critical, especially as new environmental regulations continually emerge, compelling companies to report and reduce their water footprint.

The filter system proposed in this work serves as a theoretical framework that can be further developed into a full-scale production unit. Such implementation could save several thousand euros annually under optimal conditions. Beyond economic benefits, thesis approach underscores the importance of responsible water use and sets a precedent for future research and adoption in similar industrial settings. As global water scarcity intensifies, integrating environmental considerations into industrial process design becomes paramount. Thesis contributes to broader goals of resource conservation and environmental protection.

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APPENDICES

Appendix 1. PSI500i water quality requirements

PSI500i Water Quality

Introduction

This document describes the water quality parameters for PSI500i particle size analyzer. In general, the dilution water used in the analyzer should be free of particles to avoid water affecting the measurement results. Other parameters may affect the longevity of the analyzer.

Parameters

Total Suspended Solids (TSS)

Total suspended solids in the water describes the concentration of solid particles in the water. These particles will affect the measurement reading as they will also contribute to the particle size distribution (PSD). The diluted %-solids in the analyzer measurement is typically 0.5-1% (w/w) or 5-10 g/L of sample particles. The dilution water TSS value should be < 50 mg/L or 0.005% (w/w). This way the effect of the particles in the dilution water should affect less than 1% in the analyzer PSD reading.

Water Hardness

Water hardness describes the amount of dissolved minerals, mainly calcium and magnesium, in the water. Water hardness is typically expressed as the concentration of $CaCO_3$ in water as mg/L or ppm (1mg/L = 1 ppm). Following table describes if water is considered as soft or hard:

Table 19 - Water hardness as CaCO3.

	CaCO3 (mg/L)
Soft water	0-60
Moderate hard water	61-120
Hard water	121-180
Very hard water	>181

Hard water may cause scaling i.e. mineral buildup, in pipes, pump, measurement head windows and the dilution tank. Water hardness can also be informed as degree of hardness, dH. The conversion of dH to $CaCO_3$ can be done using Equation 1.

$$\mathrm{ppm} = \mathrm{dH} * 17.85 \qquad \text{Equation 1.}$$

The water quality for PSI analyzer should ideally be <120 mg/L. 121-180 mg/L may be tolerated, but > 181 mg/L should be avoided.

Turbidity

Water turbidity is the measurement of the cloudiness of the water caused by suspended particles and/or micro-organisms. The water turbidity unit is NTU which describes the light scattered by suspended particles in water. Turbidity is related to the TSS value and can be used if TSS value is not available. The NTU value of the water should not exceed 10 NTU.

Salinity and Total Dissolved Solids

Salinity is the presence of dissolved salts in the water, which can also be described as the total dissolved solids (TDS) value. Dissolved salts may change the water diffraction properties and may affect the analyzer measurement if not consistent. If salinity content of the water is constant it can usually be removed by the light background measurement. The TDS is usually reported as mg/L or ppm, and usually contains all ions dissolved in the water and is different from water hardness. The value of TDS should be less than 1000 mg/L.

Water Conductivity

Water conductivity can be used as an indicator of the water hardness and/or the TDS, if the information is not available. Water conductivity may also promote the agglomeration of particles in the water, which could result in erroneous PSD results by the analyzer.

The conductivity of water increases with increasing dissolved ions in the water. The unit for conductivity is typically µS/cm or mS/cm. Values > 1500 µS/cm can be considered as elevated conductivity and would require hardness and/or TDS testing.

Appendix 2. Mine process water particle concentrations

	Flotation water	Process water	Plant water	Flotation water	Process water	Process water	AMD	Gold (process water)	Phosphate (effluent)	Phosphate (effluent)
pH	7.09	9.5	7.8	11.14	-	-	3.91	9.9	7.45	7.61
Temperature [C]	-	15.5	-	-	-	-	14.1	33.35	27.12	-
TSS [mg/l]	43693	-	15	-	-	-	-	141500	1525	-
Turbidity [NTU]	977	58	-	-	-	-	-	16250	-	-
Water hardness [$CaCO_3$mg/l]	-	839.1	-	855.6	778.1	1882.9	1665.0	-	512.0	678.1
Ferro content [mg/l]	115.2	7.5	-	-	-	-	730.4	4.2	-	0.01
TDS [mg/l]	130.6	-	-	-	3690	5517	3763.5	2290	4149	-
Conductivity [µS/cm]	178.3	2310.833	-	2200	-	-	2490	4565	3724	1610.685
Year	2020	2023	2019	2018	2020	2020	2009	2010	2012	2002
Source	Das & Nandi 2020	Aaltonen et al. 2023	Lin et al 2019	Retka et al. 2020	Le et al. 2020	Le et al. 2020	Kupka et al. 2012	Acheampong et al. 2013	Al-Hwaiti et al. 2016	jiries et al .2004

Appendix 3. Water risk filter indicators

https://cdn.kettufy.io/prod-fra-1.kettufy.io/documents/riskfilter.org/WaterRiskFilter_Methodology.pdf

Risk type	Risk category	Indicator *
BPH - PHYSICAL	BRC1 - Water Scarcity	B1_0 - Aridity Index B1_1 - Water Depletion B1_2 - Baseline Water Stress B1_3 - Blue Water Scarcity B1_4 - Available Water Remaining (AWARE) B1_5 - Drought Frequency Probability B1_6 - Projected Change in Drought Occurrence
	BRC2 - Flooding	B2_1 - Estimated Flood Occurrence B2_2 - Projected Change in Flood Occurrence
	BRC3 - Water Quality	B3_1 - Surface Water Quality Index B3_1_1 - *Biological Oxygen Demand (BOD)* B3_1_2 - *Electrical Conductivity (EC)* B3_1_3 - *Nitrogen (N)*
	BRC4 - Ecosystem Services Status	B4_1 - Fragmentation Status of Rivers B4_2 - Catchment Ecosystem Services Degradation Level B4_3 - Projected Impacts on Freshwater Biodiversity
BRG - REGULATORY	BRC5 - Enabling Environment	B5_1 - Freshwater Policy Status (SDG 6.5.1) B5_2 - Freshwater Law Status (SDG 6.5.1) B5_3 - Implementation Status of Water Management Plans (SDG 6.5.1)
	BRC6 - Institutions & Governance	B6_1 - Corruption Perceptions Index B6_2 - Freedom in the World Index B6_3 - Private Sector Participation in Water Management (SDG 6.5.1)
	BRC7 - Management Instruments	B7_1 - Management Instruments for Water Management (SDG 6.5.1) B7_2 - Groundwater Monitoring Data Availability and Management B7_3 - Density of Runoff Monitoring Stations
	BRC8 - Infrastructure & Finance	B8_1 - Access to Safe Drinking Water B8_2 - Access to Sanitation B8_3 - Financing for Water Resource Development and Management (SDG 6.5.1)
BRP - REPUTATIONAL	BRC9 - Cultural Importance	B9_1 - Cultural Diversity
	BRC10 - Biodiversity Importance	B10_1 - Freshwater Endemism B10_2 – Freshwater Biodiversity Richness
	BRC11 - Media Scrutiny	B11_1 – National Media Coverage B11_2 – Global Media Coverage
	BRC12 - Conflict	B12_1 - Conflict News Events B12_2 - Hydro-political Likelihood

Appendix 4. Water consumption values in PCAM.

Mineral	**Functional unit**	**Water consumption [m3]**	**Source**
Cobalt	1t of cobalt	258	Farjan et al. 2019
Cobalt	**1t of cobalt sulfate**	**104.1**	**Zhang et al. 2020**
Cobalt	1t of cobalt concentrate	208.4	Meißner 2021
Nickel	1t of nickel metal	193.8	Meißner 2021
Nickel	**1t of nickel sulphate**	**175**	**Dry et al. 2019**
Nickel (hydrometallurgy)	1t of nickel metal	303	Northey et al. 2014
Nickel (pyrometallurgy)	1t of nickel metal	67.6	Northey et al. 2014
Manganese	1t of manganese concentrate	1.4	Meißner 2021
Manganese	1t of SiMn	12.9	Westfall et al. 2016
Manganese	**1t of HC FeMn**	**8.8**	**Westfall et al. 2016**
Manganese	1t of ref. FeMn	13	Westfall et al. 2016
NH3 steam	1t NH3	0.658	Ghavam et al. 2021
NH3 electrolysis	1t NH3	1.588	Ghavam et al. 2021
NH3 (25%)	**1t NH3**	**1.147**	**Ghavam et al. 2021**
NaOH	1t NaOH	2.4	Hong et al. 2014
NaOH	1 t NaOH	5.98	Hong et al. 2014

<u>NaOH (50 %)</u>	**<u>1 t NaOH (50 %)</u>**	**<u>1</u>**	**<u>European Comission 2014</u>**
NaOH (25 %)	1 t NaOH (25 %)	1.2	European Comission 2014
<u>H2SO4 (98 %)</u>	**<u>1 t H2SO4 (98 %)</u>**	**<u>350</u>**	**<u>Aderiran et al. 2017</u>**
N2	-	-	Lewis & Lebrecht 2018
HNO3 (100 %)	1 t HNO3 (98 %)	0.86052	Alhasan et al. 2023
HNO3 (5 %)	1 t HNO3 (5 %)	0.993026	Alhasan et al. 2023

<u>Bolded and underlined</u> values are used in calculating pCAM water consumption.

Appendix 5. AWARE and WRF data used.

	https://wulca-waterlca.org/aware/download-aware-factors/															
	Sub-national region	Country	Aware_Jan_region	Aware_Feb_region	Aware_Mar_region	Aware_apr_region	Aware_May_region	Aware_Jun_region	Aware_Jul_region	Aware_Aug_region	Aware_Sep_region	Aware_Oct_region	Aware_Nov_region	Aware_Dec_region	Aware_agri_region	Aware_nonIrri_region	Aware_unknown_region
AUS.11_1	Western Australia	Australia	10,62	12,22	8,38	10,31	44,02	6,51	6,89	11,6	16,74	12,76	11,38	13,5	13,32	10,38	12,88
CHL.5_1	Atacama	Chile	99,98	99,98	99,97	99,96	92,06	7,32	8,26	8,15	20,77	43,9	78,52	99,99	96,6	64,36	95,48
FIN.5_1	Western Finland	Finland, Western Finland	1,51	1,81	1,24	0,7	0,8	1,26	1,9	2,17	2,26	1,48	1,15	1,15	1,6	1,5	1,53
	https://riskfilter.org/water/explore/data-and-methods															
Adm1 Risk 2021			Basin Physical Risk	1. Water Scarcity	2. Flooding	3. Water Quality	4. Ecosystem Services Status	Basin Regulatory Risk	5. Enabling Environment	6. Institutions & Governance	7. Management Instruments	8. Infrastructure & Finance	Basin Reputational Risk	9. Cultural Importance	10. Biodiversity Importance	11. Media Scrutiny	12. Conflict
427	Atacama	Chile, Atacama	3,04	3,41	2,95	0	1,91	2,88	4,35	2	3,14	1,3	2,43	1	1,44	2,55	3,39
5663	Western Australia	Australia, Westren Australia	2,62	2,96	2,08	3,3	1,38	1,21	1	1,5	1,26	1	4	5	1,91	4,55	3,45
4665	Satakunta	Finland, Satakunta	2,02	1,86	1,02	3,29	2,46	1,27	1	1,25	1,7	1,1	2,09	1	2,5	2,1	2,52