D2.5

Close loop recycling strategies and alternative water sources for the P&P Industry

June 8th, 2018

Deliverable Leader: CTP

1. - Table of Contents

List of Tables

List of Figures

Glossary

CDI	Capacitive Deionization
COD	Chemical Oxygen Demand
CPAM	Cationic PolyAcrylAmide
DAF	Dissolved Air Flotation
DIP	Deinked Pulp
EDI	Electro Delonization
EPS	Elevated Pressure Sonication
HP	High Pressure
OCC	Old Corrugated Cardboard
PM (or PK)	Paper Machine
TSS	Total Suspended Solids
RO	Reverse Osmosis
UF	Ultrafiltration
VFA	Volatile Fatty Acid
WSR	Wet Strength Resin
WW	White Water
WWTP	Waste Water Treatment Plant

Contributions

No	Partners	Name
1	**CTP**	Stéphanie PRASSE, Patrick HUBER, Eric FOUREST
5	**SERE**	Narinder BAINS, Sugat RAYMAHASAY
6	**XC**	Juha TIKKANEN
9	**EL**	Serge ANDRES
10	**VAL**	Pasi NURMINEN, Timo SUTELA
11	**BFI**	Martin HUBRICH, Matthias KOZARISZCZUK
14	**VTT**	Pauliina TUKIAINEN, Antti GRÖNROOS
15	**SCA**	Jenni VAINIO

2. - Introduction

2.1. - Objectives

This report presents the results achieved from M1 to M20 in the subtask *T.2.3.2. Close loop recycling strategy for the pulp and paper industry (**CTP**, EL, KL, VTT, VAL, SCA).*

The scope of Task 2.3 was to examine opportunities for developing closed-loop recycling practices in paper production processes and the required technologies that should be employed to achieve sustainable water recycling. Furthermore, alternative water sources, including treated wastewater effluents will be assessed together with the requisite technologies for advanced wastewater treatment.

Subtask 2.3.2 was dedicated more specifically to the Paper industry, with the selection and testing in realistic environment of water treatment technologies (ultrafiltration, deionization, EPS) to reduce fresh water usage in papermaking processes.

This was planned through the following:

- Potential of WWTP effluent and process water re-use in place of fresh water will be then defined according to the results obtained in T2.1. (water streams characterization and quality requirements)
- Determination of the main sources of salts and contribution of each source to the salinity build up,
- Evaluation through laboratory trials the limit value that a process can accept in term of ions content and to define the treatment level to apply.
- Evaluation of Capacitive Deionization technology at laboratory scale for the reduction of WWTP effluent salinity.
- Compare the performance of Ultrafiltration, Biocontrol concept and Elevated Pressure Sonication to control bacterial activity of bio-treated effluent at laboratory trial.

2.2. - Work progress and achievement

Baseline scenarios for specific water usages and requirements were investigated by VTT and CTP through several sampling and measurement campaigns in two paper mills from the consortium partners: Essity Nokia (Finland) producing sanitary paper from deinked pulp; Emin Leydier Nogent-sur-Seine (France) producing light packaging paper from recovered fibres. Detailed pulp and water circuits flowsheets were built and water balance were characterized (volumes, TSS, COD, conductivity, total bacterial flora…) for further simulation of optimization scenario.

The sources of water salinity for pulp and paper production was deeply investigated by CTP on the basis of fresh water, raw materials and process additives data obtained from 36 EU industrial sites producing various paper grades. Process water salinity and conductivity build-up was modelled, taking into account calcium dissolution and precipitation tendencies. The effect of salinity on process additives performance (retention aids, wet strength resin, DAF flocculants) was investigated by CTP at laboratory scale.

Several strategies and technologies for reusing process water or effluents and reducing fresh water volumes were investigated. Laboratory and pilot scale Ultrafiltration trials were performed by Valmet to treat white waters and reuse clarified water on paper machine showers instead of fresh water.

CTP also examined the possibility and limitation to reuse treated effluent from existing WWTP to replace fresh water in the process. Tertiary treatment technologies to removed

refractory compounds and inorganic salts were proposed. Capacitive deionization trials were performed by BFI at laboratory scale to achieve salinity reduction objectives.

The performance of ultrafiltration, Biocontrol concept and Elevated sonication were compared at laboratory scale by VTT, XC and SERE to control bacterial activity in bio-treated effluent.

Finally, water recycling strategies and their effect on process runnability are proposed. These strategies will be evaluated by simulation during WP3.

3. - Characterization of water streams and quality from selected paper mills

3.1. - Tissue mill: Essity Finland, Nokia (FI) (former SCA)

Essity Finland (former SCA) operates a tissue mill in Nokia, Finland. A deinking plant (DIP) produces about a half of the fibre raw material needed. The other half is purchased virgin pulp. Two paper machines (PM7 and PM9) produce tissue base paper for own converting lines and external customers. Base papers are converted into toilet tissue, kitchen towel, hand towels, hankies, wipers for consumer market and away-from-home customers.

Mill water loops are not closed and integration level between papermaking and deinking is fairly low. This is due to the internal infrastructure where deinking is located relatively far from papermaking as it was originally build in the mid 80's for a former pulp mill located on the other side of the site. There is one deinking line feeding both paper machines. DIP production runs two different DIP pulp qualities, U1 and U3, which main difference is brightness. U1 is brighter and mainly produced using higher recycled paper qualities such as pre-consumer waste paper grades from printing houses and offices. U3 is greyer in brightness and mainly made of household waste paper. Different DIP pulp grades are stored in 2500 m^3 storage towers. Storage time for DIP pulp can be up to four days. DIP pulp is pumped to the paper machines from DIP storage towers, which are approx. 400 m away from the paper machines' wet end. The long pumping distance requires a significant amount of water. Water storage capacity is low and circulated carrier water from the paper machines is typically not enough to meet the need of water. When carrier water is not available, fresh water is widely used to cover the water need.

Essity Nokia mill has established a water reduction program, which will reduce the water consumption at first from 45 m^3/t produced paper (2016 average) down to 25 m^3/t produced paper. Water reduction will be executed gradually. The mill has identified the following water reduction actions to reduce water consumption down to 20 m^3/t:

1. Increase PM7 white water storage capacity by modifying existing broke chest for white water to enable higher white water usage in pulping and DIP.

2. PM7 & PM9 showers to white water instead of fresh water.

3. PM9 dust removal repair and change to white water instead of fresh water.

4. PM7 dust washers, converting dust washers and converting Nash water to white water instead of fresh water.

5. Collect and utilize fresh and white water in DIP cooling, PM7 dust washers, PM condensate cooling, converting dust washers and Nash pumps.

6. DIP white water system improvements.

7. PM7 control system improvement and update.

8. Wastewater treatment plant (WWTP) modifications to operate with lower waste water amount and stricter discharge limits.

9. Renewal of the fresh water pumping station and fresh water treatment as the current pumping station is outdated. Renewal brings reliability and water quality (i.e. product quality) risks.

The mill has completed the reduction steps 4, 5 and 6 in early 2018. White water running on PM7 showers (step 2) has been trialled earlier but it was not successful. In the SpotView project step 2 will be trialled again by using ultra-filtered white water in PM showers instead of fresh water.

3.1.1. - Essity Nokia mill water balance

Fresh water is used in all production processes from deinking to papermaking and converting, for details see Figure 1. The latest water reduction actions aim at reducing fresh water use by collecting white water to be used in deinking instead of fresh water. This required more white water storage capacity, water loop changes in deinking and automation to control the water balance. Fresh water still needs to be used as a back-up in deinking.
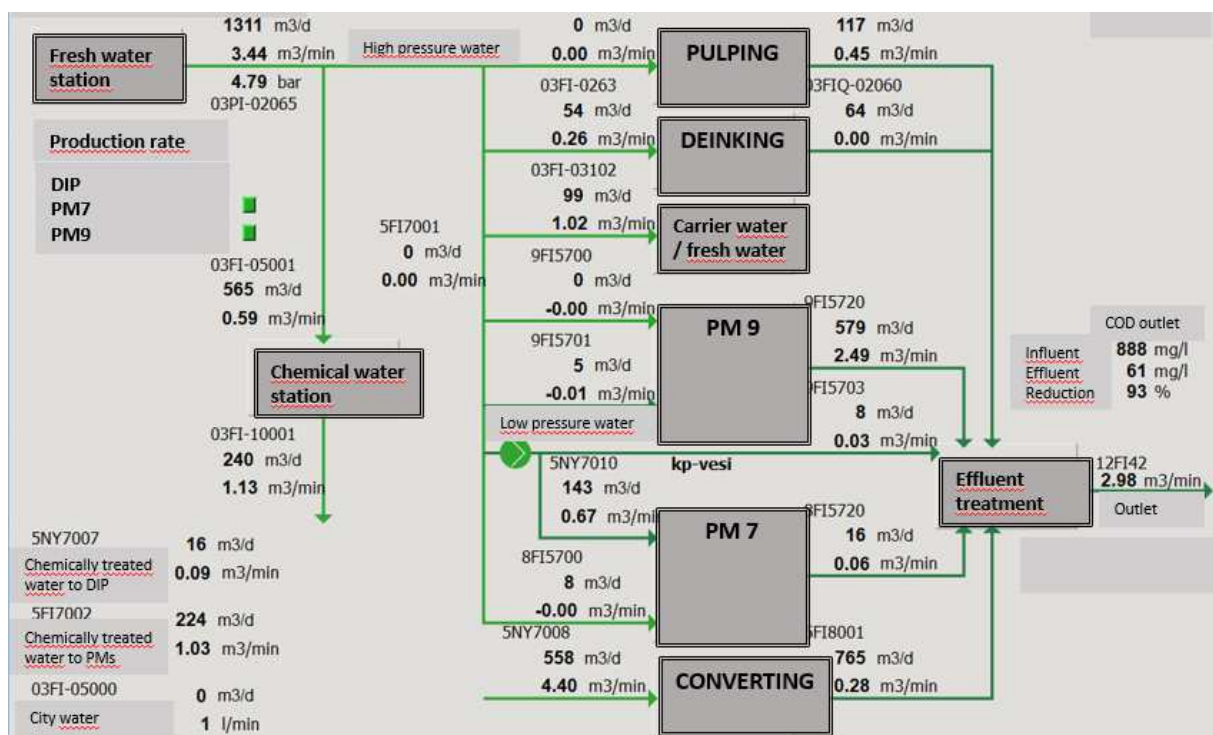
Figure 1: Essity Nokia Mill water use.

Mill water usage has to be split into a more precise water balance to understand where the highest water consumption points are. This helps in identifying water reduction needs and understanding how changes in one part of the process will affect other parts of the process. Mill water usage has been preliminary measured/estimated in August 2016 in order to define how closing of water loops will affect the water balance, see Figure 2. In SpotView WP3 mill water usage will be analysed and modelled more deeply. Better understanding of the water loops will reduce risk of adverse impacts.
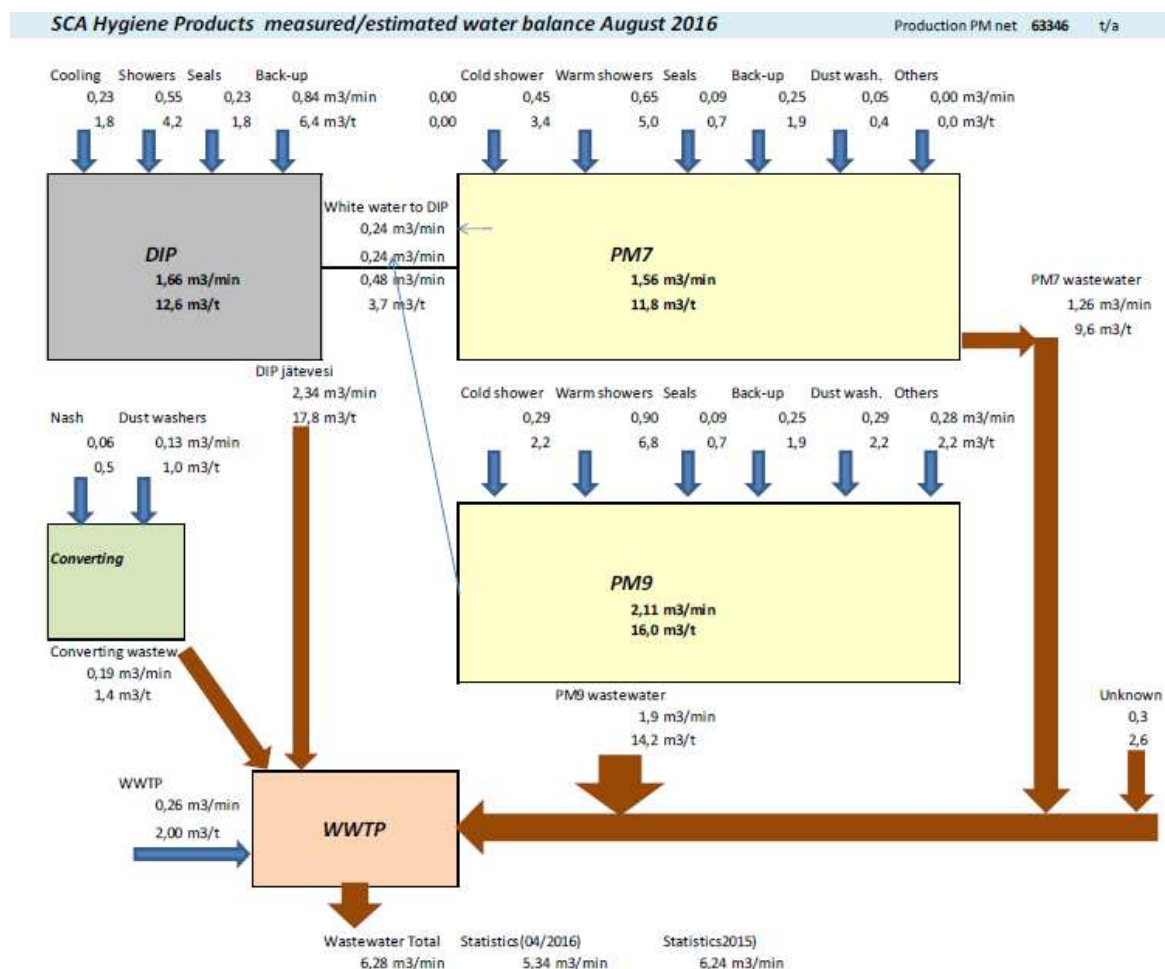
Figure 2: Essity Nokia mill water balance 2016.

3.1.2. - Essity Nokia mill fresh water and process water circuits

In September 2017, an updating of fresh water and process waters flow sheets has been realized. Two types of fresh water quality are used in the mill. The first quality (disinfection treatment) is used in DIP and virgin fibres preparations and paper machines and for sealing water. The second quality (flocculation treatment), with less TSS, is used where a better water quality is needed: chemicals preparation and paper machines showers. The fresh water consumption is 44.3 m^3/t. The details of the fresh water consumption are given in the Table 1 and Figure 3.

Table 1

Fresh water consumption details	Flow (m^3/h)	Flow (m^3/t)
DIP preparation	88	9.2
PMs	185.8	11.8
Sealing water (DIP and PMs)	2.3	0.2
Chemicals preparation	78	8.2
HP waters WWTP	10.2	1.1
Converting	0.6	0.1
Other	9.9	0.2
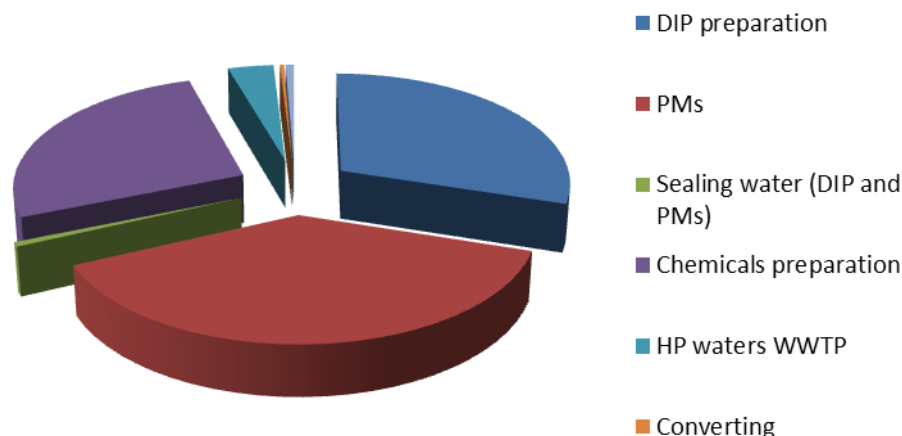
Figure 3: Fresh water consumption details

Concerning the DIP and stock preparation, the wash water from the first loop are treated in a dissolved air flotation system and reused as dilution water in this first loop. The wash waters from the second DIP loop are not treated. They are mix with the treated wash waters from the first DIP loop. Just before the storage in four towers, pulp is thickened in a screw press. The obtained filtrates are reused upstream, just before the bleaching tower. Finally the strictly loops separation of DIP and stock preparation process waters is well respected and the process waters circulate at counter current, what respects the water management best practices.

Concerning the PMs waters, PM7 white waters are treated in a polydisk. The clear and super clear filtrates are not separated. The filtrates are used to dilute pulp of PMs. The PM9 white waters are treated by dissolved air flotation and the filtrates are reused as dilution water at PMs level. As for process waters from DIP, filtrates from PMs waters are reintroduced in the process at counter current.

Waste water treatment plant is feed with DIP, PM7 and PM9 effluents. The effluents are firstly treated by a primary clarifier and then by activated sludge. The bio-treated waters are rejected in the river.

3.1.3. - Water characterization

Mill water characterization at Essity Nokia mill in SpotView started by adding online measurements in paper making for pH, redox and conductivity measurements. Sampling rounds were arranged in order to characterize chemical and microbial state in different parts of the water circulation. Large number of sampling points were covered in the sampling rounds. Sampling rounds took place in March, May and September 2017. Sampling rounds reflected different tissue base paper qualities and circumstances where paper machines were running 100 % recycled base paper, 100 % virgin pulp base paper and mixed base paper recipes with recycled and virgin pulp.

Results of the sampling rounds indicated that influent coming to the effluent treatment plant from different sub-processes like from papermachines has fairly big variation for example in total COD load (organics) and conductivity (salinity). It was found, that the biggest source of the total COD was DIP, even the variation of COD was the lowest.

COD results:

- Effluent into waste water treatment plant CODtot 770 →1600 mg/l

- PM9 effluent CODtot 640 →1400 mg/l

- Deinking primary clarifier feed 2800 → 3000 mg/l

- Deinking primary clarifier clarified water 1100 → 1500 mg/l

In the

Figure 4 it is shown the COD load from different sub-processes calculated using analysis results obtained during sampling period carried out in May 2017. As can be seen, the COD load to effluent treatment came mainly from DIP either via paper machines or straight. Only minor part of the COD load came from pulp/broke handling.
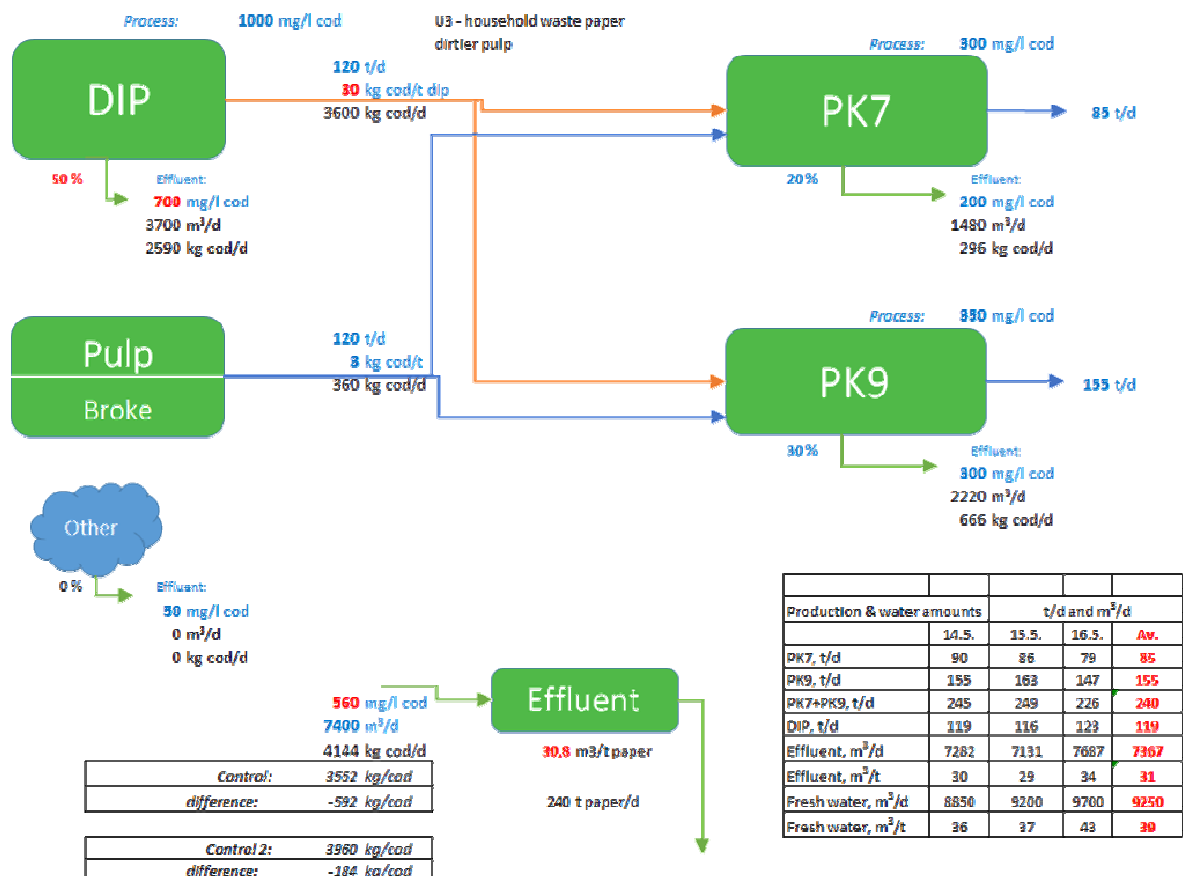
Figure 4: COD load from different sub-processes 15.-17.5.2017.

In the case of conductivity the biggest values as well as the biggest variations were observed in DIP.

Conductivity results:

- Effluent into waste water treatment plant 68.5 → 80.2 mS/m

- DIP pulp storage towers 39.2 → 106.6 mS/m

- PM7 effluent 27.5 → 49.9 mS/m

- PM9 effluent 23.9 → 54.5 mS/m

Analysis results pointed out the sources of COD and salinity (measured as conductivity) from different sub-processes and this will help in modelling and assessing the impact of future water reductions. Together with COD and salinity, also microbiology will be affected in water reduction activities and it will have a big impact on tissue quality, runnability, efficiency etc. Tissue is sensitive with regard to odour. Thanks to high volume of fresh water usage, Essity Nokia mill has no issues with odour in tissue but when closing the water loops it's likely to have odour issues in tissue if not controlled.

Different DIP pulp grades are stored in 2500 m^3 storage towers. Storage time for DIP pulp can be up to four days. Microbial growth in broke towers decreases the amount of dissolved oxygen in the broke tower and the environment becomes anaerobic. The growth of acid-producing anaerobic bacteria results in a drop in pH as a consequence of volatile fatty acids being formed under anaerobic conditions. The broke tower is a possible reservoir for spore-forming bacteria. By monitoring pH and redox it's possible to detect conditions that may lead to odour issues in tissue. Microbiology related risk for product quality could be reduced by reducing storage time in broke towers.

Water characterization verified also, which water fractions could be used as feed water to Valmet Ultrafiltration. Valmet Ultrafiltration is being installed to generate high pressure shower water for PM wire section. This installation will allow Essity Nokia to use circulated water instead of fresh water and reduce their fresh water consumption.

3.2. - Packaging mill: Emin Leydier Nogent (FR) (CTP, EL)

Emin Leydier, with two production sites (Nogent and Champblain), produces 750 000 t of containerboard from 90 to 210 g/m² for corrugated packaging, annually. The paper mill in Nogent has one paper machine producing light weight board from recovered papers.

3.2.1. - Fresh water and process water circuits

The fresh water is treated by a biocide to prevent microbiological growth. Their different uses are presented in Table 2 and *Figure 5*. The total specific fresh consumption is 7 m^3/t.

Table 2

Fresh water consumption details	Flow (m^3/h)	Flow (m^3/t)
Sealing water	16,4	0,41
Chemicals preparation	40,4	1,01
PM showers	133,1	3,33
Others	9,6	0,24
Addition in process waters	13,8	0,35
Boiler	13,1	0,33
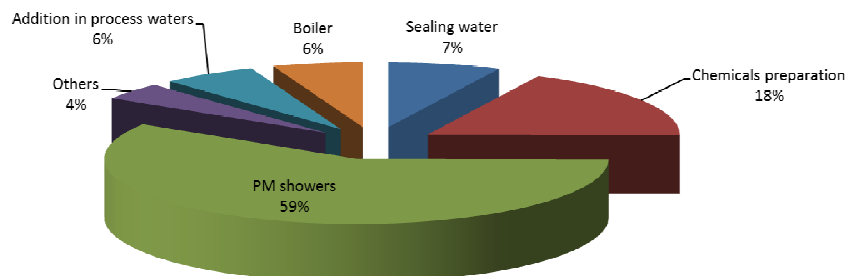
Figure 5: Fresh water consumption

3.2.2. - Stock preparation

Recovered papers bales are slushed to pulp in a continuous drum pulper and after several and sharp screening steps to remove plastics, sands, glues…, pulp is split in two main flows to produce short fibres and long fibres before being thickened up and stored at high consistency in two chests supplying the PM. The filtration water produced by the final thickening step is reintroduced upstream in the stock preparation loops as a counter-current washing flow, before being send at the end to the effluent treatment plant.

3.2.3. - Paper machine

On PM side, short and long fibres pulps are highly diluted with drainage water from the forming section and then pumped under pressure into the head box nozzles of the PM.

Paper sheet is formed by dewatering highly diluted pulp on continuous sieve belts. Drainage water, called "white waters 1", is re-introduced upstream to dilute high consistency pulp from

the pulp chests at the end of the stock preparation plant. The excess water called "white waters 2" is filtered as "clear filtrates" and "super clear filtrates". "Clear filtrates" are re-introduced at the PM level and upstream at different points in pulp preparation. The water management best practices, i.e. loop separation and counter-current circulation, are applied in Emin Leydier Nogent paper mill. "Super-clear filtrates" was tentatively used at PM showers, but as a consequence of frequent plugging of the nozzles, ground water or cooling water is currently used.

3.2.4. - Water characterization

The process waters have been characterised according to the following analysis: pH, temperature, redox, conductivity, chemical oxygen demand (COD), volatile fatty acids (VFA), chlorides, sulphates, bromides, calcium, magnesium, silicon, iron, potassium, sodium, aluminium, inorganic carbon and carbonates.

Concerning the physico-chemical measures, temperature varies around 35°C in the process waters. Fresh water temperature is at 15°C and the outlet effluent is at 20°C. The measures were realised in May 2017 which was a hot month this year. The COD, conductivity, pH and redox are presented *Figure 6*, *Figure 7* and *Figure 8*.

COD (*Figure 6*) in pulp circuits is around 5500 mg/L and in the PM circuits at around 4500 mg/L (as a consequence of loop separation and counter-current management). The COD come mostly from the pulping of recovered papers. The decrease of COD between the pulp circuits and the PM circuits is relatively weak, ratio 1.2, this ratio characterises the efficiency of the loop separation. For a good efficiency, it is 2. In this case the loop separation is not very efficient. A very weak COD value (40 mg/L) in the PM showers tank is observed. The explanation is that the PM showers tank is filled with fresh water. The COD decrease in the waste water treatment plant is 97.5 %. Conductivity (*Figure 7*) in pulp and PM circuits is around 3 mS/cm. The fresh water conductivity is at 407 µS/cm. As observed for the COD, the PM showers tank has a very low conductivity, 424 µS/cm. This conductivity is the one of fresh water. Conductivity decreases strongly in the outlet effluent after aerobic treatment. This is probably due to the strong decrease of calcium ion, from 400 mg/L to 130 mg/L (*Figure 10*) at the same step. The pH of fresh water is at 7.8 and the redox potential at 300 mV (*Figure 7*) which represent aerobic conditions. pH and redox potential of process waters are respectively around 6.5 and −150 mV which confers an anaerobic environment for micro-organisms and then induce VFA production (*Figure 11*). In the anaerobic treatment, reducing conditions that are essential for methane production are well respected (pH = 5, redox potential = -350 mV). VFA are very high in the process waters (1500 mg/L). They contribute to the acidification of the process waters and the high conductivity level (*Figure 12*). VFA have also an indirect impact on calcium and carbonates precipitation or dissolution due to their influence on pH (*Figure 9* and *Figure 10*). Due to the use of recovered papers as raw material, calcium reload is important in OCC paper mills, in Emin Leydier paper mill dissolved calcium concentration is at around 400 mg/L. According to the physico-chemical conditions at different points in the paper mill (pH, temperature, total suspended solid) the risk of scaling is high. Concerning the other ionic species, potassium, magnesium, aluminium, iron and silicon, they are minor with a concentration inferior at 35 mg/L. Sulphates, sodium and chlorides concentrations vary from 80 to 170 mg/L.

Finally, process waters of Emin Leydier paper mill in Nogent favour VFA production which can indirectly cause corrosion and scaling at special points in the circuits (i.e. where CO_2 is stripped, like the back of vacuum foils). The major ionic species contributing to conductivity are VFA and calcium. A CTP previous study (Scale2) has demonstrated that reintroduction of treated waters by WWTP can reduce VFA production and buffer the pH. The next step (WP3, T3.4) will test different WWTP effluent reuse based on simulation. The model has been built thanks to the waters characterisation of this task.
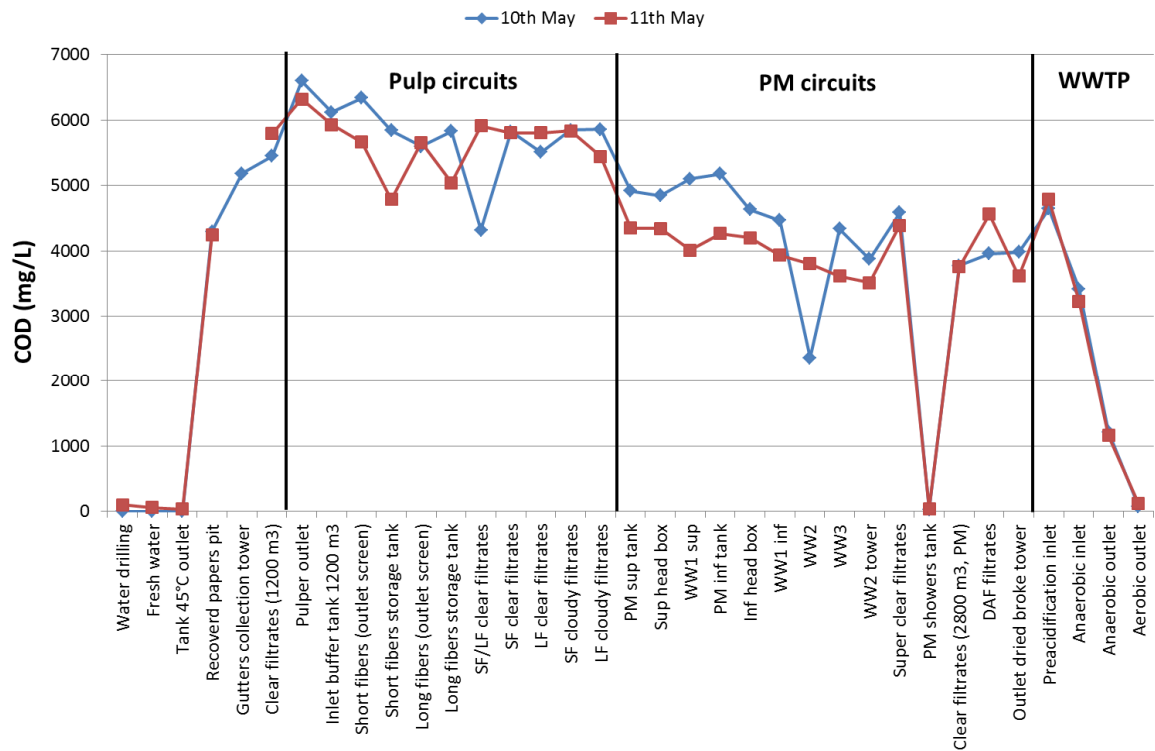
Figure 6: COD in process waters
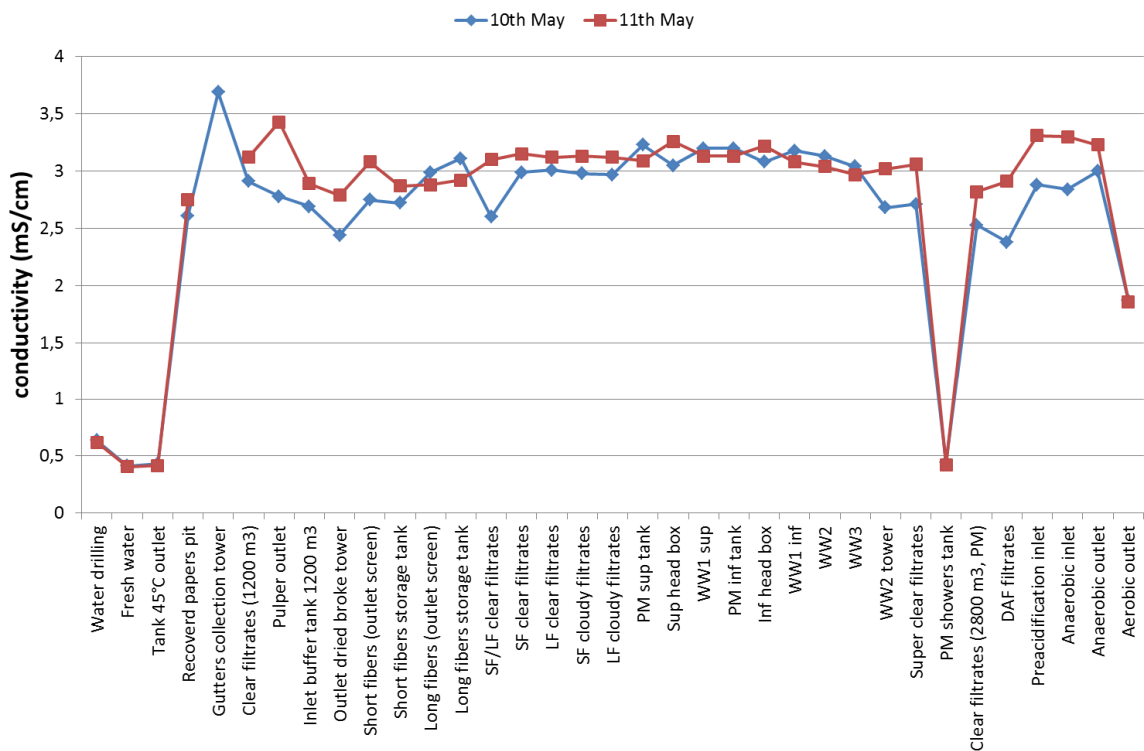
Figure 7: Conductivity in process waters
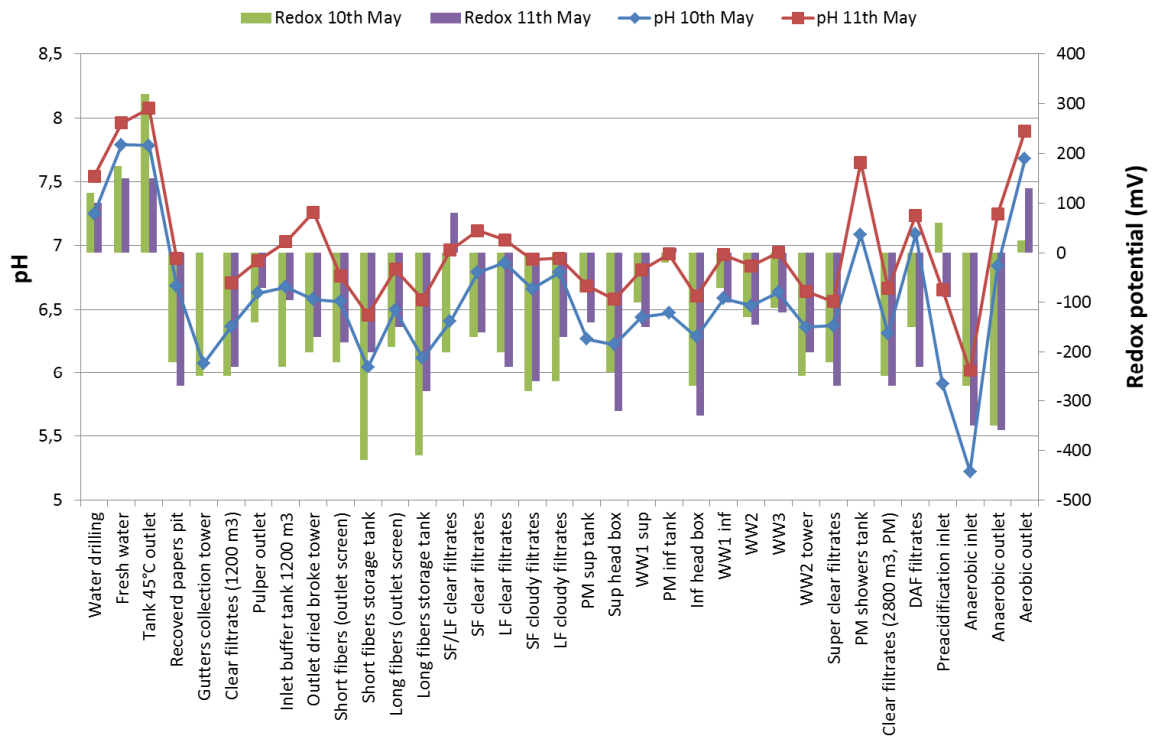
Figure 8: pH and redox potential in process waters
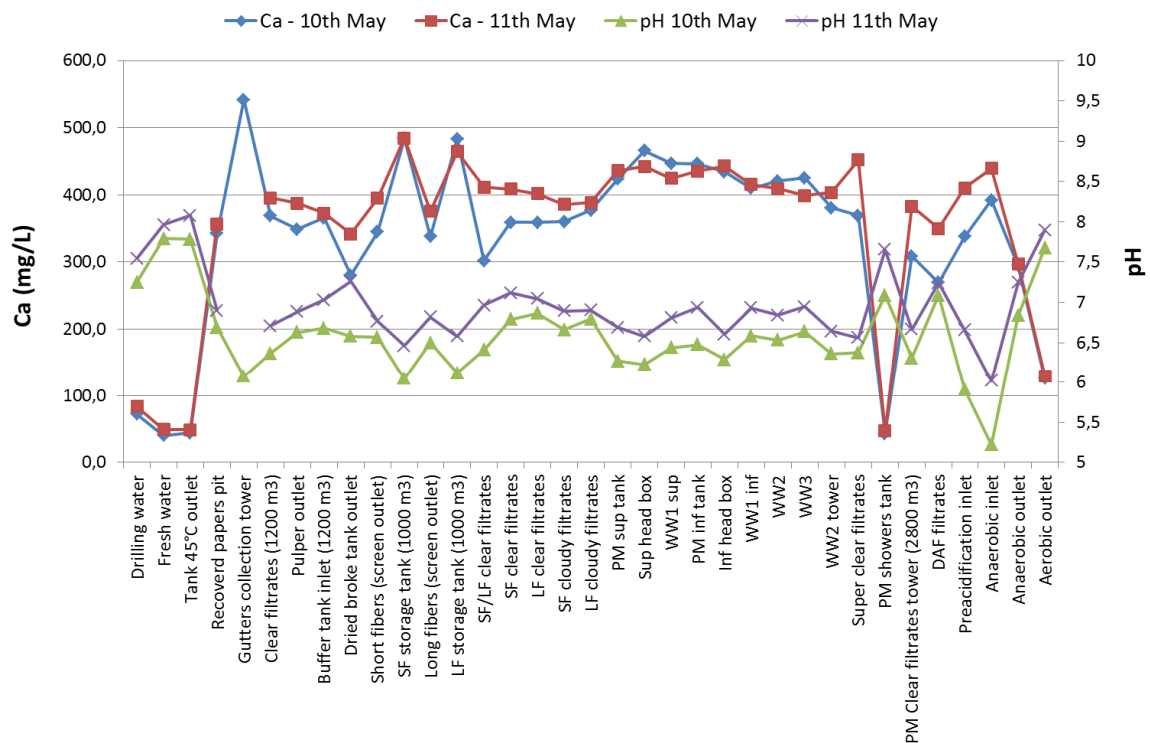
Figure 9: Dissolved calcium and pH relations in process waters
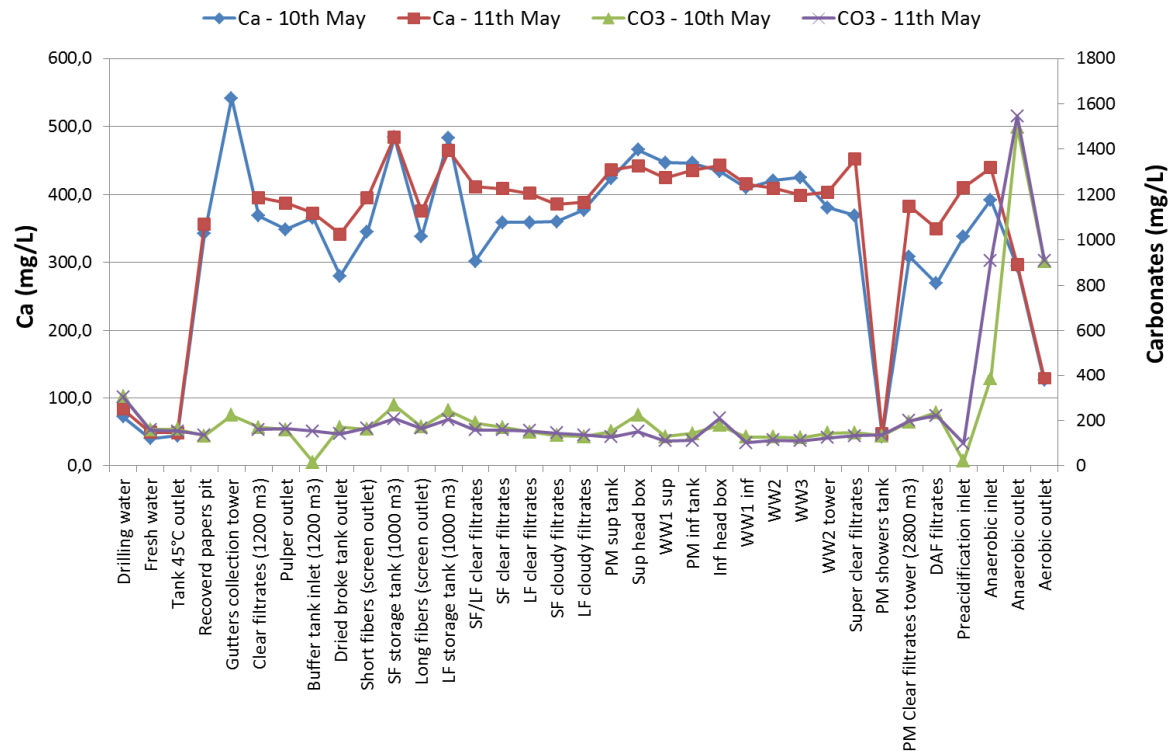
Figure 10: Calcium and carbonates concentrations in process waters
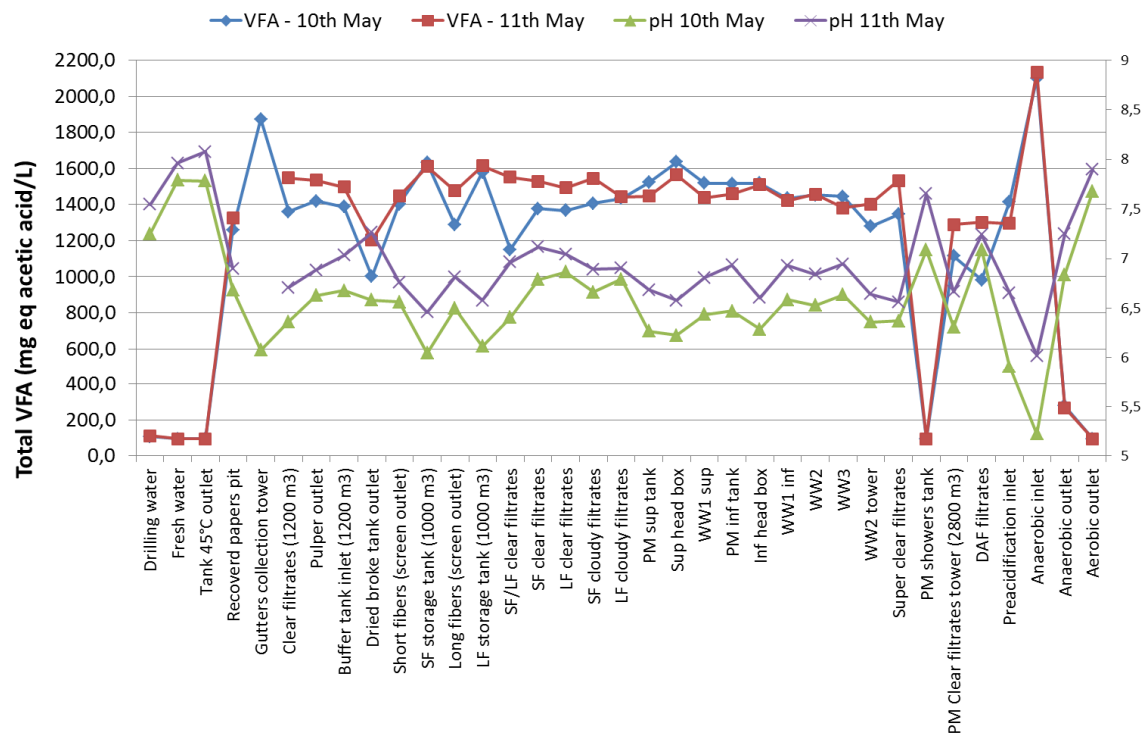
Figure 11: VFA concentrations and pH relation in process waters
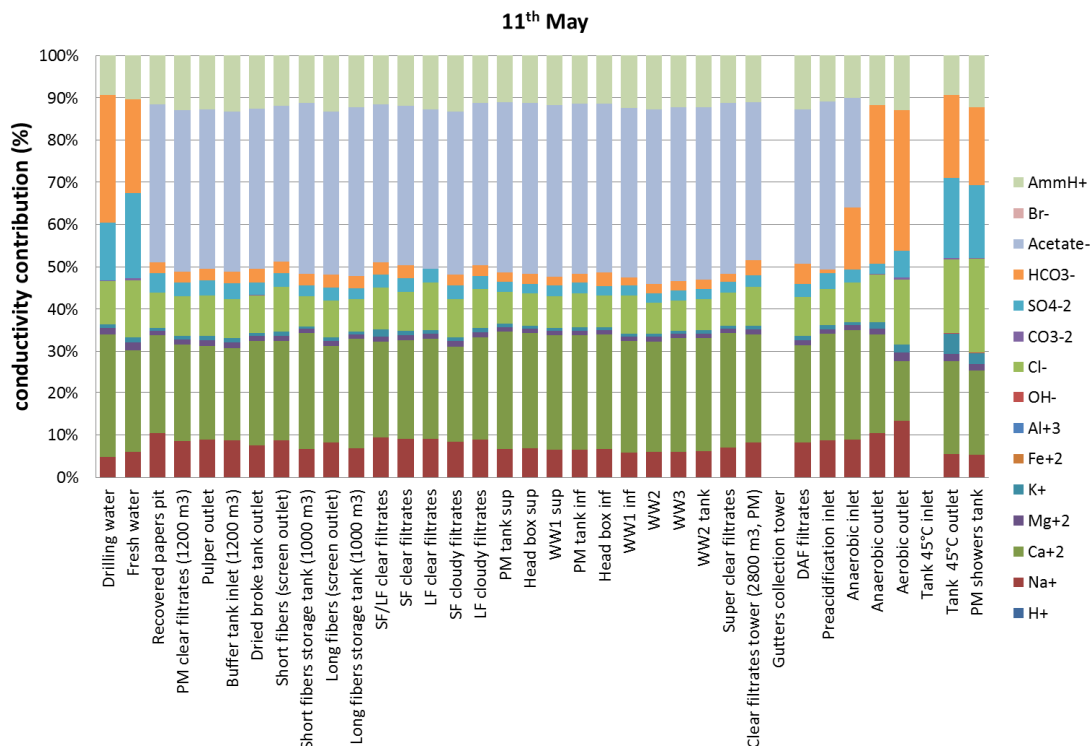
Figure 12: Conductivity contribution of measured ionic species

4. - Origin and consequences of water conductivity build-up

4.1. - Determination of the main sources of salinity

Inorganic substances come from raw material, feed fresh water or chemical additives, but also from phenomena in process water due to anaerobic bacteria activity. Indeed in lack of oxygen, some bacteria produce VFA which cause acidification of process water, calcium dissolution and in favourable conditions, scaling.

The aim of the task is to determine the relative contributions of each source.

4.1.1. - Contribution of raw material

Various raw materials (Table 3) were pulped in deionized water at laboratory scale to determine their contribution to process water salinity.

Pulped raw materials	
Virgin pulp	Unbleached Kraft pulp
	Bleached Kraft pulp (softwood)
	Bleached Kraft pulp (hardwood)
	Market CTMP (softwood)
	Newspaper 1 (100% TMP)
DIP	Market deinking pulp 1
	Market deinking pulp 2
Recovered papers	Newspaper 2 (100% DIP)

| | Corrugated board |
| | Corrugated paper |

Table 3: Tested raw materials

At the end of pulping, samples were collected. The following analyses were done:

- On pulp fraction: mineral content – $CaCO_3$ content
- On water fraction: COD, pH, conductivity, chloride (Cl), sulphate (SO_4), calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), silica (Si), aluminium (Al), iron (Fe), inorganic carbon, Volatile Fatty Acid (VFA).

The analyses on water fraction show that paper produced from recovered fibres releases more conductivity (5 to 6 (µS/cm) / (g of paper/L)) than those produced from bleached Kraft pulp (1 (µS/cm) / (g of pulp/L)) (*Figure 13*). According to the ionic species analyses, it seems that sodium, calcium and sulphate are the main ions to increase conductivity. These three ions are also the most concentrated ions in recovered papers (*Figure 14*). Potassium and chloride are part of major ions but in a lower proportion compared to calcium, sulphate and sodium. Any specific major ions seem to contribute to conductivity in unbleached and bleached Kraft pulp. The minor ions species are silica, aluminium, iron and inorganic carbon (*Figure 15*). Concerning the VFA, they are present in low quantities (< 2.5 mg eq acetate/ g of paper, *Figure 16*) or absent in raw materials. Recovered papers contain the most important concentrations of VFA (2.5 mg eq acetate/ g of paper), followed by deinking pulp (2.5 mg eq acetate/ g of paper (around 1 mg eq acetate/ g of paper) and Kraft and CTMP pulps (> 0.5 mg eq acetate/ g of paper). Finally raw materials are ionic sources; their contribution to conductivity varies widely, depending on their nature: bleached Kraft pulp or recovered fibres.

These results concerning mineral content and $CaCO_3$ on pulp fraction and COD and pH on water fraction do not bring anything new for the rest of the project. They just confirm what is now well known. They are presented in annexe 1.
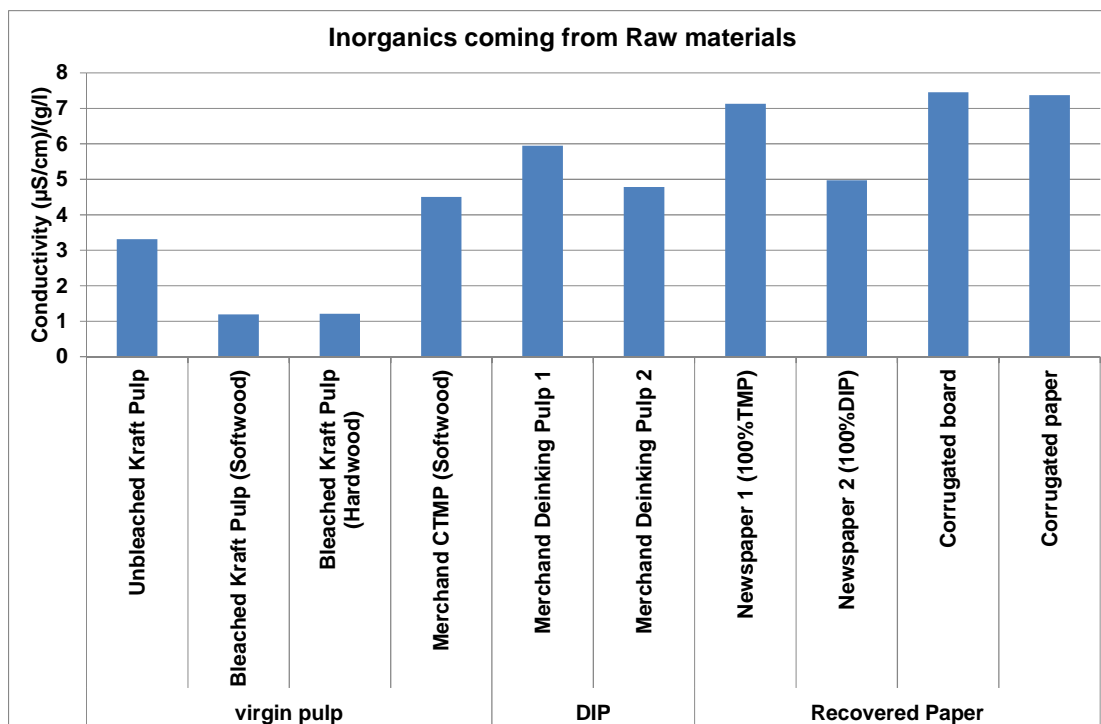
Figure 13: Raw materials contribution on conductivity
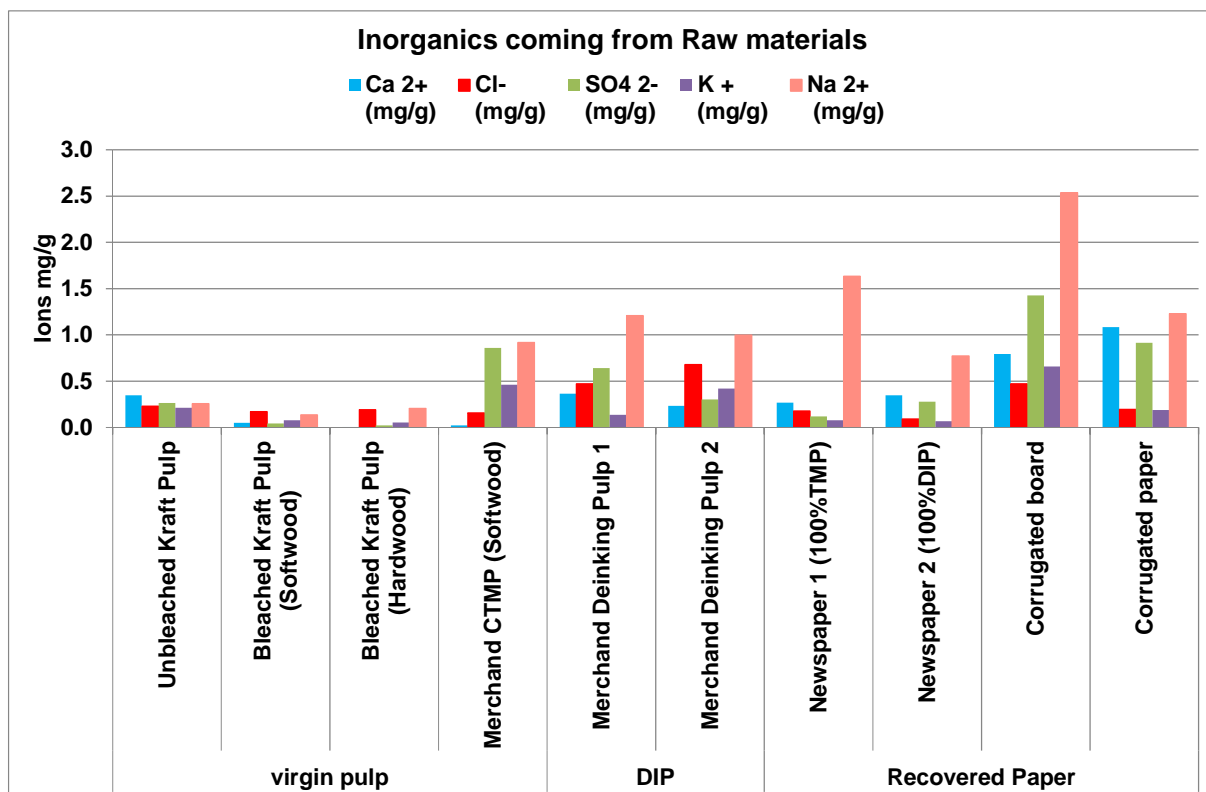
Figure 14: Raw materials contribution on major ionic species
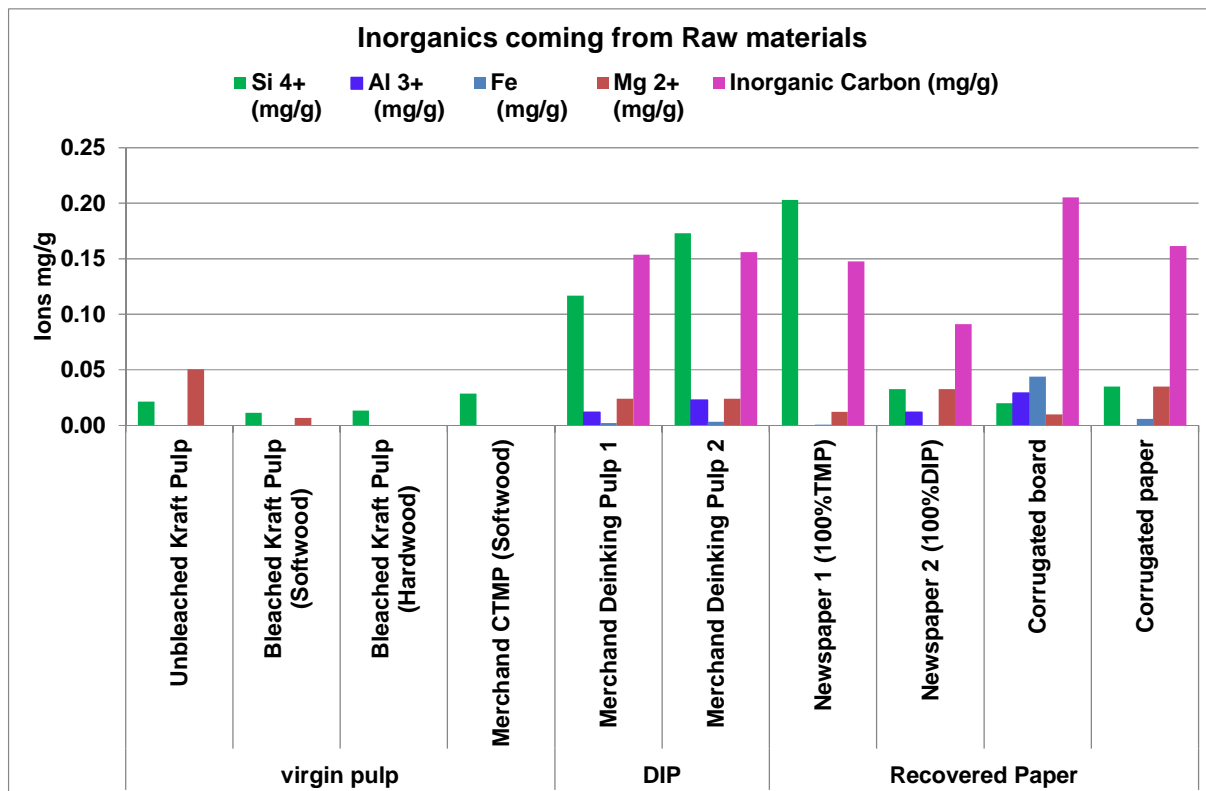
Figure 15: Raw materials contribution on minor ionic species
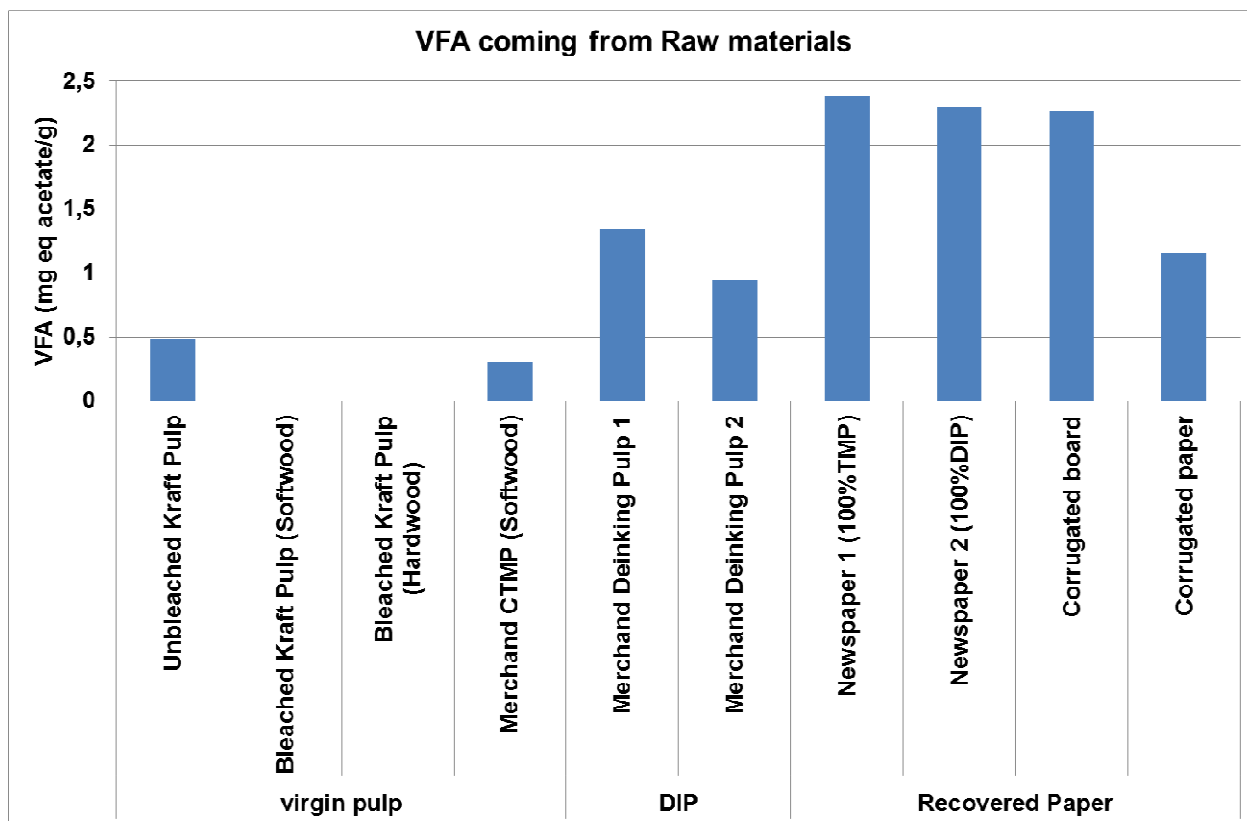
Figure 16: Raw materials contribution on VFA

4.1.2. - Contribution of feed fresh water

Thanks to CTP database, 36 fresh water characterisations could have been analysed. The minimum and maximum values of several physico-chemical and chemical parameters are presented in Table 4.

	based on 36 papermills	
	min	max
pH	6.93	8.7
temperature °C	6.5	29.5
COD mg/l	6	149
Conductivity µS/cm	79	1220
calcium mg/l	11	156
chloride mg/l	9	140
sulphate mg/l	10	286

Table 4: Fresh water parameters

Conductivity and ions concentrations can be very different from fresh water to other (factor 15). Consequently fresh water can be an important source of ions in some cases.

4.1.3. - Impact on WW1 conductivity – Simulation approach

To better understand the contribution of the raw material to the conductivity of process water, PS 2000 simulation tool has been used. A very simplified model of a paper mill with a stock preparation and a paper machine has been built. In this first approach, conductivity was assumed to follow mass balances equations. Three types of conductivity contribution at two specific consumptions (6 and 10 m^3/t) have been assessed:

- From raw materials (Table 5)
- From fresh water (Table 6)
- From raw materials and fresh water (Table 7)

These simulations confirm that the most the circuits are closed the most the conductivity is high. This is due to the dissolved matters which are at the same concentration but in a smaller amount of water. The contribution of fresh water with high conductivity is comparable to that of recycled raw material. In this case, conductivity does not rise with circuits' closure. The contribution of fresh water and raw material is the addition of the two conductivities, which is not what it really happens in a chemical point of view. But it allows comparing these simulated values with measured values in the CTP database. Figures from CTP database show that:

- the conductivity in WW1 of an OCC line from recovered fibres, with specific water consumption of 6m^3/T and a medium ionic quality feed fresh water is around 3500 µS/cm
- and the conductivity in WW1 of a tissue line from bleached Kraft pulp, with specific water consumption of 10m^3/T and a medium ionic quality feed fresh water is around 800 µS/cm

The simulated conductivity is 1570 µS/cm for OCC line with fresh water consumption at 6 m^3/T is much lower compared to 3500 µS/cm measured (database value). Other conductivity sources must then be determined. Concerning tissue mill conductivity, 170 µS/cm are missing. From these simulations it appears that fresh water and raw materials are not the only contributors to conductivity, a major contributor is missing. It could be chemicals.

Type production	Raw material input conductivity (µS/cm)/(g/l)	Resulting WW1 conductivity (µS/cm)	
		Fresh water consumption = 6 m^3/t	Fresh water consumption = 10 m^3/t
OCC	7.4	1130	760
Bleached kraft pulp (tissue)	1.2	180	124

Table 5: Raw materials conductivity contribution on white waters conductivity

Fresh water conductivity (µS/cm)	Resulting WW1 conductivity (µS/cm)	
	Fresh water consumption = 6 m^3/t	Fresh water consumption = 10 m^3/t
80	70	73
550	440	460
1200	1060	1100

Table 6: Fresh water conductivity contribution on white waters conductivity

Raw material input conductivity (µS/cm)/(g/l)	Fresh water conductivity (µS/cm)	Resulting WW1 conductivity (µS/cm)	
		Fresh water consumption = 6 m^3/t	Fresh water consumption = 10 m^3/t
7.4	550	1570	1220
1.2	550	640	630

Table 7: Fresh water and raw materials conductivities contribution on white waters conductivity

4.1.4. - Contribution from wet-end chemicals

The contribution of additives to conductivity was evaluated by measurement of conductivity of each additive formulation with several dilutions. The specific contribution to conductivity was evaluated as the slope of the dilution curve in the range of high dilution (Figure 17). The additives that show the highest specific contribution to conductivity are the caustic soda and the coagulant for the primary treatment (Figure 18). When taking into account the dosages, the additives that contribute mainly to conductivity are: caustic soda, sodium bisulphite, DAF flocculant in pulp preparation and Wet-Strength Resin (WSR) (Figure 19). The contribution from the other additives is negligible.
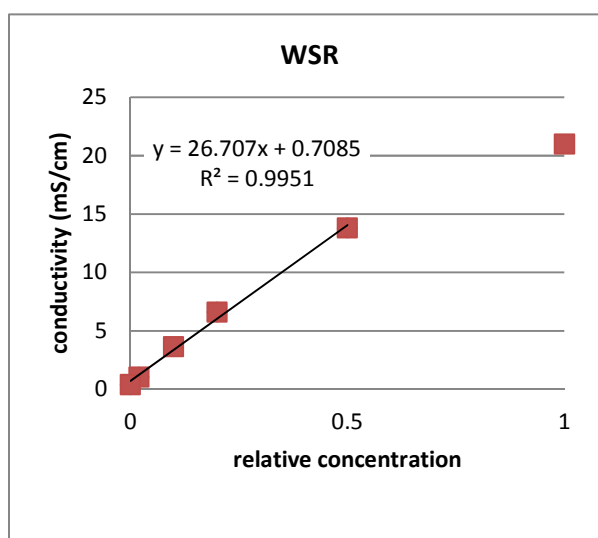
Figure 17: Example of dilution curve for the WSR to estimate the specific contribution of the chemical to conductivity
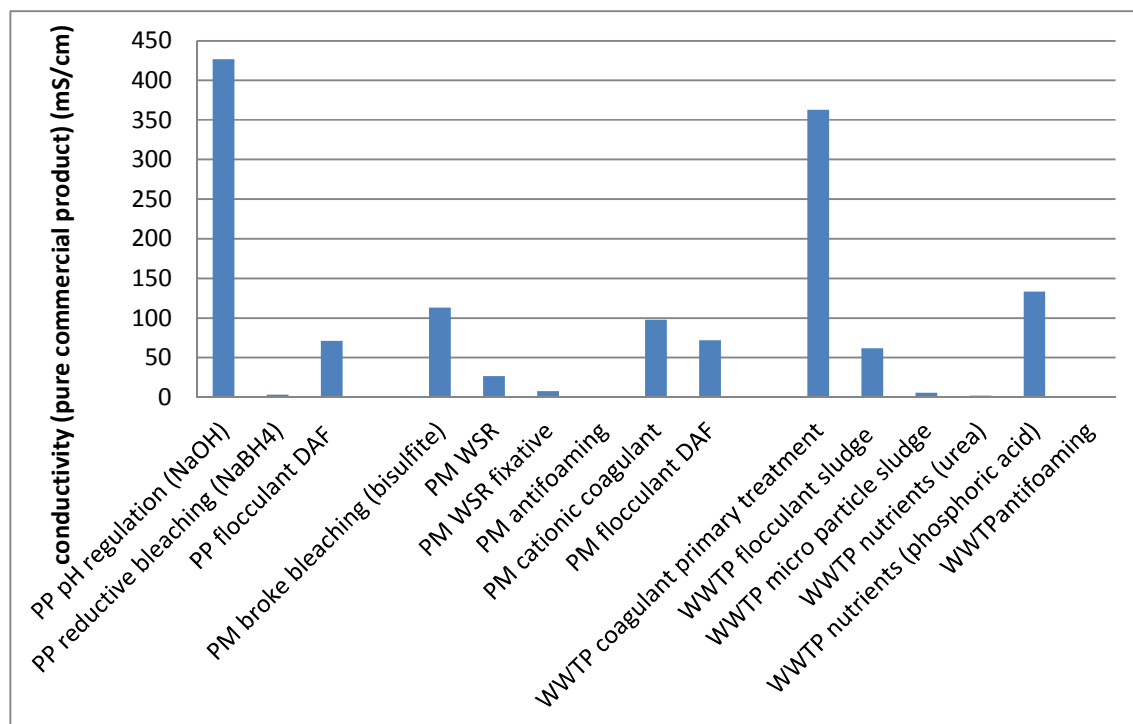
Figure 18: Specific contribution of the additives to conductivity (estimated from the slope of their dilution curves)
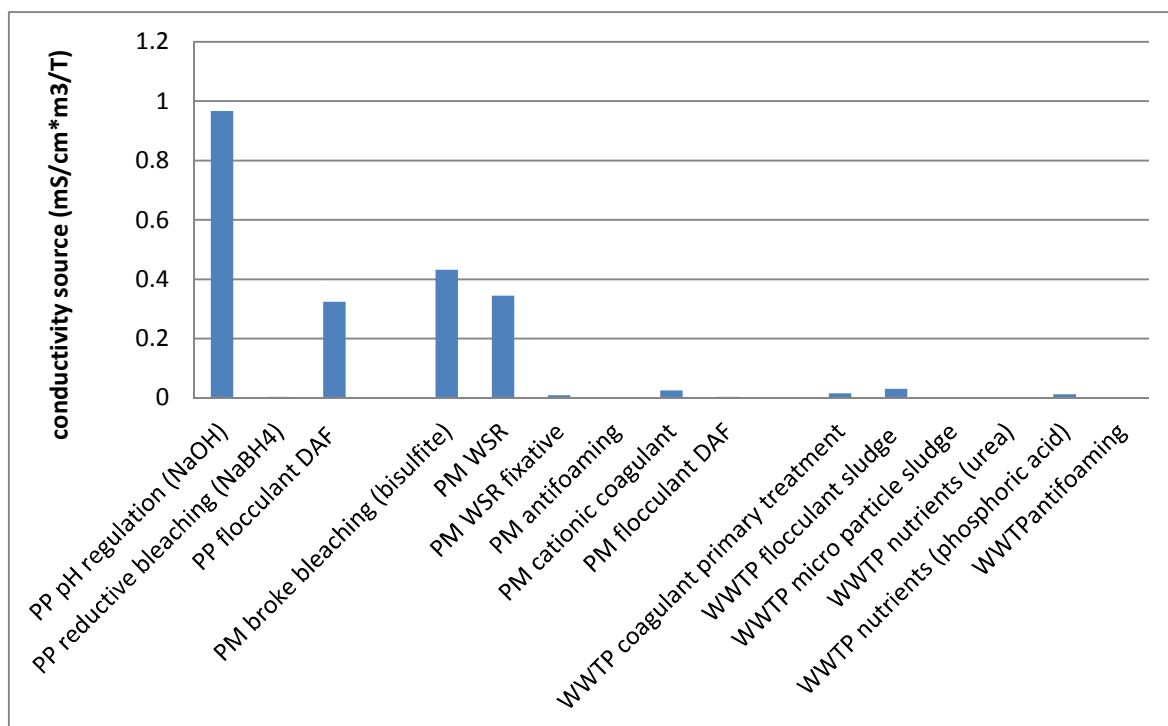
Figure 19: Source of conductivity when taking into account the dosages of the additives.

4.1.5. - Conclusion

The aim of this task was to determine the relative contribution of ions sources such as raw materials, fresh water and wet-end chemicals in a paper production process. The raw materials contribution has been assessed by pulping of ten different papers (bleached and unbleached Kraft pulps, CTMP, TMP, deinking pulps, newspapers and corrugated boards) at laboratory scale and analysing the pulp and water fractions. The fresh water contribution has been evaluated thanks to the CTP database (36 fresh waters analyses). The combination of the two inputs (raw materials and fresh water) has been studied with the CTP simulation tool PS 2000. And the contribution of chemicals has been assessed by measurement of conductivity of each additive formulation with several dilutions.

From these different experiments, it appears that raw material contribution varies widely depending on their nature. However recovered papers contribute mostly to conductivity than Kraft pulps. The major ions are sodium, calcium, and sulphate. Fresh water can be a non-negligible ions source depending on the geographical situation of mills. Chemicals are an important ions source, especially sodium and bisulphite in the studied tissue mill.

4.2. - Acceptable limit value in term of ions content

4.2.1. - Introduction

The objective of this work is to establish the effect of increasing conductivity on the performance of DAF flocculants and development of wet-strength, in the conditions of a tissue production from recycled pulp. This will set limits on the maximum acceptable salts build-up upon recycling of bio-treated water.

4.2.2. - Summary of previous CTP results

4.2.2.1. - Effects of salt build-up on retention aids efficiency (Cyclad project 2002-2006)

Concerning the use of treated effluent for dilution of chemicals we studied the effect of the main ion species present in "bio-treated effluent on the efficiency of retention aids

For this part, 2 different impacts were studied:

- Firstly the impact on the retention aids efficiency when the last dilution is made with bio-treated effluent,
- secondly, the impact on the retention aids efficiency taking into account the ionic species build up due to bio-treated effluent recycling.
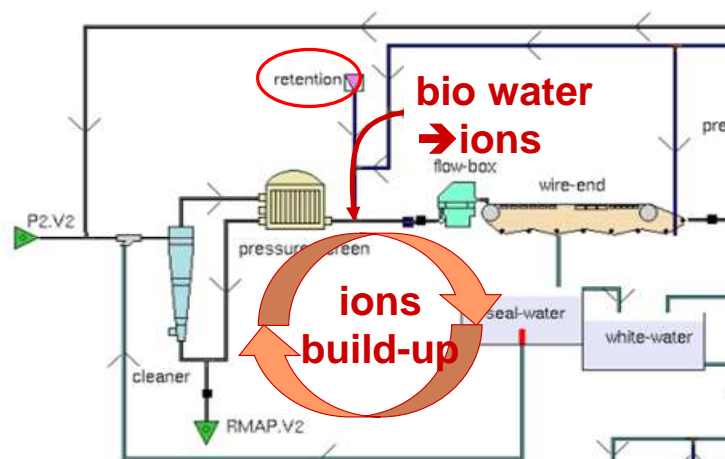
The main conclusions were:

- No detrimental effect for retention or drainage when retention aids are diluted with bio-treated effluent
- But salts build-up in the short circulation is detrimental for retention with CPAM+bentonite system. We determine that divalent salts are more detrimental than monovalent and in presence of salts. The best CPAM had high Degree of Substitution, and low Molecular Weight. CPAM dosage can be increased when bio-treated effluent contains mostly monovalent ions but is inefficient with divalent ions

4.2.2.2. - Scaling potential in water circuits (sCAle project 2010 – 2012)

The scaling potential of a solution is defined by its supersaturation. Above a given supersaturation threshold, scaling may occur in a two-step process. Firstly, nucleation gives birth to crystal germs, and then growth of these germs forms the scale deposit. Nucleation can occur under either homogeneous (direct precipitation from the bulk solution) or heterogeneous regime (precipitation on existing surfaces, e.g. surface of the pipes, suspended solids (fibres, fines, filler…).

Supersaturation (S) is the key parameter that determines precipitation: it is defined as the ratio of the activities of the precipitation species over their value at equilibrium.

$$S = \frac{IAP}{K_s} = \frac{[Ca^{2+}] \cdot [CO_3^{2-}]}{[Ca^{2+}]_{eq} \cdot [CO_3^{2-}]_{eq}}$$

The chemical speciation software PHREEQC (Parkhust and Appelo 1990) resolves all known chemical equilibria, without approximations and then, the ionic activity product (IAP) can be extracted, and compared to the solubility product of the considered solid phase.

- If IAP<Ks then the solution is under-satured solution and there is dissolution of existing CaCO3 solid
- If IAP=Ks then the solution is at equilibrium with the solid
- If IAP>Ks then the solution is supersaturated, out of equilibrium. This is a metastable state and external disturbance (for instance: temperature or pH shocks, contact with air or aeration phases) cause the solution to evolve to nucleation and crystal growth, leading to calcium carbonate scaling in our case.

The work performed on $CaCO_3$ dissolution at laboratory scale and with the speciation software PHREEQC highlighted the main influencing parameters:

- $CaCO_3$ dissolution takes place all along the papermaking process, at each pulp dilution as long as dilution waters are aggressive towards $CaCO_3$. So pulper consistency does not affect the total dissolved $CaCO_3$ amount if dilution waters, from pulper to head box, are aggressive, as it is the case in OCC paper making.
- Temperature decreases dissolved $CaCO_3$ amount but speeds up dissolution kinetics.
- Dilution water pH has an influence upon $CaCO_3$ dilution AND $CaCO_3$ dissolution buffers final water pH.
- VFA production by micro-organisms increases $CaCO_3$ dissolution.

4.2.3. - Methods for conductivity impact assessment

4.2.3.1. - Conductivity control

Conductivity rise in process water due to bio-treated effluent recycling was simulated with either model salts (NaCl or $CaCl_2$), or using bio-treated effluent (after concentration under gentle evaporation, with added biocide DBNPA, 10 ppm). The conductivity range was set from 2 to 6 mS/cm. The minimum corresponds to the actual conductivity level measured in the process water of a mill producing tissue from DIP pulp with a high conductivity level due to severe water restriction, while the maximum corresponds to the conductivity predicted by the chemical process simulation when recycling the maximum possible amount of bio-treated water to the process.

4.2.3.2. - Wet-strength development

The pulp was a wood-free market DIP pulped in deionised water. The pH was adjusted to 7.5 with HCl.

The charges brought by the additives were measured by colloidal titration. The ionic demand was measured with a Mütek PCD03 streaming current detector. The WSR (Polyamidoamine epichlorohydrin resin) was titrated with PVSK (potassium polyvinyl sulphate). The Fixative (APAM) was titrated with PEI (polyethyleneimine).

In order to directly assess adsorption of (charged) additives on the furnish, their influence on zeta potential (ZP) of the furnish was measured. Additives were added to the furnish under gentle stirring (at 3.5 g/L, 40°C). Samples were taken over time, and the furnish zeta potential was measured with a Mutek SZP-04 (where a pulp pad is formed against a wire under pressure, and the streaming potential is measured).

For the selected addition sequence (WSR addition (15 kg/T, 2 min), followed by fixative addition (1.5 kg/T, 1 min), handsheets were produced (60 g/m², Rapid Köthen former, standard pressing and drying). The handsheets were then cured in an oven (80°C, 30 min) to polymerise the resin and develop the wet-strength. The dry and wet tensile were measured using standard methods (ISO 1924-2).

4.2.3.3. - DAF flocculant

Suspended matter to be recovered in the DAF was simulated by isolation of the fine fraction of the wood-free market DIP by micro-hole fractionation. The thickened pulp was diluted to 5 g/L using either NaCl, $CaCl_2$ or bio-treated water. The flocculant (CPAM) was added with 5 minutes contact time (0.5, 1, 2 kg/T, reference mill dosage = 1 kg/T). The turbidity of the supernatant was measured after centrifugation at 40 g during 5 min. The clarification performance is defined relatively to the centrifuged turbidity of the blank without added flocculant.

4.2.4. - Results

4.2.4.1. - Wet-strength development

The wet-strength resin has a specific charge that is 3.6 times larger than the fixative (in absolute value). When taking into account the applied dosages, the charge brought to the furnish by the WSR is 36 times larger than that brought by the fixative (*Table 8*).

	specific charge (μeq/g)	kg/T (commercial)	purity	kg/T (pure)	added charge (μeq/g)
WSR	2599	15	0.2	3	7.796
fixative	-718	1.5	0.2	0.3	-0.215

Table 8: Charges brought by the additives

The adsorption of the WSR on the furnish is clearly showed by the time evolution of the zeta potential (Figure 20). In the first 2 min, the zeta potential rises largely due to loose adsorption of cationic polymer chains on fibres in an extended conformation. A maximum is reached after roughly 3 min contact time. The zeta potential then slowly decays as more cationic sites adsorb on the surface in a more flat conformation. The maximum and final zeta potential increase with the WSR dosage.
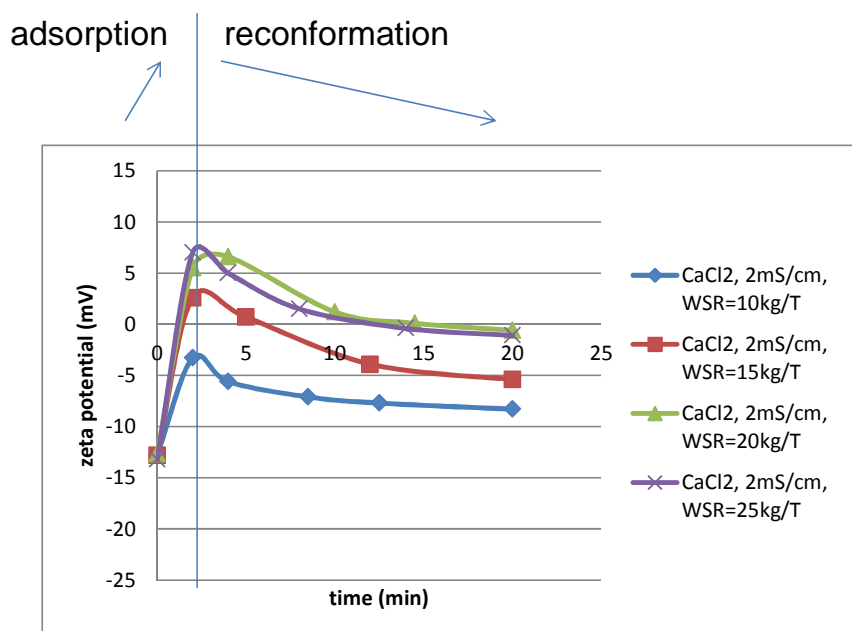
Figure 20: Adsorption of WSR on fibres: example of zeta potential time evolution (reference conductivity = 2 mS/cm, model salt = CaCl$_2$)

The evolution of maximum zeta potential vs. WSR dosage with the 2 model salts is plotted in Figure 21. The maximum zeta potential increases with the WSR dosage, for the two salts. The zeta potential reached with CaCl$_2$ is however much higher than when using NaCl. In the reference usage conditions of the WSR (15 kg/T), the zeta potential reaches a neutral value. There is a risk of over-cationisation of the furnish for higher WSR dosages. It is recommended to maintain the zeta potential below -5 mV in order to limit destabilization of the furnish and deposit problems.
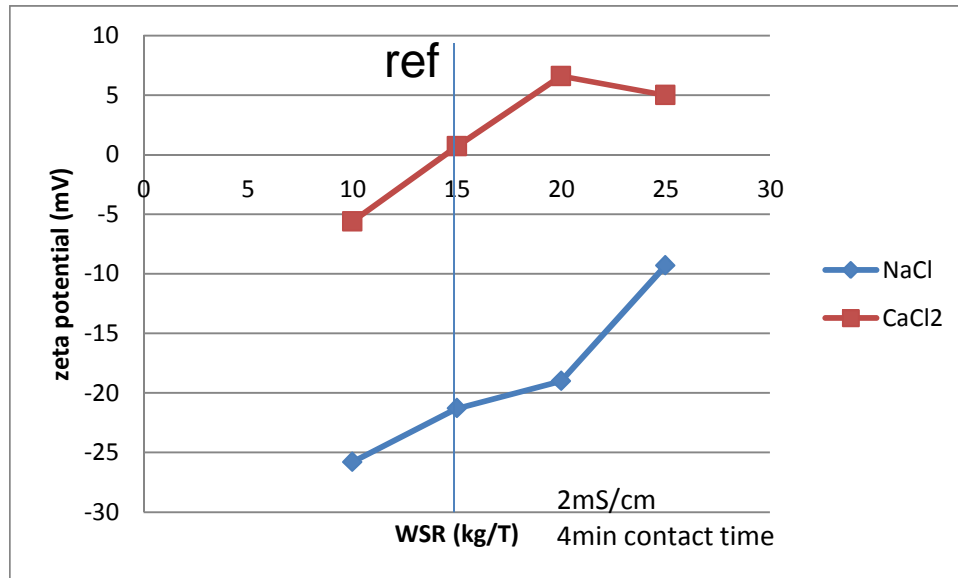
Figure 21: Adsorption of WSR on fibres: effect of dosage (reference conductivity = 2 mS/cm, 4 min contact time)

The evolution of the zeta potential vs. conductivity is plotted in Figure 22. As expected, the zeta potential increases with conductivity, as a result of the compression of the electrical double layer. At the reference WSR dosage, with a divalent salt, the risk of over-cationisation may be critical for conductivity > 2 mS/cm. With the monovalent salt, the zeta potential is kept below -10 mV at the highest conductivity. The ionic distribution of the process water is not exactly described by a mixture of $CaCl_2$ and NaCl. We tentatively plot the expected trend for the mill process water by inferring the zeta potential corresponding to the calculated ionic strength (estimated from detailed process water analysis). The ionic strength of the mill process water is close to that of the $CaCl_2$ situation, so that the risk of over-cationisation should be closely monitored at higher conductivity.
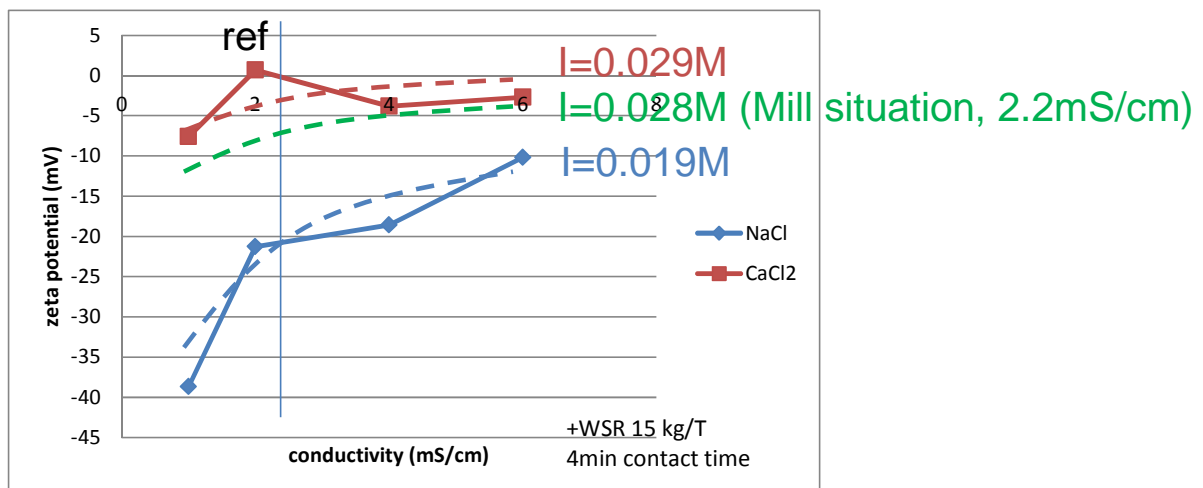
Figure 22: Adsorption of WSR on fibres: effect of conductivity (reference WSR dosage = 15 kg/T, 4 min contact time)

Finally, the zeta potential resulting from the reference addition sequence is presented (Figure 23). As already mentioned, higher zeta potential is reached at higher conductivity. However it can be seen that the fixative lowers the zeta potential. With a divalent salt, the zeta potential is kept is the safe range when conductivity < 4 mS/cm.
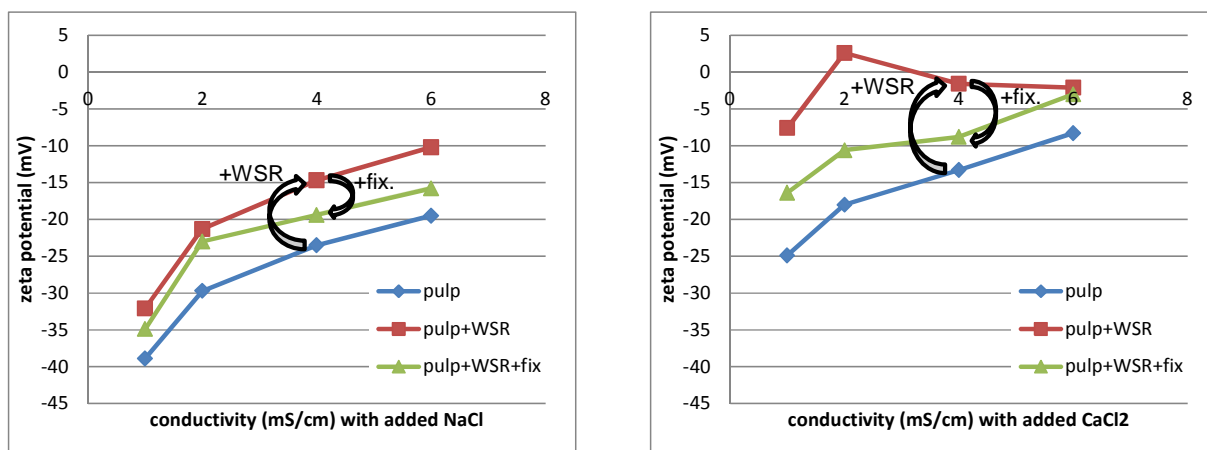
Figure 23: Evolution of zeta potential vs. conductivity for a sequence of WSR addition (15 kg/T, 2 min), followed by fixative addition (1.5 kg/T, 1 min) (conductivity controlled with NaCl (left), or CaCl$_2$ (right)).

The conductivity rise controlled with model salts has limited impact on the development of wet-strength (Figure 24). There was a slight reduction of wet-strength ratio with CaCl$_2$. There was no significant impact on WSR retention (Figure 25). When rising the conductivity with the concentrated bio-effluent, there was a slight reduction of wet-strength ratio, which was barely significant (Figure 26).
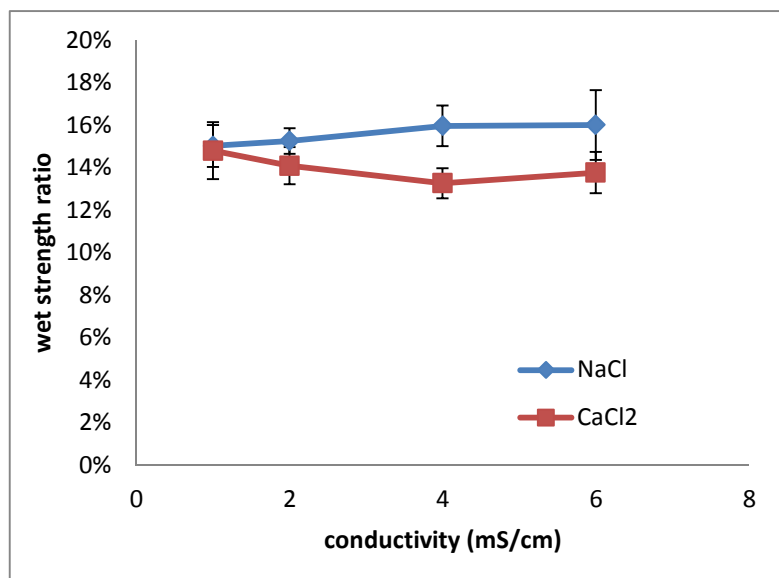
Figure 24: Handsheet properties: evolution of wet-strength ratio vs. conductivity controlled with model salts
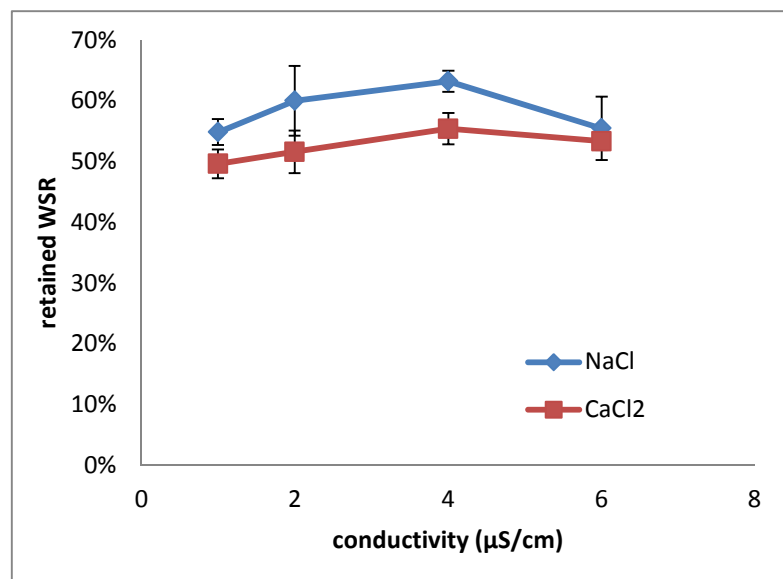
Figure 25: Handsheet properties: evolution of retained wet-strength resin vs. conductivity
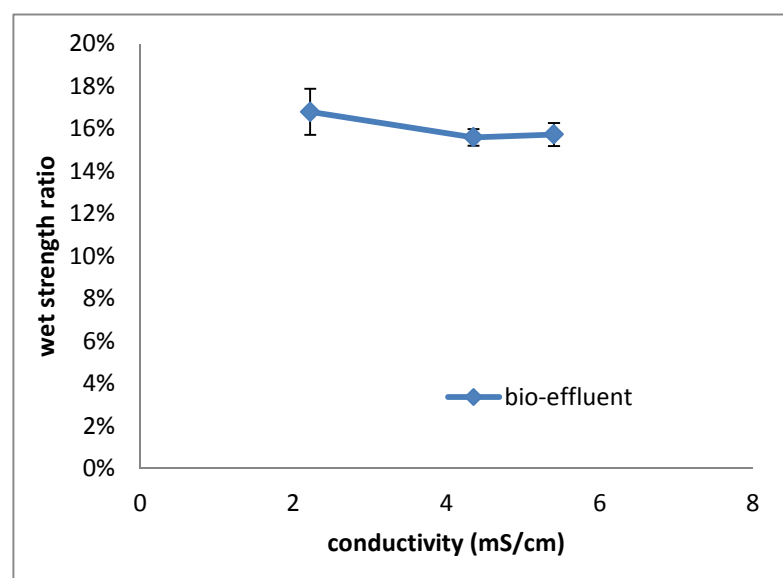
Figure 26: Handsheet properties: evolution of wet-strength ratio vs. conductivity controlled with concentrated bio-effluent

4.2.4.2. - DAF flocculant

The effect of conductivity increase on DAF chemistry efficiency was firstly investigated with model salts. With NaCl addition, there was little effect on the clarification performance of the polymer (Figure 27). No detrimental effect of conductivity increase on the polymer efficacy was observed. An optimum polymer dosage was found at around 1 kg/T. With $CaCl_2$, no detrimental impact was found either (Figure 28). There was possibly even a positive effect of the divalent salt on the clarification performance of the polymer (to be confirmed). The slight beneficial effect of conductivity increase may be related to charge reduction of fines (enhanced by divalent salts). The expected polymer coiling due to charge screening that would reduce bridging efficiency is obviously not the predominant effect. Also, the polymer may have been designed specifically to resist coiling at high ionic strength.
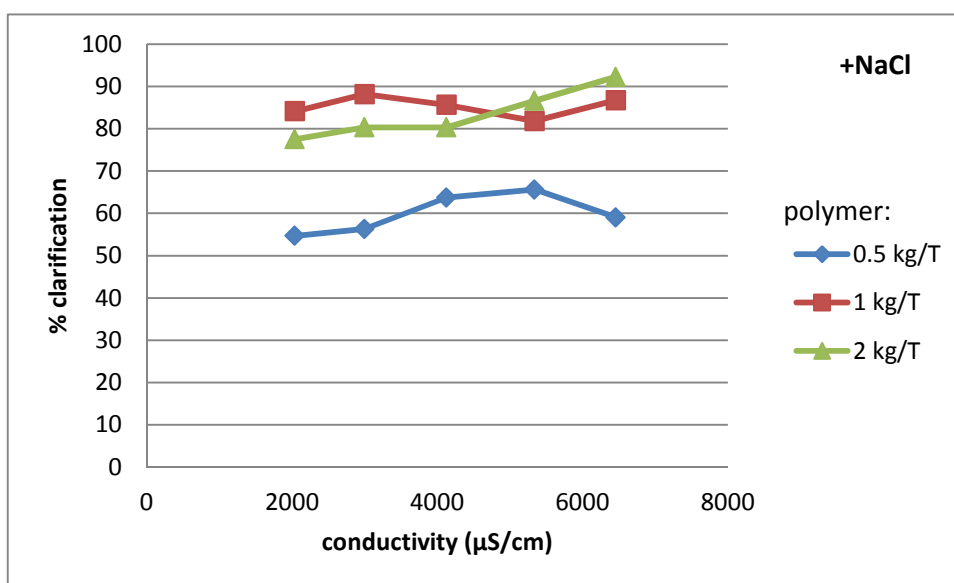
Figure 27: Effect of conductivity (controlled by model salts, NaCl addition) on the clarification performance of the DAF polymer
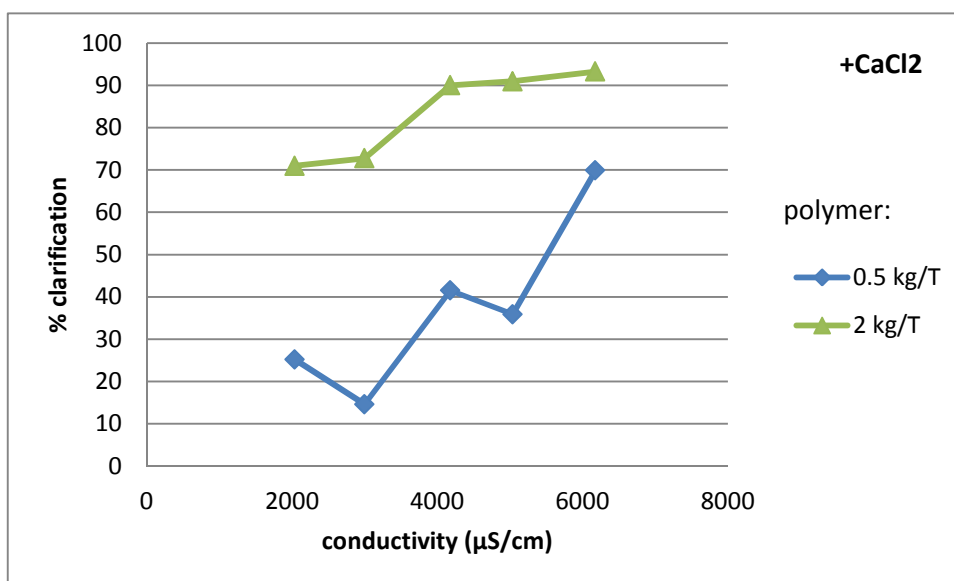
Figure 28: Effect of conductivity (controlled by model salts, CaCl2 addition) on the clarification performance of the DAF polymer

When the bio-treated water was added to increase the conductivity, the clarification efficiency was however significantly reduced, at all polymer dosages (Figure 29). In this situation, the concentration of the bio-treated water not only caused the conductivity to rise, but also induced a build-up of all other dissolved species. The cationic demand increased from 15 to 35 µeq/L. Such a cationic demand level is still considered as weak, but may partly explain the observed reduction of polymer performance, through irreversible neutralization of charged groups on the polymer chain. Usually, it is considered that a cationic demand < 200 µeq/L is not detrimental when diluting a retention polymer (Ryoso and Manner, 2001). It is possible that the polymer used here is particularly sensitive to charged colloids. It could be

interesting to try neutralizing the bio-treated water with a coagulant before recycling to the process.

Also in this case, there was no optimum polymer dosage (over the studied range), as the clarification efficiency increased with higher polymer dosages. Thus, the detrimental effect of bio-treated water recycling can hopefully be compensated by increasing the polymer dosage: the performance obtained with the reference polymer dosage of 1 kg/T could be maintained in the highest conductivity conditions by increasing the polymer dosage to about 1.5-2 kg/T. Alternatively, a polymer with higher DS may be employed.
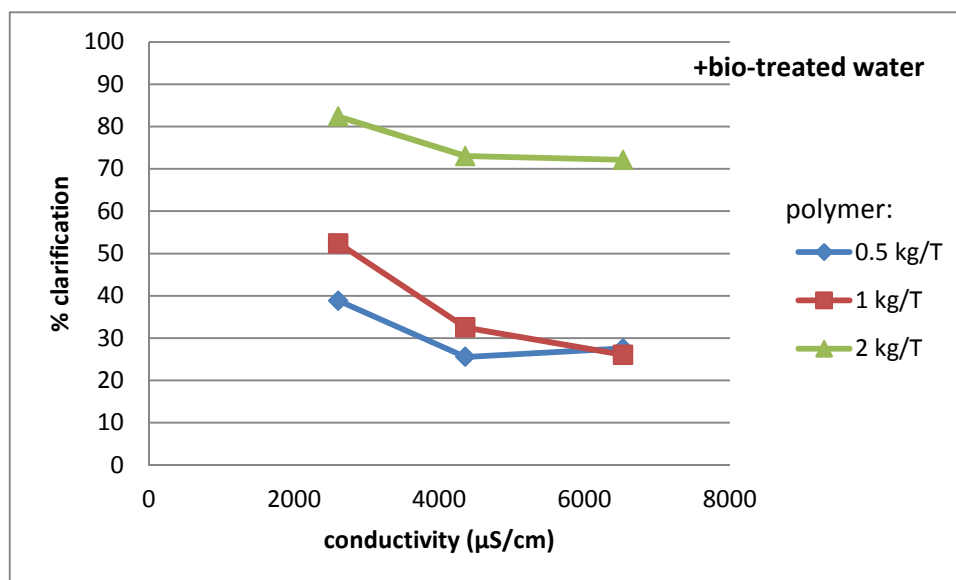
Figure 29: Effect of conductivity (controlled by bio-treated water addition, concentrated to various levels) on the clarification performance of the DAF polymer

4.2.5. - Conclusions

At higher conductivity, addition of WSR may cause destabilisation of the furnish (positive zeta potential). Addition of fixative helps keeping the zeta potential in the safe range. Higher conductivity has limited impact on WSR retention and development of wet-strength.

The DAF polymer performance was not affected by conductivity rise. However, it seems that higher cationic demand may be detrimental for clarification performance. That negative effect could be compensated by increasing polymer dosage. Also, it may be useful to neutralize the cationic demand of the bio-treated water with a coagulant before recycling to the process, or to use a polymer with higher specific charge.

All in all, recycling bio-treated effluent is not expected to impact wet-strength development. It may however reduce the clarification performance of the DAF polymer, due to residual cationic demand.

5. - Water treatment technology assessment

5.1. - Valmet Ultrafiltration (VAL)

5.1.1. - Technology description and objectives

Water is a scarce natural resource, and its consumption is something that needs to be considered in all industries today. Valmet's ultrafiltration technology is a unique solution for decreasing paper mills' fresh water consumption.

Valmet Ultrafiltration Tissue process produces high quality ultrapure water (permeate) for the paper machine's wire section high-pressure showers to decrease the fresh water consumption. Permeate can also be used for paper machine's other showers on wire and press sections as well as for the dilution of chemical additives.

The permeate produced with Valmet Ultrafiltration technology is

- Free from solid substances
- Free from colloidal material
- Free from turbidity
- Free from bacteria
- Free from secondary and micro sticky and
- It contains 50-70 % less anionic trash

When the permeate is used for replacing the warm fresh water there are also savings in the energy used for heating the water suitable for PM processes. Removing of trash material from process water helps also maintaining good paper making performance and efficiency.

The Valmet Ultrafiltration feed water is normally paper machine white water, e.g. clear filtrate from fibre recovery disc filter.

The benefit of Valmet Ultrafilter CR (cross rotational) is the low operating pressure difference and thus there is no clogging of the membrane. This results in high and stable filtrate capacity as well as long membrane life time.

Valmet's technology uniqueness and comparison vs state-of-the-art is that Valmet Ultrafiltration Tissue is the first new designed cross rotational ultrafiltration system for tissue mills white water recycling and purification. State of the art nowadays is warm fresh water for the critical consumption points.

For the tissue lines a new Valmet CR Filter model and its process has been developed in SPOTVIEW project (Figure 30). During the project, the first customer trials in Essity Nokia will be done. Technology effectiveness and impact for the process will be verified.

Figure 30: Valmet Ultrafilter CR prototype for tissue process.

Valmet Ultrafiltration Tissue process is a factory built and IO-tested fully automated modular system. The heart of the process is the new CR1010/30 ultrafilter. The membrane area is 42 m² with 30 filter cassettes and its dimensions are 2.3 m x 2.1 m x 1.4 m (height x width x length). The modular system can easily be extended by adding filter units to increase the membrane area.

With the typical tissue machine (production of 100-300 t/d) the Ultrafiltration process including one or two CR ultrafilters can reach the fresh water reduction of 1-2 m³/t of produced paper.

Using permeate instead of fresh water decreases the overall water consumption in the tissue-making process and creates savings in the energy used for heating the fresh water. A modern tissue machine consumes 5–15 m³ of water per ton of paper, and Valmet's solution decreases the consumption by 1–2 m³.

The process is designed to be service friendly and with exchange filter cassettes the membrane change is fast, easy and economical.

5.1.2. - Technology trials

5.1.2.1. - Laboratory scale Valmet Ultrafiltration trials at Essity Nokia mill

The potential feed water types for Valmet Ultrafiltration were investigated at Essity Nokia (former SCA) paper mill. The laboratory scale CR250 membrane filter was used in the tests. The results obtained by CR250 are comparable to larger scale. Thus, the purpose of the laboratory scale trials was to evaluate the suitability of the different process water at the PM7 and PM9 for the new prototype CR1010/30 Tissue filter and to figure out the best type of membrane for the prototype testing.

The trial runs were conducted at ambient temperature and with 1.0 bar pressure difference (trans membrane pressure). The membranes used in the trials were Valmet P, Valmet PS, and Valmet RC. They are made of PES (polyethersulfide), PS (polysulfone), and regenerated cellulose respectively. All the membranes have anionic surface charge in neutral pH and

thus they are widely used in membrane filtration of pulp and paper process waters at different MWCO's (molecular weight cut-off). To CR250's membrane module it can be installed two membrane samples at the same time and they can be tested simultaneously.

The first trials were conducted with PM7 (PK7) clear filtrate, which was considered to be the best suitable feed water for Valmet Ultrafiltration. The clear filtrate had 300 ppm COD, 14 ppm TSS, its pH was 7.6 and charge 49 µeq/kg. Conductivity of the filtrated sample was 1.0 mS/m. The tested membranes were Valmet P and Valmet RC. During the trials, the both membranes had a capacity (permeate flux above 200 L/m²h). At 35 °C as can be seen in Figure 31. That equals to 150 L/min with CR1010/30 Tissue filter.

Figure 31 The permeate flux of Valmet P and Valmet RC membranes during the CR250 filtration trial with PM7 clear filtrate at 35℃ and 1.0 bar.

The next trial runs were conducted with PM9 (PK9) Krofta (flotation) accept, which contained 500 ppm COD and 60 ppm TSS. Its pH was 7.9; charge 53 µeq/kg, and conductivity 84 mS/m. The tested membranes were Valmet P and Valmet RC. The both membranes had a stable capacity above 200 L/m²h) during the trial at 35 °C and 1.0 bar (Figure 32).
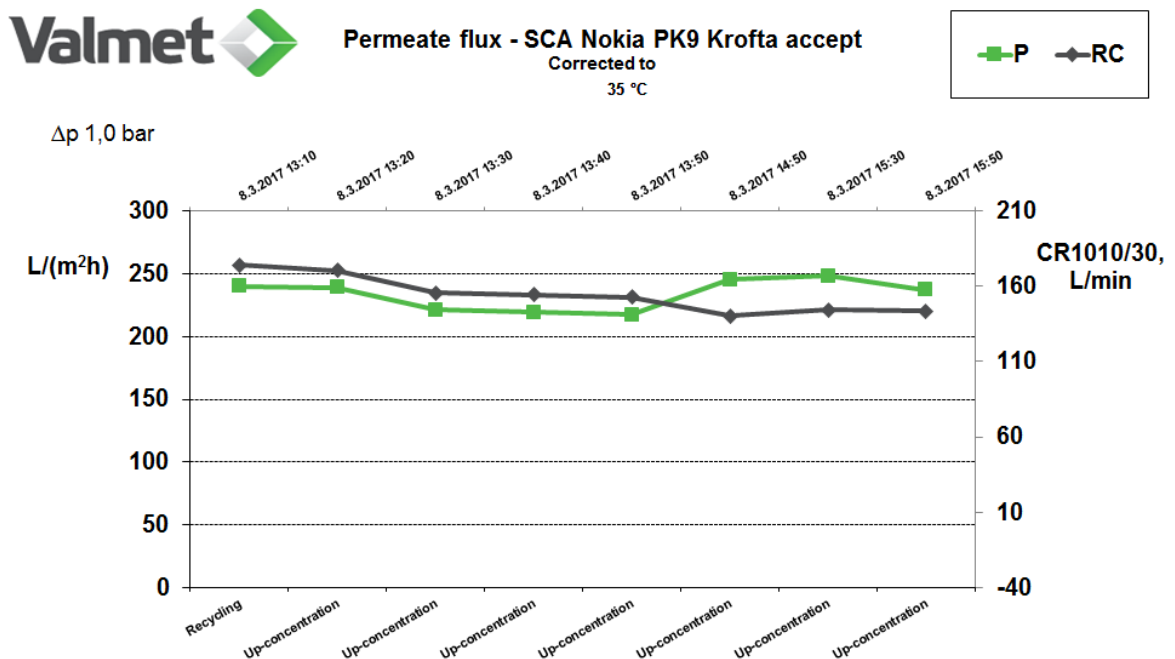
Figure 32: The permeate flux of Valmet P and Valmet RC membranes during the CR250 filtration trial with PM9 Krofta accept at 35℃ and 1.0 bar.

The next trials were conducted with Krofta feed, that contained 800 ppm COD. Its pH was 8.5, and conductivity 56 mS/m. The tested membranes were Valmet PS and Valmet RC. The Valmet RC membrane had higher capacity, over 200 L/(m^{2}h), as compared to the Valmet PS membrane, 150 L/(m^{2}h) at 40 °C and 1.0 bar (Figure 33).
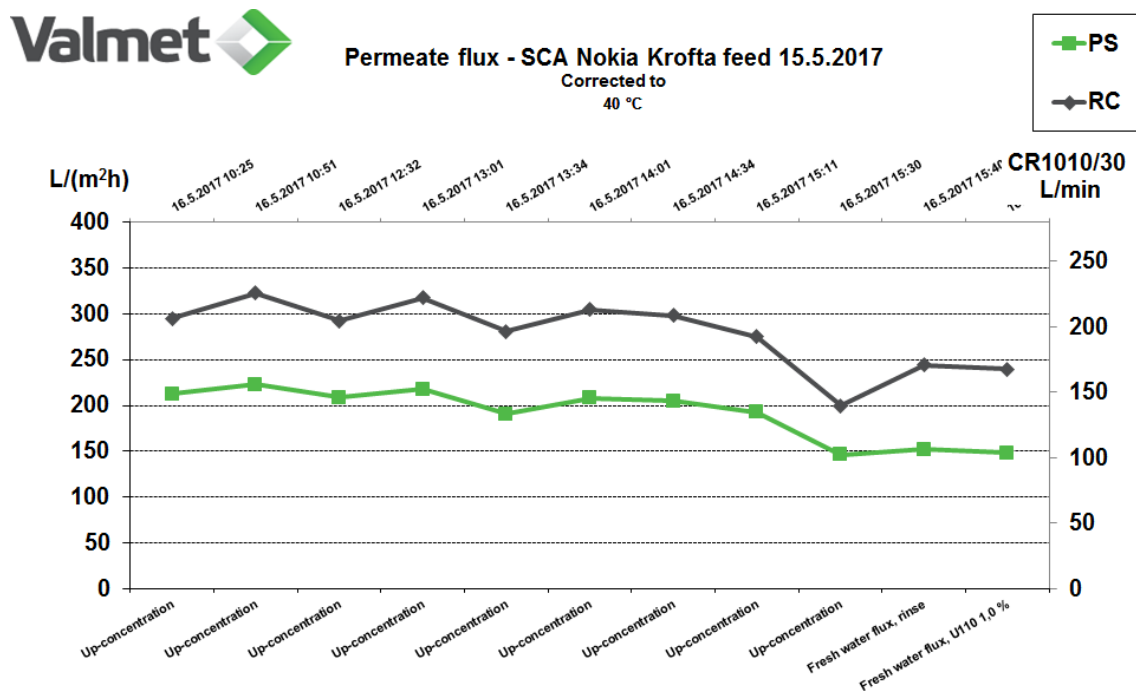
Figure 33: The permeate flux of Valmet PS and Valmet RC membranes during the CR250 filtration trial with PM9 Krofta feed at 40℃ and 1.0 bar.

There was a change in the Krofta process chemicals after the first trials with Krofta feed. Therefore, it was tested again with the same membranes. The results were similar to the previous test. The both membranes had a somewhat higher capacity as in the first trials (Figure 34).
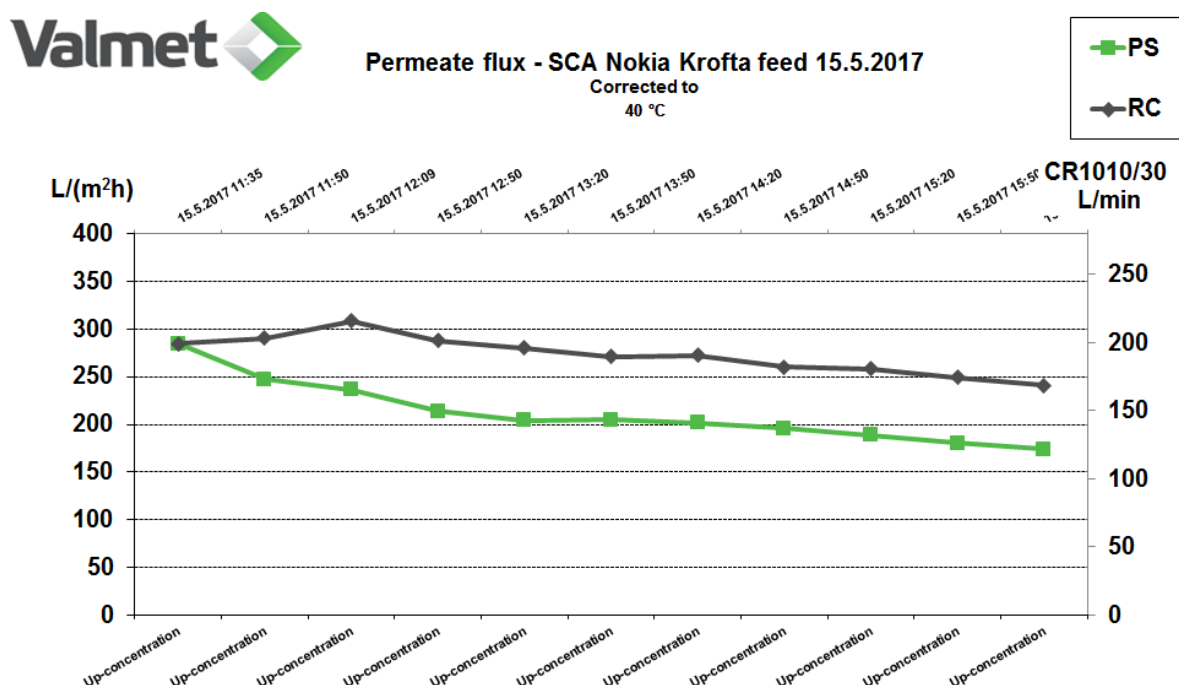
Figure 34: The permeate flux of Valmet PS and Valmet RC membranes during the CR250 filtration trial with PM9 Krofta feed at 40℃ and 1.0 bar.

The results were verified by so-called dead-end trials with the most potential feed waters. In those trials, the up-concentration was sped up by closing the concentrate valve. Then, only permeate was flowing out from the filter and higher VRF (volume reduction factor) could be achieved in relatively short time. The Krofta filtrate + Krofta feed mixture (one part feed, 7 parts filtrate) contained 350 ppm COD and 110 ppm TSS. Its pH was 7.9; charge 41 µeq/kg and conductivity 20 mS/m. The tested membranes were Valmet RC and Valmet PS. Valmet PS seemed to have a higher flux as compared to Valmet RC membrane. Both membranes' capacity was 200 L/m²h) or more while the VRF was up to 80 (Figure 35). The capacities increased after the feed dilution by opening the concentrate valve. This means that there has not been severe membrane clogging during up-concentration. The filtration temperature was 35 °C and pressure difference 1.0 bar.
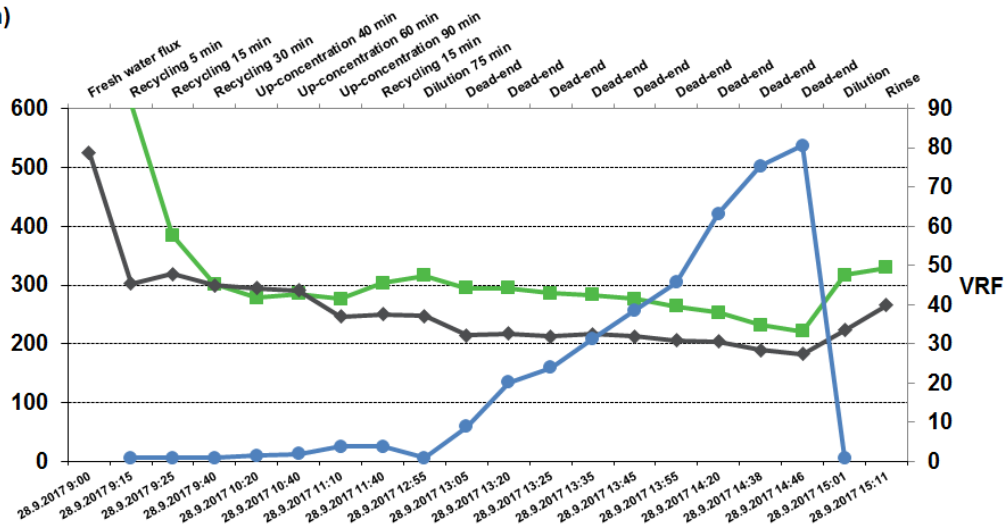
Figure 35: The permeate flux of Valmet PS and Valmet RC membranes during the CR250 filtration trial with PM9 Krofta feed and filtrate mixture (1/7) at 35℃ and 1.0 bar.

A similar dead-end filtration trials were conducted also with PM7 clear filtrate, which contained 330 ppm COD and 98 ppm TSS. PM7 clear filtrate's pH was 7.7, charge 40 µeq/kg and conductivity 41 mS/m. The tested membranes were Valmet PS and Valmet RC. Temperature was 40 °C and the pressure difference 1.0 bar. The both membranes had a capacity around 150 L/m^{2}h) while the VRF increased up to 80 (Figure 36). After the dilution, the capacities increased to 250 L/m^{2}h). Thus, there has not been severe membrane clogging during up-concentration.
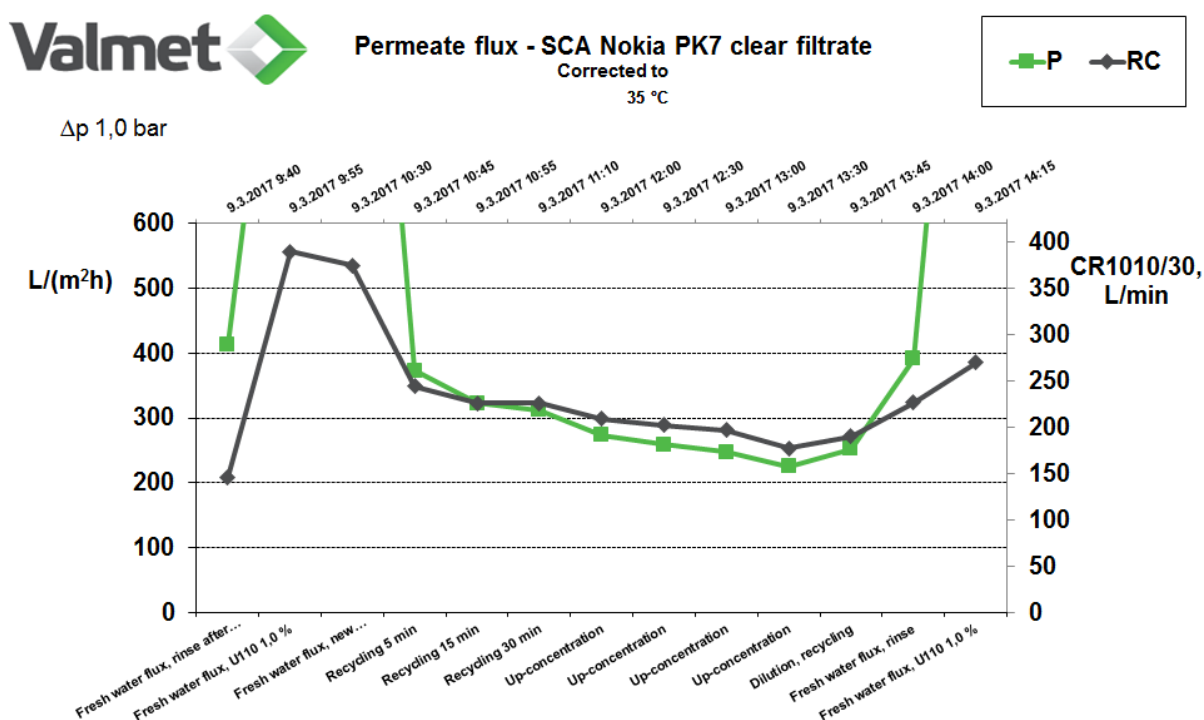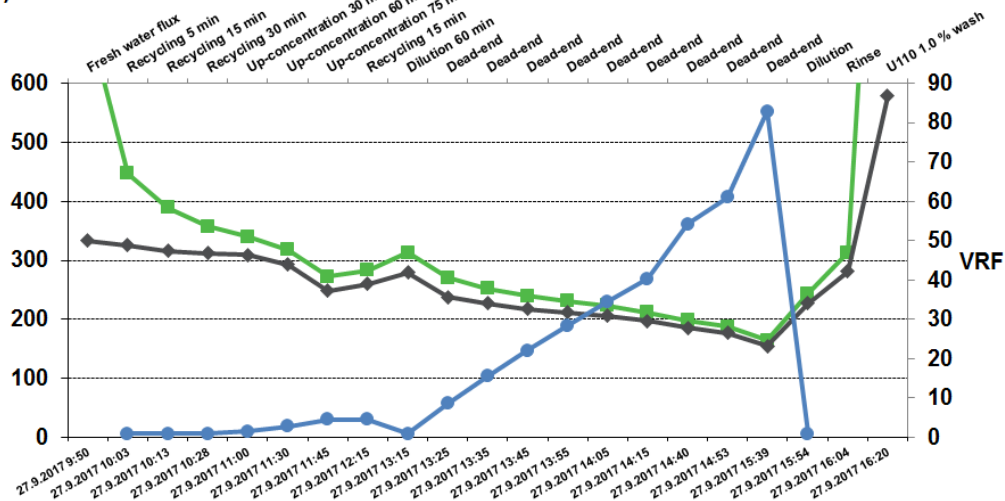

Figure 36: The permeate flux of Valmet PS and Valmet RC membranes during the CR250 filtration trial with PM7 clear filtrate at 40℃ and 1.0 bar.

The permeate produced during the laboratory scale CR250 trials was analysed for its quality. It was free from solid substances, colloidal material, turbidity, and bacteria. Charge reduction was 60% for the permeate produced from PM7 clear filtrate and 80% for the permeate produced from PM9 Krofta filtrate, *i.e.* there was 60-80 % less anionic trash in permeate than in the feed waters.

According to the lab scale results with CR250, all the waters studied are suitable for a long time trial with the CR1010/30 Tissue prototype filter.

5.2. - Enhancement of existing effluent treatment processes (CTP)

5.2.1. - Existing techniques for pulp and paper effluents treatment

Existing effluent treatment plants in the pulp and paper industry include primary treatment to recover suspended solids (TSS), and secondary biological treatment to eliminate biodegradable substances (BOD, COD). Primary effluent processes, sometime integrated in the papermaking process to recover valuable cellulosic fibres and pigments, include disk filters, micro-flotation and settling tanks equipment. These technologies can eliminate 95 to 99% of TSS, with treated effluent below 50-100 mg/L TSS. Primarily treated effluent quality is already suitable for recycling in some processes, mainly for pulp dilution.

Secondary biological treatment, including anaerobic or aerobic processes (activated sludge, biofilters, moving bed biofilm reactors or suspended carriers) can eliminate 85 to 95% of BOD_5 and 75 to 90% of COD. Removal efficiency of soluble and colloidal organic compounds depends on several factors including the incoming concentration and biodegradability of incoming pollutants, food/biomass ratio (i.e. hourly COD per kg of microbial biomass) or hydraulic retention time in the basins. Incoming effluent characteristics largely depends on the type of pulp and paper production, raw material (virgin or recovered fibres) and process additives. Proper design and maintenance of the treatment plant are prerequisite for well performing biological systems.

In the case of Essity Nokia producing sanitary papers, Pulp preparation and paper machine effluents are treated by a primary clarifier to eliminate suspended solids. The total volume of clarified effluent is then treated by an aerobic biological treatment (activated sludge with secondary clarifier).

In the case of Emin Leydier producing packaging paper, part of the primary treatment is integrated in the process as a disk filters to partially recycle clear and cloudy filtrates for pulp dilution. Another part of the primary treatment cleans some rejects by Dissolved Air Flotation before secondary treatment. The secondary treatment is a two-step anaerobic/aerobic treatment (activated sludge with secondary clarifier).

Table 9: biological effluent treatments of pulp and paper mills[1]

Process	Application (average BOD inlet concentration)	Advantages	Drawbacks	Remarks
Aerobic submerged biofilters (single-stage)	20 – 100 mg/l	Safe process; immobilised biomass; low concentration of suspended solids in the effluent	Sensitive to higher concentration of suspended solids	NA
Aerobic submerged biofilters (two-stage)	100 – 300 mg/l (or more)	NA	NA	NA
Low to medium capacity trickling filters	<400 mg/l	Simple construction; low energy consumption; cooling of the waste water, quick recovery after short-term toxic shock (¹)	In some cases risk of clogging; odour caused by stripping, higher P emission required for optimum operation (1.0 – 1.5 mg/l)	Risk of clogging and odour are minimal with proper nutrient management. Lifetime expectancy of 15 years or more when properly operated
High capacity trickling filters + activated sludge	200 – 800 mg/l	NA	NA	NA
Activated sludge (single-stage)	100 – 1 000 mg/l	Conventional process with a number of variants; well-established treatment technique	Energy consumption; excess sludge; problems with bulking or floating sludge	NA
Activated sludge (two-stage)	300 – >1 000 mg/l	NA	NA	Separation of sludge circuits is important
Activated sludge (two-stage with high sludge load step)	600 – 1 200 mg/l	Improved properties of activated sludge process	Energy consumption; excess sludge	NA
Moving bed biofilm reactors, MBBR (fixed biomass on mobile carrier material)	300 – 1 500 mg/l	Fixed biomass; smaller reactor volumes; no return sludge; less sensitive to peak loads	Excess sludge	Allows high volume load
Rotating biological contactors (RBCs): Fixed biofilm system/biodiscs	Applied as bulk removal step or for advanced treatment	Cost-effective for smaller mills; low energy demand (<0.3 kWh/kg BOD₅ removed)	In many European countries there is less experience with RBCs	Successful application in US and Italy in paper industry
Activated sludge as sequencing batch reactor (SBR)	100 – 1 000 mg/l	More flexible process operation	More efforts for process control; discontinuous process	NA

NB: NA = not available
(¹) *Source*: Water treatment handbook, Chapter 11.2 trickling filters, 6th edition, Degrémont.
Source: [113, PTS 1998], amended by EIPPCB.

5.2.2. - Effluent quality after biological treatment

Effluent from pulp and paper processes after secondary treatment can reach BOD below 20 mg/L and COD values of 50 to 150 mg/L. TSS after secondary clarification reach 10 to 50 mg/L, with turbidity level from 1 to 5 NTU.

Comparative analysis of bio-treated effluent and process water quality was performed for five paper mills already having low specific water consumption (Table 10) and producing different grades: coated paper with and without wood, corrugated paper from recovered fibres and newsprint from deinking pulp and mechanical pulp.

---

[1] Table 2.17 from BREF document for the Production of Pulp, Paper and Board: , in: http://eippcb.jrc.ec.europa.eu/reference/BREF/PP_revised_BREF_2015.pdf, 2015.

	specific consumption m3/T
Mill A - coated paper mill with wood	15
Mill B - coated paper mill without wood	10.3
Mill C - coated paper mill without wood	15
Mill D - corrugating paper mill	6.5
Mill E - newsprint paper mill - DIP/TMP	12.5

Table 10: Water consumption and type production of studied paper mills

The bio-treated effluents have been characterised according to the following measures:

- Dissolved and colloidal organic fraction (COD and colour),
- Dissolved and colloidal inorganic fraction (conductivity as a global evaluation and three major ionic species: calcium, sulphate, chloride),
- Microbial activity (measurement of total aerobic flora on petri dish)

Dissolved and colloidal organic material

As expected the COD of biotreated effluent is low (< 200 mg/L), much lower than the COD of process water (from 700 to 4500 mg/L), but slightly higher than in fresh water (< 50 mg/L).
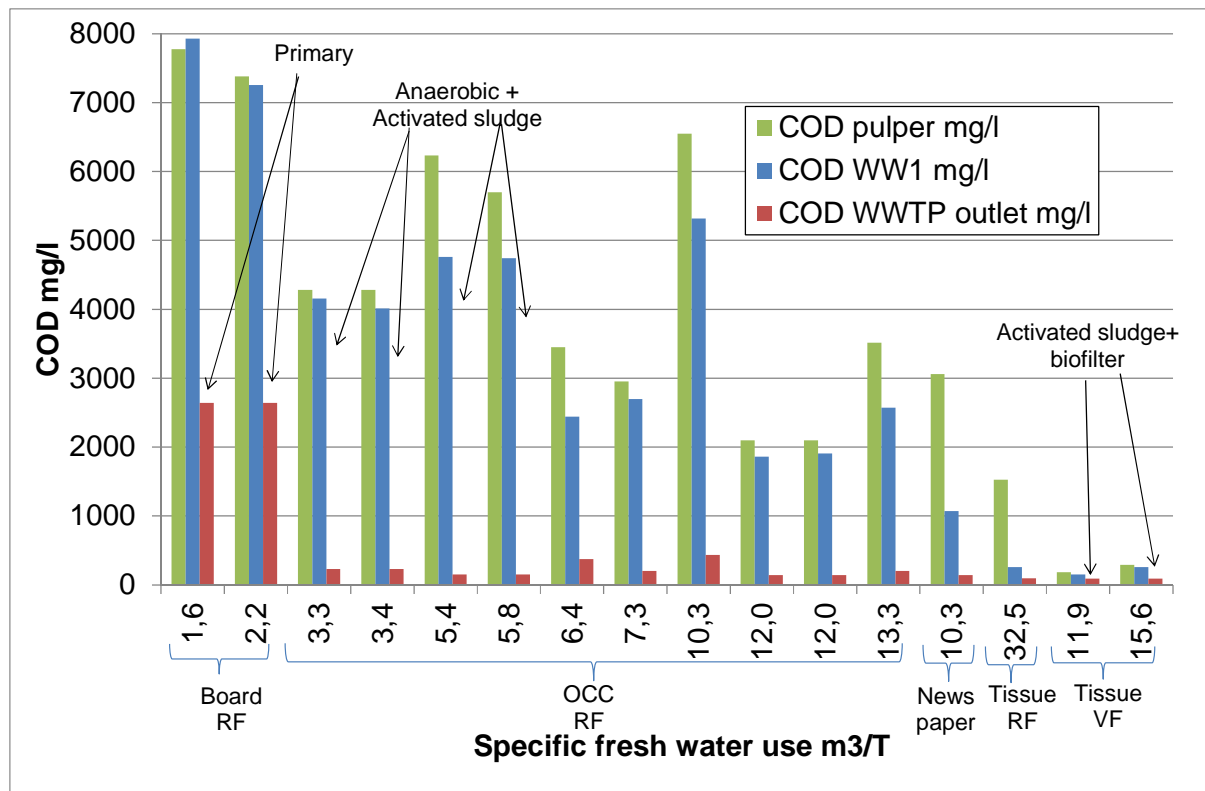
Figure 37: COD of bio-treated effluents

Total Flora

Considering the total flora, we made also measurement for raw fresh water and for treated fresh water. Aerobic bacteria development in bio-treated effluent exists, but can be equivalent that in fresh water even with treatment and is not higher that in process water. It means that the microbiology have to be under control as it must be the case in process water.
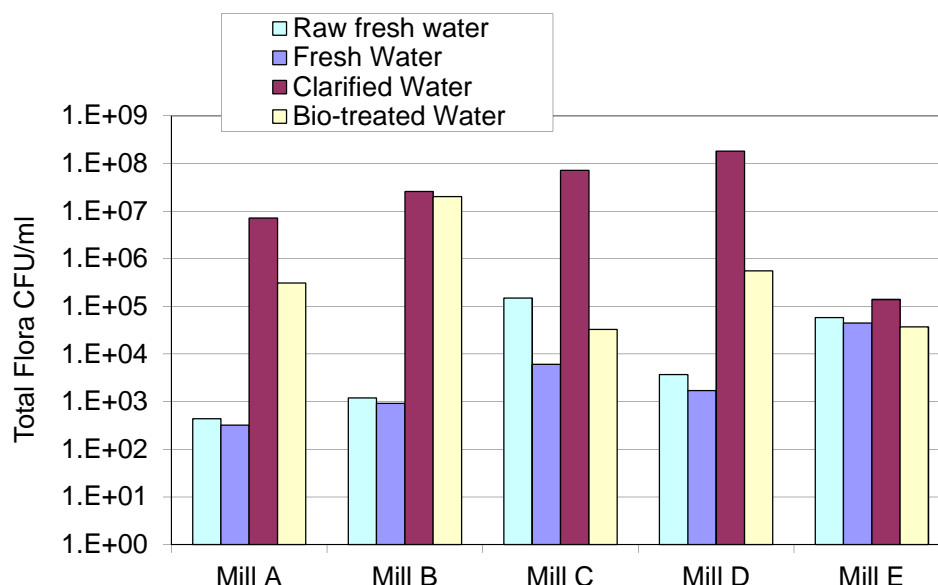
Figure 38: Total flora of bio-treated effluents

Conductivity

Through the numerous analysis campaigns performed for more than 15 years in paper mills, CTP created a data base compiling conductivity measures (Figure 39) and major ions concentrations in fresh water, WW1 and bio-treated effluent namely: calcium (Figure 40), chloride (Figure 41) and sulphate (Figure 42).

The COD of bio-treated effluent is generally much lower than that of process water, and the organic compounds responsible of this COD are poorly biodegradable.

The conductivity of the bio-treated effluent is, in general, slightly lower than that of the process water, except when the plant has a tertiary treatment on the effluents (by coagulation flocculation) or when the site has several production units (TMP, coating) but only one waste water treatment plant. It would seem that conductivity increases when circuits' closure increases. This effect seems to be strong, under 6 m^3/t. Fresh water conductivity impact depends on the geographical location of the mills. The measures on the main presumed ions (calcium, sulphate and chloride) show that they have, in general, a highest concentration in white water 1 than in bio-treated effluent. This is due to calcium precipitation in activated sludge and sulphate biodegradation during biological treatment, especially in anaerobic treatment. The decrease of chloride is not explained. The waste water treatment plant is not expected to reduce chloride concentration.
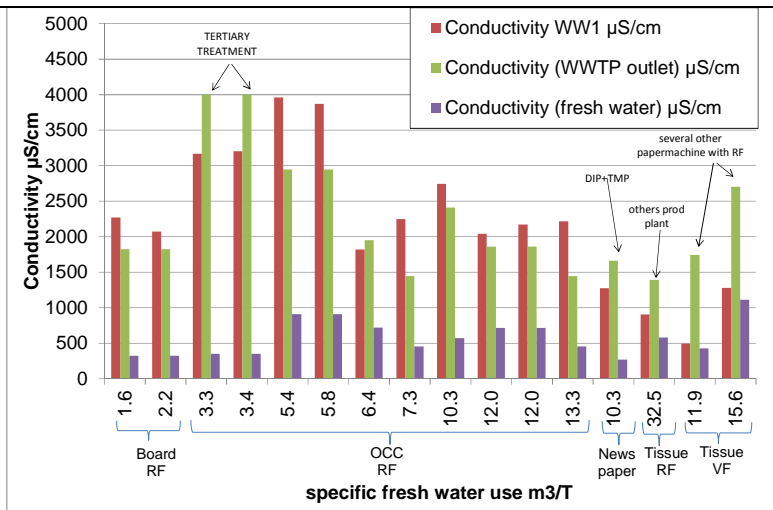
Figure 39: water conductivity data
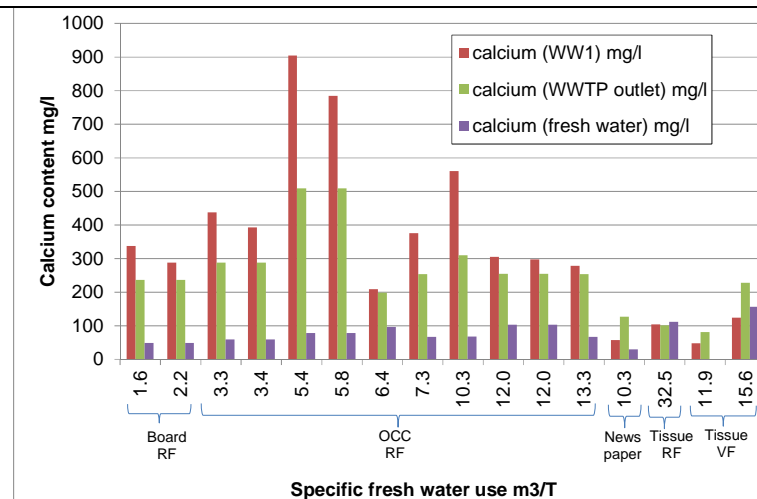
Figure 40: calcium contents
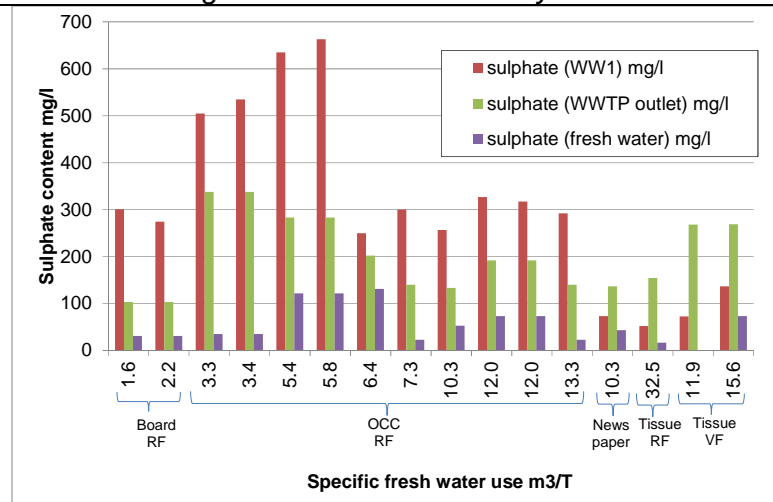
Figure 41: sulphate contents
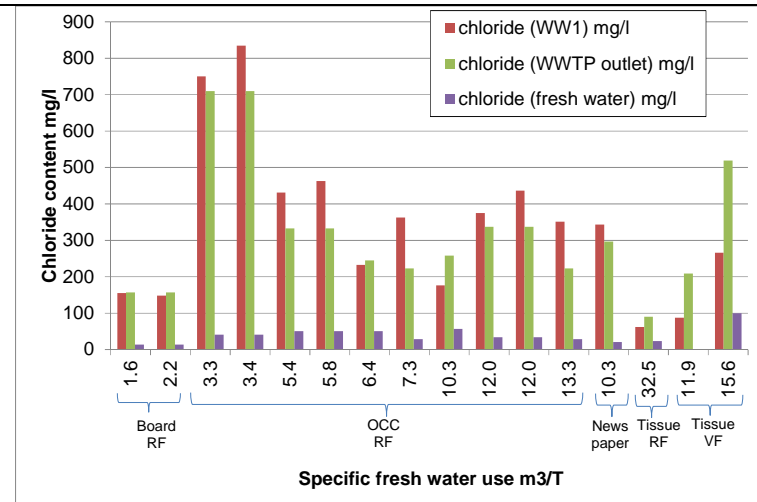
Figure 42: chloride contents

5.2.3. - Limitations of existing effluent treatment for reuse

5.2.3.1. - Hydraulic limitations

Three categories of hydraulic limitations can be considered when modifying the effluent treatment plant circuit:

1. Limitation due to pumping and piping capacities: nominal and maximum flow acceptable. Exceeding the limit is only possible by changing the equipment. Reducing the effluent volume would also generate larger flow rate fluctuation or air cavitation if the pump/pipes are over-dimensioned.

2. Equipment volume limitation that influence the hydraulic retention time in reaction tanks. Biological treatment processes are dimensioned for a maximum daily COD or BOD loading rate. Reducing the volume and retention time may lead to overpass the nominal volumetric loading of the basin (i.e. kg $COD/m^3/day$) and limit the biological reaction and the COD/BOD removal efficiency. Increasing the retention time in settling tanks or non-mixed and non-aerated tanks would also generate uncontrolled anaerobic conditions and solid deposits.

3. Equipment surface limitation that influence the superficial fluid velocity in the equipment. Exceeding critical superficial velocity in primary or secondary decanter would generate flocs and suspended solids reject. Contrarily, reducing hydraulic velocity of fluidized bed reactors such as anaerobic UASB or EGSB would cause granular sludge bed settling and clogging.

An audit of the hydraulic capacity of the effluent treatment plant is thus recommended before modifying the water management system.

5.2.3.2. - Biochemical limitations

Each category of pulp and paper effluent can be characterized by the biodegradability of organic compounds, simplified by its COD/BOD ratio, leading to refractory residual COD after optimal biodegradation in aerobic conditions. In pulp production processes from wood, lignin aromatic compounds are mostly responsible for recalcitrant COD fraction (up to 20%) and effluent colour. In papermaking process effluents the refractory COD fraction is generally limited to 5-10%, depending on the nature of additives used, and their retention in the production process (surfactants, dyes, polymers, fixatives…). Previous studies by CTP[2] have shown that aerobic biological treatment could also generate refractory compounds through humification process or release of extracellular polymeric substances.

For this reason, best available effluent treatment techniques cannot eliminate up to 99-100% of the COD and soluble organic compounds. Residual effluent BOD can reach detection limit, but COD between 50-150 mg/L is generally considered as a minimum achievable concentration after optimized biological effluent treatment. This COD removal rate is generally sufficient to avoid most problems associated with treated effluent reuse, if this residual COD is not linked with excessive colour, turbidity, microbial flora or ionic demand. Turbidity around 1 NTU, total flora below 10^3 CFU/mL and ionic demand below 50 µeq/L are generally sufficient for many water reuse applications. Further tertiary effluent treatment is only necessary to achieve higher quality levels.

---

[2] F. BERTAUD, et al (2008). Characterisation of recalcitrant substances responsible for residual COD load: development of an analytical protocol of biodegraded effluent. *Revue ATIP* Vol. 62 No 2 – p. 2-12.

5.2.3.3. - Chemical limitations

Conventional effluent treatment installations in pulp and paper industrial sites are generally not designed to eliminate soluble inorganic substances (anionic or cationic salts, mainly). The main reason is that salinity is not a regulatory parameter for water emission in this industrial sector.

However it has been observed that aerobic biological treatment can eliminate calcium ions to a large extent, due to the alkalinisation of effluent and HCO_3^- production, leading to $CaCO_3$ precipitation. Most part of mineral solids is eliminated with the mixed liquor extracted from the aeration tank, but the residual effluent hardness should be controlled before effluent reuse, to avoid scaling in water circuits. Other cations (Mg^{2+}, Fe^{2+}, Al^{3+}…) can also be reduced by adsorption or precipitation in the biological treatment process. Monovalent cations, particularly Na^+ or K^+, are much poorly eliminated. Only ammonium ions (NH_4^+) are assimilated as nutrient by effluent purifying micro-organisms.

Sulphate anions (SO_4^{2-}) can only be removed by anaerobic effluent treatment though microbial sulphate reduction producing H_2S in the biogas. Conversely, chloride ions are not removed in conventional effluent treatment plants.

When necessary, the reduction of inorganic salts in effluent to produce reusable water compatible with process conditions could be achieved by using tertiary deionization techniques. High deionization rate is only necessary to produce water for steam production. In most water reuse application, water conductivity from 500 to 1000 µS/cm can be sufficient. Effluent softening or other scale prevention systems may also be required when the hardness or $CaCO_3$ saturation index indicate high scaling tendency.

To conclude, limitations of existing effluent treatment plants could be associated with potentially disturbing factors as follow:

- Residual soluble and colloidal organic compounds, associated with effluent turbidity, colour and cationic demand that can be detrimental to process additive performance (retention and flocculation polymers).
- Residual micro-organisms and nutrients (carbon, nitrogen or phosphorous) that could lead to biofilm and odours development.
- Residual calcium and hardness compounds that can generate circuit scaling
- Residual chloride and sulphate anions that could induce corrosion.
- Residual Na+ that could contribute to increasing conductivity.

The situation of each pulp and paper mill can be specific and should thus be examined in detail when implementing water circuit closure strategies. The quality of effluents from secondary biological treatment could be sufficient for many applications in papermaking processes. Simple indicators, such as turbidity, conductivity, cationic demand, hardness can be sufficient to monitor the effluent quality for recycling. Tertiary effluent treatment requirement should be evaluated according to the water quality priorities.

5.3. - Tertiary effluent treatments techniques

It is not an objective of the SpotView project to examine and compare the efficiency of all existing tertiary effluent treatment techniques. The purpose of this chapter is to present a synthesis of the most adapted techniques for reducing soluble or colloidal organic compounds and for salinity reduction after conventional primary and secondary effluent

treatment. The results obtained by BFI with a new desalination technique, Capacitive deionization (CDI), are presented in more details.

5.3.1. - Technique for refractory organic compound removal

Four main categories of technologies are available to remove refractory organic compounds:

1. Chemical flocculation followed by flotation or filtration
2. Advanced oxidation techniques, including ozonation and biofiltration
3. Membrane ultrafiltration or nanofiltration
4. Adsorption techniques

These techniques have advantages and drawback presented as follow:

Techniques	Advantages	Drawbacks
Chemical flocculation + micro flotation or filtration	Efficiency (50-80% COD) Robust and well tested Low maintenance cost	Flocculants cost Chemical sludge production
Advanced oxidation techniques	Efficiency (50-80% COD) Colour removal Disinfection Flexible performance No sludge production	High capital and operating costs (Energy) Require post bio-treatment
Membrane ultrafiltration or nanofiltration	Efficient for colloids and HMW compounds removal	UF poorly efficient on LMW soluble COD (NF required) High capital and operating costs (cleaning + maintenance) to avoid clogging
Adsorption techniques (i.e. activated carbon, zeolite…)	Low investment cost	High operating cost to replace adsorption media

Few examples of tertiary effluent techniques exist in the pulp and paper industry.

- Tertiary physico-chemical precipitation associated with micro-flotation or sand-filtration are the most applied techniques (>10 units for tertiary effluent treatment in EU) due to their robustness and easy maintenance. These techniques are also widely used in the Pulp and paper industry for fresh water conditioning from surface water, sometime associated with oxidation for iron and manganese removal.
- Many advanced oxidation were extensively tested at laboratory or pilot scale, such as ozonation, catalysed ozonation (UV, H_2O_2, TiO_2), Fenton oxidation (H_2O_2/Fe^{2+}), but only two ozonation + bio-filtration installations exist at industrial scale in EU. A major drawback of ozone effluent treatment is its capital and energy cost.
- Membrane bio-reactors can also be found in few pulp or paper effluent treatment plants. The reason to adopt such technique is mostly the installation compactness, because secondary clarifiers are replaced by submerged or external membrane systems. Microfiltration or UF membrane can produce effluent without suspended solid and very low turbidity, but the reduction of soluble organic compounds is not significantly improved.

The limitation of these techniques is their poor performance to reduce effluent salinity.

5.3.2. - Technique for inorganic salts removal

Four main categories of technologies are available to remove inorganic salts:

1. Ion exchange resins (IE)
2. Reverse osmoses (RO)
3. Electro-deionisation (EDI)
4. Lime Softening

These demineralization techniques are mostly used to produce fresh water from sea-water, or to produce deionized water for steam production. These techniques are associated with high salinity concentrates (>20% of treated volume) that can be difficult to discard. RO and EDI can require high power consumption (1 - 2 kWh/m³). Several stages of deionization techniques (IE, RO) can be associated to remove anions and cations. Softening can be achieved by using cation exchange resins or reverse osmosis, but lime precipitation of Ca and Mg carbonates can also be achieved at a reduced cost. Lime softening produces large volumes of a mixture of calcium carbonate and magnesium hydroxide in a very finely divided white precipitate which may also contain some organic matter flocculated out of the raw water. This precipitate is generally removed by flotation. Processing or disposal of this material may be a cost to the process.

5.3.3. - Capacitive deionization (BFI)

5.3.3.1. - Technology description and objectives

Capacitive deionization (CDI) is a new ionization method for the removal of ions from water by electrostatic adsorption on two opposed charged electrodes by a low-voltage electromagnetic field (1.5 V in Voltea's design). In format of the porous electrodes, ion exchange membranes are installed to improve the removal efficiency of the process. After loading the electrodes with ions a cleaning cycle is performed by reversing the polarity of the electrodes and discharging the ions in a concentrate stream, figure 1. A large number of cells can be connected in parallel in order treat large volume flows.

| Desalting | Cleaning by polarity reversal | ´ Lab CDI |
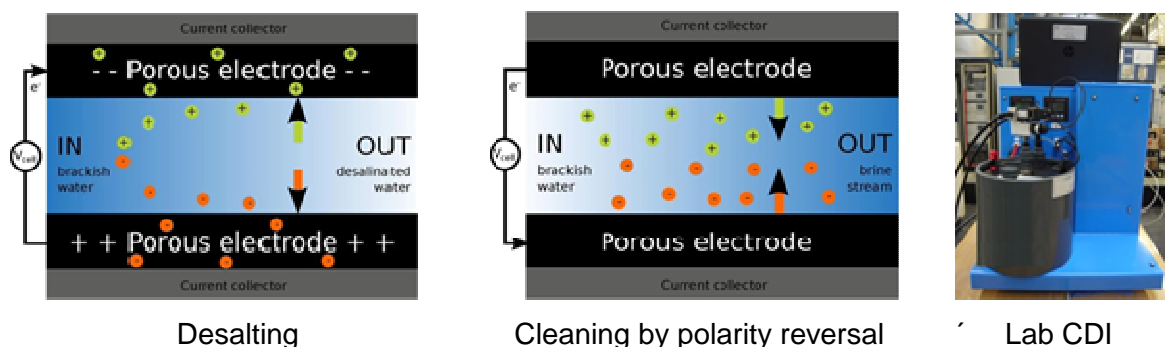
Figure 43: Working principle of CDI and lab CDI at BFI

The CDI differs from electro deionization (EDI), which is used with much higher voltages for ultrapure water production. The EDI produces a permanent waste water flow of about 5 – 7 % of in feed flow rate, whereas CDI only generate a small waste volume during the cleaning process. Furthermore, the energy consumption of the CDI differs from the treatment with RO and EDI depending on the water composition.

Objective of the work was the testing of the technologies under laboratory set-up with operational (real) wastewater samples to determine its applicability respectively the determination of a pre-treatment if necessary.

5.3.3.2. - Technology trials

For the trials, a lab CDI was used with a capacity of 60 l/h - 210 l/h and the parameter: pure time = desalting time, waste time – cleaning by polarity reversal, pre-pure time = rinsing time after polarity reversal as well as the flow rates of pure / waste and the current were varied. Aim was the reduction of the conductivity below 200 µS/cm according the requirements of CTP with a 300 l sample of waste water of a biological treatment plant of a paper mill.

The initial conductivity of the waste water was about 2440 µS/cm with a chloride content of 370 mg/L respectively a sulphate content of 440 mg/L. The organic content consisted of 36 mg/L dissolved organic carbon (DOC) and 76 mg/L dissolved inorganic carbon (DIC). The COD value of 88 mg/L is in the range between 50 mg/l for permanent load and 100 mg/L for short term load mentioned as maximum content from the CDI manufacture.

The first <u>trials</u> with the <u>waste water</u> showed that by varying the above mentioned parameters the conductivity could be decreased in maximum about 39% to 1491 µS/cm, while the chloride content was reduced about 68% from 310 mg/L to 118 mg/L. The hardness components as Ca and Mg were decreased about 57 – 63%: In opposite to this, the sulphate content stayed nearly constant with a reduction of 8%. A water recovery of 59% with an energy demand of 2.29 kW/m³ feed was achieved.

To decrease the conductivity further on, the <u>produced clean water (pure) was treated again in the CDI</u>. In this trial the settings as in the previous trial were used but in the following the current increased to maximum available. At a certain point, the increase of the current did not lead to a further improvement of the removal because the voltage level reaches its maximum. Finally, the conductivity could be reduced about 30% to 900 µS/cm, while the removal of chloride stayed stable leading to a final chloride content of 29 mg/L, Figure 44. Further on a significant increase of the sulphate removal to 66% compared to the trials with the waste water (removal efficiency: 8%) or in the case of PO_4 from 34% to 54% was overserved. The achieved sulphate content was about 283 mg/L after the treatment. Furthermore a decrease of the dissolved inorganic carbon content (DIC) was about 65% was noticed.

An overview of the achieved desalted water and the occurring concentrate composition is given in Table 11 and Table 12.

Table 11 Composition of feed, pure, concentrate and removal efficiency

Sample	pH-value	Con-ductivity [µS/cm]	Content [mg/L]				Removal efficiency [%]				
			Cl	SO$_4$	Ca	Mg	Con-ductivity	Cl	SO$_4$	Ca	Mg
Feed	7,8	2.440	370	440	84	22	---	---	---	---	---
Pure 1. CDI treatment	7,5	1.491	118	405	31	10	39	68	8	63	57
Concen-trate I	8,0	3.530	651	466	130	36	---	---	---	---	---
Pure 2. CDI treatment*	6,8	900	29	283	12	3	30	61	66	23	11
Concen-trate II	8,4	2.520	267	397	71	20	---	---	---	---	---

*Feed 2 CDI-treatment = produced clean water (pure) of 1. CDI treatment

Table 12 Composition of feed, pure, concentrate and water recovery or energy demand

	COD [mg/L]	DOC [mg/L]	DIC [mg/L]	PO$_4$ [mg/L]	Water recovery [%]	Energy demand [kW/m³ feed]
Feed	88	36	76	11,8	---	---
Pure 1.CDI treatment	---	34	42	7,8	58,4	2,29
Concentrate I	82	37	118	8,4	---	---
Pure 2.CDI treatment*	---	31	15	3,6	58,5	2,27
Concentrate II	80	35	70	6,5	---	---

*Feed 2 CDI-treatment = produced clean water (pure) of 1. CDI treatment
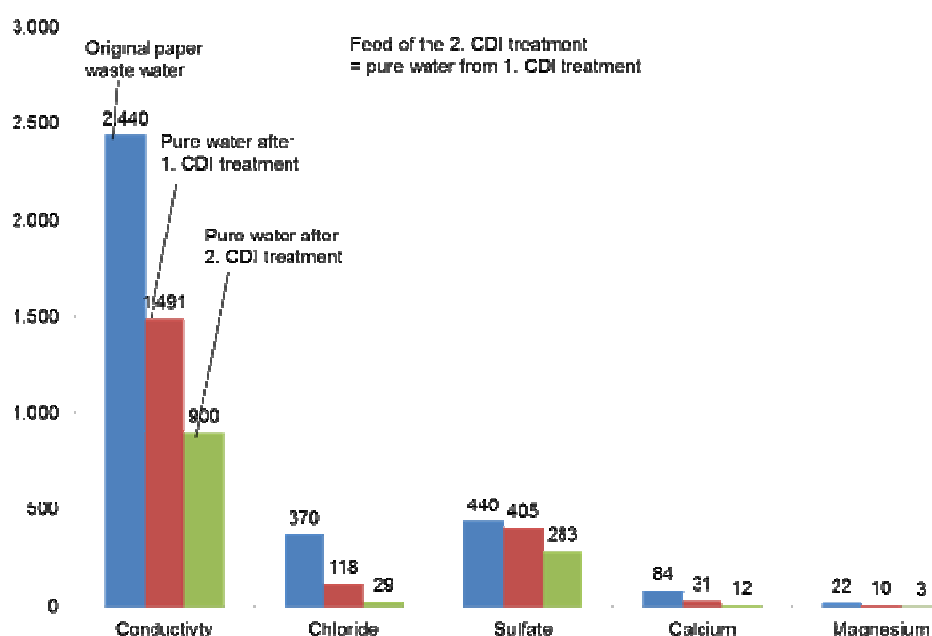
Figure 44: Comparison of feed and pure composition

Before and after the trials, <u>reference trials with tap water</u> have been performed to determine possible interactions between waste water compounds and the membrane respectively the electrodes of the CDI module. A decrease of the removal efficiency of about 3% comparing before and after the trials with the waste water was determined, indicating the formation of a layer in the module. After flushing the module with tap water, the initial removal efficiency was achieved, again.

<u>Summarizing</u>, the CDI is suitable for the removal corrosion and scaling causing components as Cl, Ca and Mg between 57% to 68% with a water recovery of 58.4%. The achieved conductivity was reduced from 2440 µS/cm to 1491 µS/cm and further by a second CDI treatment to minimum 900 µS/cm. A possible long term effect of the COD content of 88 mg/L (limit from manufacture: 50 mg/L short term, 100 mg/L long term) influencing the removal efficiency should be investigated with a larger sample amount (1 m³) in an e.g. 24 h trial. Further on, the CDI is possible to softening the water and to remove PO$_4$ besides the desalting.

The produced <u>concentrates were sent to VVT</u> for trials, investigating the possibility to use the chloride of the concentrate as source for an onsite production of biocide. The preferred chloride content of VVT would be 500 – 1000 mg/L, which is fulfilled by concentrate I (after the first CDI treatment) with 650 mg/L. Further on, possible interactions of the COD and DOC forming components in the concentrate with the biocide production process

5.4. - Performance of Ultrafiltration, Biocontrol concept and Elevated Pressure Sonication to control bacterial activity of bio-treated effluent

5.4.1. - Background and objectives of the study

The European paper industry is strongly reducing their fresh water in-take, in many cases targeting near to zero discharge. At the same time, environmental regulations for example chemical oxygen demand (COD) are tightening. Ever-increasingly, paper mills have to take into consideration alternatives to internal recycling of waters in the process. Reuse of biologically treated effluent as process water is one serious alternative. When there are variations in production rate and PM white water is not available enough, effluent purified by internal purification methods is particularly useful for the stabilization of the water balance.

An activated sludge process is capable of removing more than 90 % of the total suspended solids and dissolved organic material, but does not remove inorganic material efficiently. The brown colour and microbial activity of the biologically treated effluent are major sources of concern for effluent reuse.

The objectives of the study were to compare the performance of Ultrafiltration, Biocontrol concept and Elevated Pressure Sonication (EPS) to control bacterial activity of bio-treated paper mill effluent at laboratory trials.

5.4.2. - Methods

Methods used to compare the performance of Ultrafiltration (UF), Biocontrol concept and Elevated Pressure Sonication (EPS) to control bacterial activity of bio-treated effluent at laboratory trials are presented in this chapter.

5.4.2.1. - Ultrafiltration

In the Valmet Ultrafiltration CR (Cross Rotational) filters, high crossflow and turbulence are created with special rotors between membrane elements causing fouling control. Valmet Ultrafiltration CR is suitable for crossflow microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) studies. In the Valmet Ultrafiltration CR250 test unit used in the study there is two membranes with total filtration area of 0.09 m^2. Between membranes there is a rotor operating at 1000 rpm, which creates turbulence in order to enhance the filtrate capacity and reduce the fouling effect (see Figure 45).

Figure 45: Construction of Valmet Ultrafiltration CR (left), photographs of CR250 (middle) and membrane module opened showing the rotor (right).

In the UF trials, wastewater treatment plant (WWTP) effluent from Essity Nokia mill was filtrated using Valmet Ultrafiltration CR250 -device with Valmet P membranes. Valmet P membranes are made of polyethersulfide (PES), having anionic surface charge in neutral pH. Thus, they are widely used in membrane filtration of pulp and paper process waters.

5.4.2.2. - Elevated Pressure Sonication

Elevated Pressure Sonication (EPS) technology is a low thermal chemical-free technology which uses elevated CO_2 pressure (50-100bar), low temperature (c.40-50°C) and low intensity sonication (20kHz) that has proven in previous studies to achieve up to 6.8 $\log_{10}$ reductions in aerobic and anaerobic bacteria counts in short treatment times (< 30seconds). EPS technology operating at 40-50°C leads to potential reductions in biocontrol and disinfection with low energy input requirements. The EPS lab-scale plant used in the study is presented in Figure 46.

1 CO2/N2 gas cylinder: 2 pumps; 3 heat exchangers: 4 back pressure regulator: 5 mass flow meter: 6 liquids fed tank; 7 ultrasonic controller; 8 ultrasonic probe: 9 Pressure-Ultrasonic sterilizer: 10 sampling vessel: 11 high pressure vessel: 12 waste tank: 13 collector: 14 sterilize bath; 15 gas meter
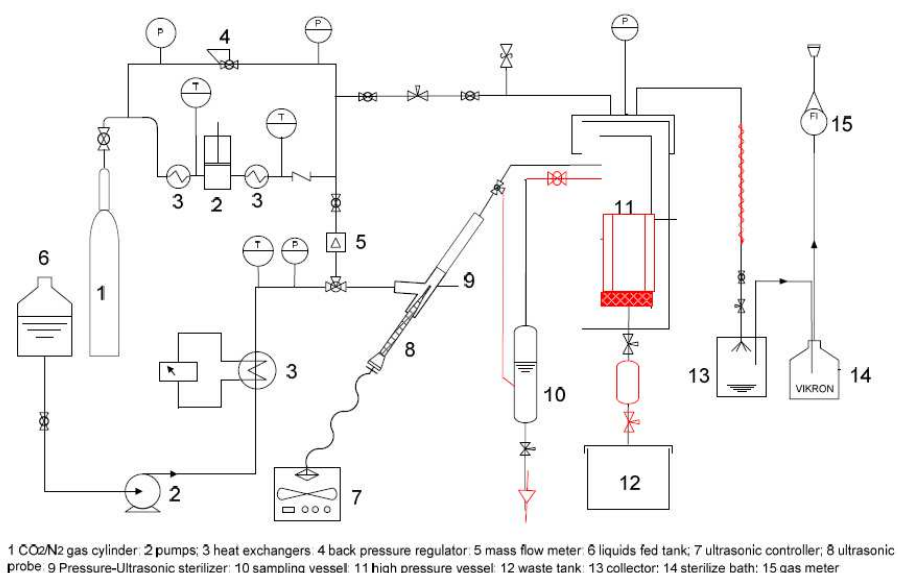
Figure 46: Elevated Pressure Sonication (EPS) lab-scale plant set up.

5.4.2.3. - Biocontrol concept

In biocontrol concept biocide is produced directly on -situ from the salt substances in the process water by electrolysis. Pre concentration of the salts is done with reverse osmosis (RO) or NF membranes (see Figure 47). In this study, two procedures were used: 1. electrolysis of wastewater treatment plant effluent without pre-treatment, and 2. biocide treatment of WTTP effluent with biocide produced from tissue mill white water with Biocontrol concept.

The electrochemical cell EC-Electro MP (Electrocell, Denmark) was employed for electrolysis. It is a modular multipurpose cell intended for process evaluations and experimental tests in laboratory scale. The projected electrode area is 200 cm^2, and the distance between cathode and anode is 3 mm. Titanium was employed as cathode, while DSA (Dimensionally Stable Anode) as anode. DSA is iridium and ruthenium oxide coated titanium. Flow rate in trials was 100 ml/min and current used 4 A.
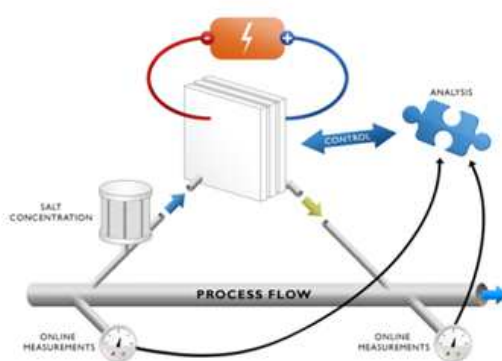
Figure 47: Biocontrol concept.

5.4.3. - Results

5.4.3.1. - Ultrafiltration

In the UF trials, WWTP effluent was filtrated in the concentration mode *i.e.* concentrate was fed back to feed tank and permeate was flowing out from the filter. The filtration data is shown in the *Table 13*.

Variable	Value
Feed volume	58.1 kg
Permeate volume	51.8 kg
Concentrate volume	6.0 kg
Filtration pressure	1.2 - 2,3 bar
Filtration temperature	24 - 29 ºC
Pure water flux before filtration	830 LMH
Flux during filtration	310 → 265 LMH
Pure water flux after filtration	370 LMH
Filtration time	2 h

Table 13: UF filtration data of WWTP effluent.

Physical, chemical and microbial characteristics of the feed sample and UF permeate sample are shown in *Table 14*.

Sample	pH	Conductivity; µS/cm	N_{tot}; mg/L	P_{tot}; mg/L	COD; mg/l	Aerobic bacteria; CFU/mL	Aerobic spores; CFU/mL
WWTP Effluent	7.8	1 020	1.8	< 2	70	300 000	470
WWTP Effluent UF permeate	8.1	990	< 1.0	< 2	47	1 300	< 10

Table 14: Analysis data of WWTP effluent and UF treated WWTP effluent of Essity Nokia mill.

The lab scale UF trials of WWTP effluent from Essity Nokia mill using Valmet Ultrafiltration CR250 -device with Valmet P membranes went well. Flux decrease was only little. However, there was some membrane clogging/fouling, because the pure water flux after filtration was much lower than pure water flux before filtration. UF worked well also in controlling of bacterial activity of bio-treated effluent. Colony Forming Unit (CFU) -values of WWTP Effluent UF permeate was much lower than that of WWTP Effluent.

5.4.3.2. - Elevated Pressure Sonication

Wastewater treatment plant (WWTP) effluent from tissue paper mill was used in the study. The first sample (Sample 2) was a WWTP effluent as such and the second sample (Sample 3) was a permeate of WWTP effluent sample after Ultrafiltration (for details see chapter 5.4.3.1, *Table 14*).

The samples were processed at 50°C temperature and at 50 and 100 bar CO_2 pressure in combination with 30% US power. The main target of the EPS treatment was to achieve several log reductions in aerobic and anaerobic bacteria. The external lab used was unable to conduct anaerobic and spore counts as the species were not known. Therefore, only aerobic counts were determined in the analysis conducted. *Table 15* shows the results of the EPS treatment of the two WWTP effluent samples. It was clearly found that the EPS treatment has resulted in further reduction in bacteria counts in both of the samples provided. The counts have gone from initial 250,000cfu (cfu counted by external lab) down to 130cfu at 50bar/50°C EPS in the WWTP effluent sample. In the UF treated sample, EPS reduced aerobes from 1200cfu to 10cfu at 50bar/50°C EPS treatment. The 100bar/50°C EPS achieved 37cfu in the effluent and <10cfu in the UF sample. This is promising as an initial test condition using EPS treatment on Pulp and Paper industry effluent directly and in combination with UF.

plate counting results								
Sample	Before EPS treatment			Post EPS treatment				
				50 bar			100 bar	
	pH	Aerobic bacteria	Aerobic spores	pH	CFU_{Aero}	Δlg(CFU)	pH	CFU_{Aero}	Δlg(CFU)
Sample 2 WWTP Effluent	7.8 (7.66)	300000 (250000)	470	6.81	130	3.28	6.91	37	3.83
Smaple 3 WWTP Effluent UF Filtrate	8.1 (8.07)	1300 (1200)	< 10	7.21	10	2.08	6.80	<10	3.08

Table 15: Analysis of aerobic counts after EPS treatment by SERE. Before EPS treatment results without brackets are measured at VTT and with brackets by SERE.

The EPS process affected a pH change from alkaline to acidic on the samples during processing due to the injection of supercritical CO_2 (see *Table 16*). However, when pressure returned to ambient, the CO_2 disengageed the effluent and reverted the pH back towards neutrality. There were minor insignificant changes to the conductivity during EPS processing. Both pH and conductivity were measured at ambient conditions.

ID	US Ampl. (%)	P (bar)	T (°C)	pH	T (°C)	Cond (mS)
Sample 2 Starting Material	-	-	-	7.66	19.8	0.999
E-15 (Sample 2 - 50 bar)	30	50	50	5.87	19.5	1.031
E-13 (Sample 2 - 100 bar)	30	100	50	6.28	18.6	1.029
Sample 3 Starting Material	-	-	-	8.07	19.6	0.996
E-16 (Sample 3 - 50 bar)	30	50	50	5.86	20.2	1.013
E-14 (Sample 3 - 100 bar)	30	100	50	5.92	19.9	1.016

Table 16: Test conditions of EPS treatment by SERE.

Figure 48 illustrates the log reduction in aerobic bacteria kill in Sample 2 during EPS processing and compares the untreated sample 2 with 50bar and 100bar EPS conditions. EPS achieved 3.28 $\log_{10}$ reduction at 50 bar and 3.83 $\log_{10}$ reduction at 100 bar.
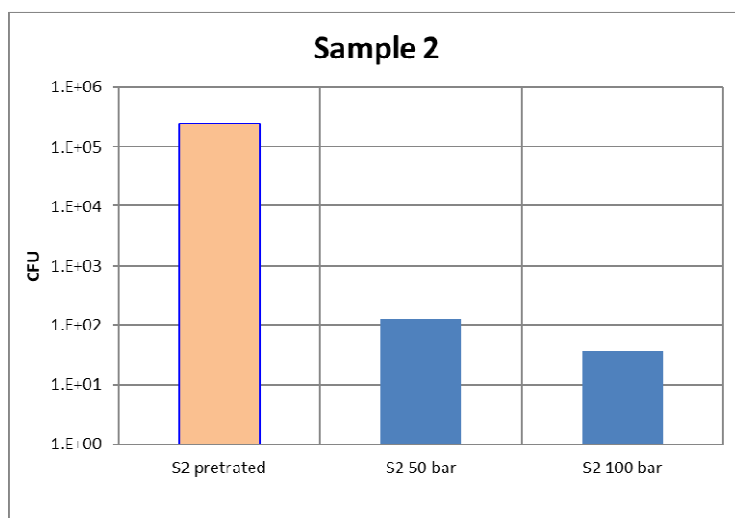
Figure 48 : Log reduction of aerobic bacteria in Sample 2 (WWPT effluent from Tissue paper mill) using EPS treatment.

Figure 49 illustrates the log reduction in aerobic bacteria kill in Sample 3 during EPS processing and compares the UF treated sample 3 with 50bar and 100bar EPS conditions. EPS achieved 2.08 $\log_{10}$ reduction at 50 bar and 3.08 $\log_{10}$ reduction at 100 bar.
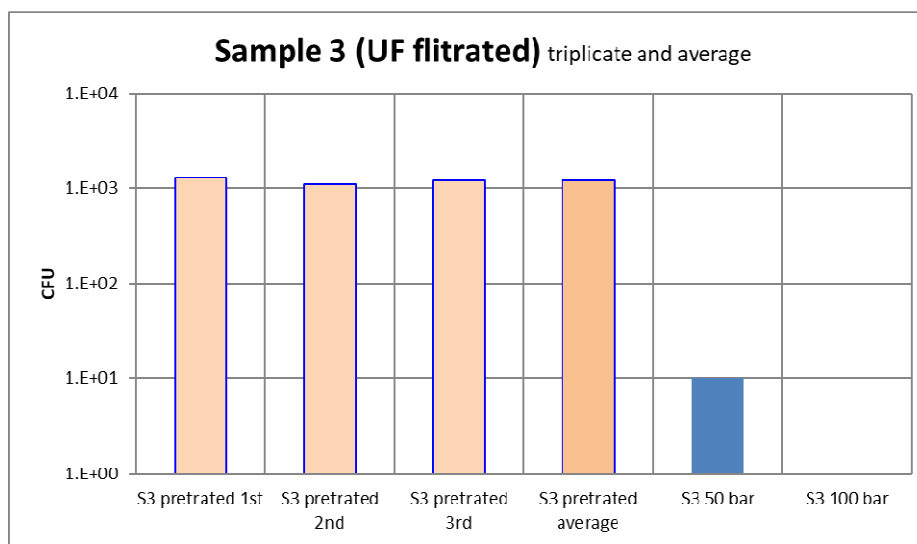

Figure 49 : Log reduction of aerobic bacteria in Sample 3 (Ultrafiltrated WWPT effluent from Tissue paper mill) using EPS treatment

The results are encouraging as the first test for biocidal properties of EPS treatment with Pulp and Paper effluent and potentially integrating opportunities with UF treatment. Although these preliminary tests were not optimized clear aerobic bacteria kills were seen. Further tests are recommended for replicability and reliability as these were one of tests conducted.

5.4.3.3. - Biocontrol concept

In the study, two procedures to control bacterial activity of bio-treated paper mill effluent were used: 1. electrolysis of waste water treatment plant (WWTP) effluent without pre-treatment, and 2. biocide treatment of WTTP effluent with biocide produced from tissue mill white water with Biocontrol concept. Analysis data of WWTP effluent before and after electrolysis is shown in *Table 17*. Direct electrolysis of effluent eliminated microbes efficiently. Effluent pH increased slightly due to formation of NaOH during the electrolysis. Conductivity of the effluent did not change significantly.

Sample	pH	Conductivity	Aerobic bacteria	Spores	Chlorine
		µS/cm	CFU/mL	CFU/mL	mg/L
WWTP effluent	7.8	1090	8000	460	0
WWTP effluent after electolysis	8.3	1030	20	10	28

Table 17: Analysis data of WWTP effluent before and after electrolysis (flow=100 ml/min, current 4A).

Also the biocide treatment of WTTP effluent with biocide produced from tissue mill white water with Biocontrol concept eliminated microbes efficiently (see *Table 18*). For elimination of spore forming bacteria high biocide dosages were needed. Biocide dosages needed are case specific for each mill since both process chemistry and microbiology vary from mill to mill. It is well known that bacterial spores are more resistant to biocides than vegetative cells. Oxidative biocides are able to damage spores preventing their germination. However, a much higher concentration of the biocide is needed for removal of spores, than for removal of vegetative cells.

Biocide dosage Chlorine, mg/l	Aerobic bacteria CFU/mL	Spores CFU/mL
0	1,00E+04	5,80E+02
1	7,30E+03	4,00E+02
2	3,50E+03	3,60E+02
3	4,00E+03	5,70E+02
5	5,80E+02	5,70E+02
10	5,90E+02	5,50E+02
20	9,00E+01	2,00E+01

Table 18: Results of biocide treatment of WTTP effluent with biocide produced from tissue mill white water with Biocontrol concept.

5.4.4. - Summary

Laboratory scale studies showed that all the methods tested (UF, Elevated Pressure Sonication and Biocontrol concept) were efficient in controlling bacterial activity of bio-treated paper mill effluent. In UF trials flux decreased only little. However, some clogging/fouling of membranes was observed, which is normal when filtering biologically treated waters. The EPS results proved the biocidal properties of EPS treatment when using Pulp and Paper effluent. Integrating opportunities of EPS with UF were also found. In the biocontrol studies, both the procedures studied were active in controlling bacterial activity of bio-treated paper mill effluent. However, high biocide dosages were needed for elimination of spores. Process chemistry (chloride concentration, amount of organic material and especially dissolved organics, some transition metals, reductive agents, and pH level) has an impact on performance of Biocontrol concept. The conditions are different in each process and therefore performance should be verified with standardized testing procedures. Optimal microbial control strategy is highly application specific. Optimization of the concept needs to be performed case-by-case at mill scale and techno-economic feasibility of studied technologies needs to be evaluated before mill scale trials.

6. - Water recycling strategies

6.1. - White water ultrafiltration for water recycling (VTT, VAL, SCA)

The motivation of Valmet for the SPOTVIEW project was to propose innovative water management strategies and to develop closed loop recycling and process water reuse. This will be done by combining existing technologies and creating new technologies and taking advantage of the kidney effect (Valmet Ultrafiltration) to produce high quality paper with minimal fresh water, reducing energy demand and valuing recoverable substances. In Figure 50 it is shown the filtration performance of ultrafiltration compared to other separation technologies.
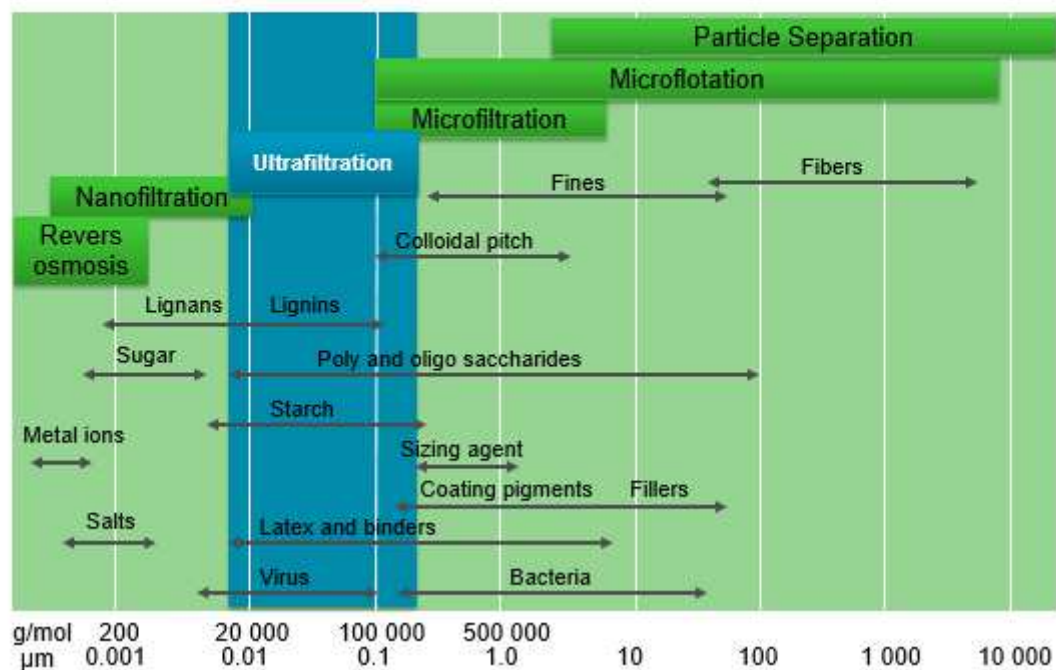

Figure 50: The effect of ultrafiltration compared to other separation technologies.

Presently, the acceptable limits of water circuit closure vary according to production types and raw materials. Efficient water management strategies allow reducing consequences on productivity and environment. Optimisation of fresh water consumptions and rationalisation of recirculation loops of process waters allow to reach a maximum circuit closure without impairing the machine operating conditions and the quality of finished products. To go beyond these specific consumptions while keeping a satisfactory productivity and product quality, it is necessary to combine and to integrate in the circuits existing technologies or systems acting like a "kidney" to recover or eliminate a part of contaminants, which accumulate and limit a more sophisticated circuit closure.

With the Kidneys like Valmet Ultrafiltration the acceptable maximum contaminant concentration levels of paper production line white water are controlled. At the same time, the paper machine's runnability is maintained and production is maximized. The purity requirements of process water are defined by application to be used. With kidneys, the amount of anionic trash, the amount of sticky and micro sticky and the amount of secondary sticky are controlled. With kidneys, also microbial activity is reduced. If necessary, the level of conductivity can also be controlled.

With kidneys, it is also possible to save energy when warm process water is reused instead of cold fresh water. When recycling the warm process water, it is possible to rise up the process water temperature naturally with the process's own thermal energy recovery. The energy review shall also aim to assess the drying energy reduction of the influence of process heat rise and the reduction in operating costs. In every cases, the kidneys need to be optimized and the investment costs minimized.

In the SPOTVIEW project, Valmet Ultrafiltration will be used at Essity Nokia mill in water reuse. Disc filter's clear filtrate from PM7 and Krofta's filtrate from PM9 will be filtrated to be reused in paper machine's wire section high-pressure showers to decrease the fresh water consumption. The use of Valmet Ultrafiltration permeate instead of fresh water reduces the overall water consumption in the tissue-making process and creates savings in the energy used for heating the fresh water. A modern tissue machine consumes 5–15 m³ of water per ton of paper, and Valmet's solution decreases the consumption by 1–2 m³.

6.2. - Reuse of effluents from biological treatment plant (CTP)

6.2.1. - Impact of re-using the effluent on calcium solubility

Previous works have demonstrated the interest of re-using bio-treated effluent in corrugating paper production circuits instead of process water (at constant specific fresh water consumption) to take advantage of the kidney effect of the WWTP to deconcentrate process waters in both organics and (precipitated) inorganics. From the point of view of calco-carbonic equilibrium, bio-effluent has a very high scaling tendency. By mixing this water with aggressive process water, it is possible to reach equilibrium state versus $CaCO_3$. This water management strategy has numerous advantages: lower chemicals addition, lower sludge production, very limited power requirements, and virtually no investment cost. The drawback is the increased WWTP hydraulic capacity required, so that implementation of this solution may not be possible in all mills. Simulations have been performed to determine bio-effluent flow rate to be mixed with process water to reach this equilibrium. We can reasonably think that this strategy leads to a decrease of microbial activity as fewer carbon source will be available.

1. Thanks to the simulation tools, several scenarios could be studied: the bio-effluent has been mixed with process water, in pulper dilution water tank,

2. or in stock preparation filtrate tank,

3. or in paper machine filtrate tank,

4. or in the 3 previous tanks simultaneously.

The flow of bio-treated effluent to be recycled was calculated to reach calcium dissolution equilibrium (SI=0) in process water tank. Figure 51 explains the recycling bio-treated effluent strategies.
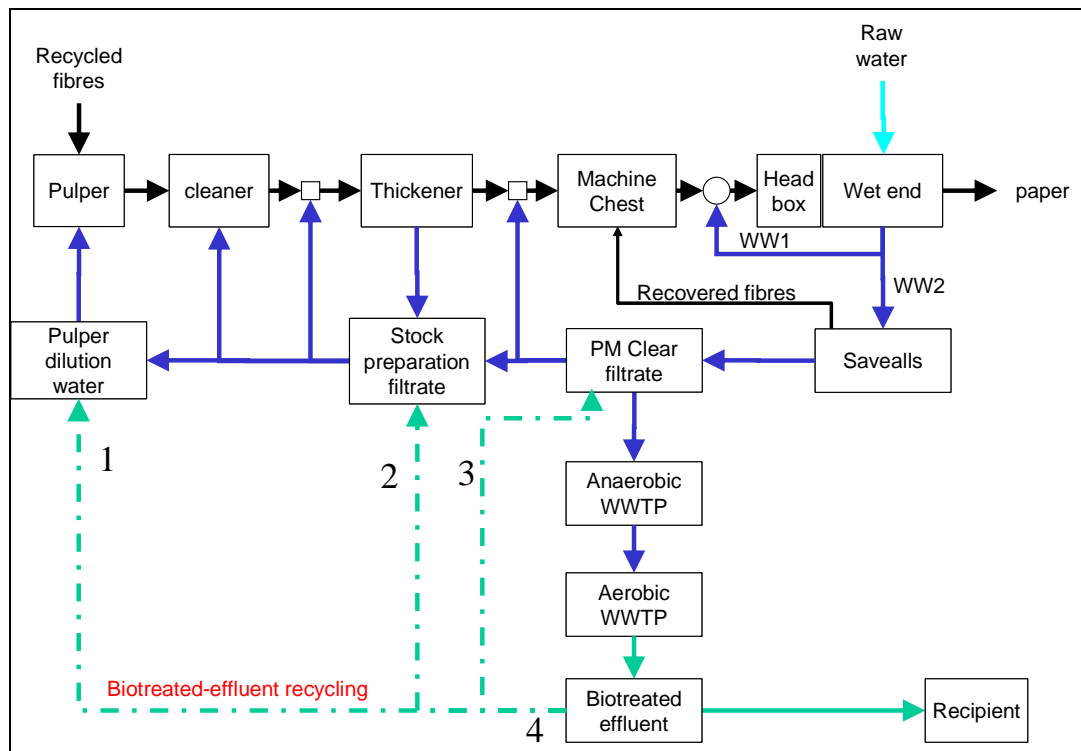
Figure 51   simplified flowsheet of recycling strategies

Simulations were done with the two different hypothesis:

1. hypothesis 1: recycling biotreated-effluent has no effect on bacterial activity and more precisely on VFA production,

2. hypothesis 2: bacterial activity is reduced when biotreated-effluent is recycled: with a reduction of VFA production by 20% and by 60%.

Figure 52 gives the result of the simulations done with the hypothesis 1 and indicates the evolution of concentration of calcium ions in process water when biotreated effluent is recycled in different process water tank considering that the recycling has no effect on bacterial activity.

The results in term of efficiency are good with a large decrease in the Ca release, but the biotreated effluent flows needed to neutralise process waters are quite important. To give an idea, in the simulated case, the waste water treatment plant would have to treat a hydraulic flow up to 5 times higher than its present flow rate. In these conditions, it would be impossible to keep the same WWTP.

Figure 53 gives the result of the simulations done with the hypothesis 2 and indicates the evolution of concentration of calcium ions in process water when biotreated effluent is recycled in main process water tank considering that the recycling decrease bacterial activity.
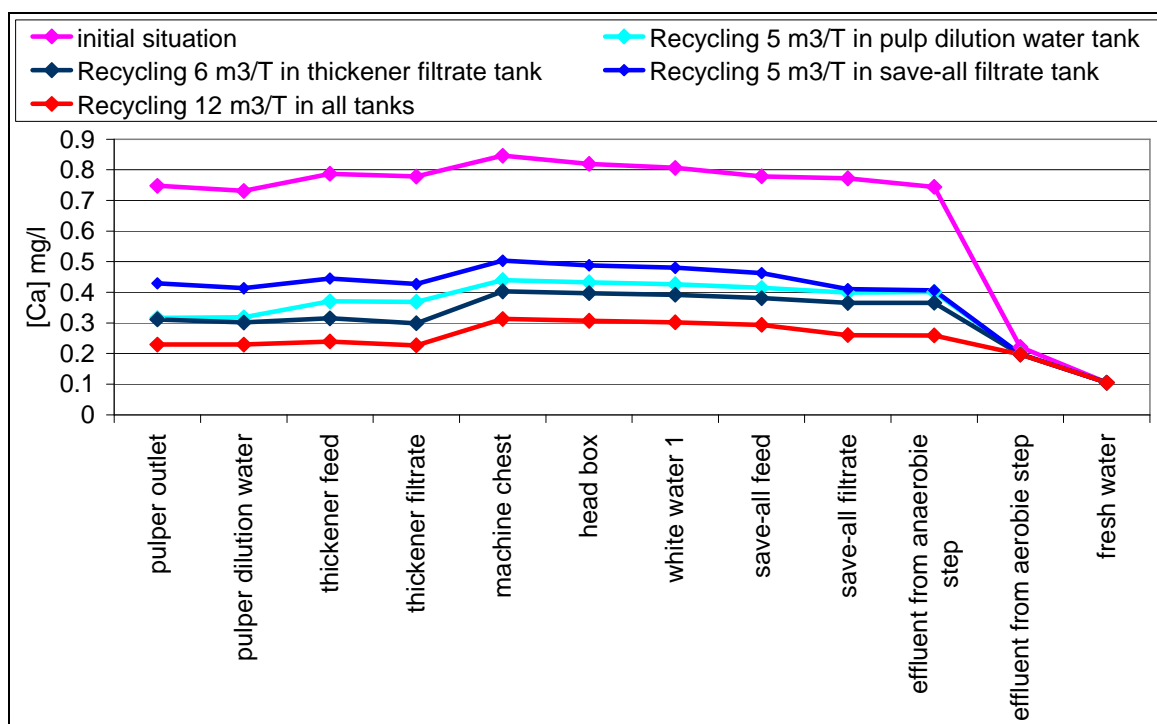
Figure 52   Simulation results: Recycling bio-effluent to process water – hypothesis 1
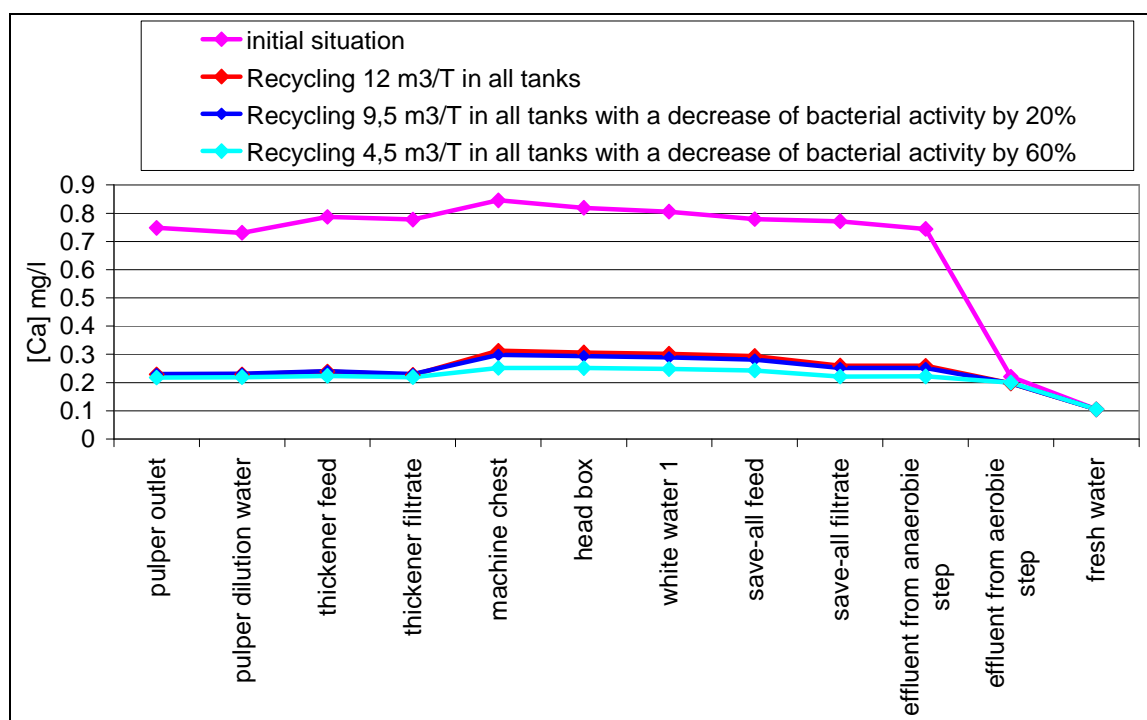

Figure 53   Simulation results: Recycling bio-effluent to process water – hypothesis 2

For the second hypothesis, we suppose that bacterial activity is reduced when bio-effluent is recycled (we have simulated a reduction of VFA production by 20% and by 60%). To "neutralise" the aggressive tendency of the dilution process water, only a lower biotreated-effluent flow has to be recycled in order to have same effect (Figure 53). And then, this practice becomes more realistic versus the flow rate to be recycled.
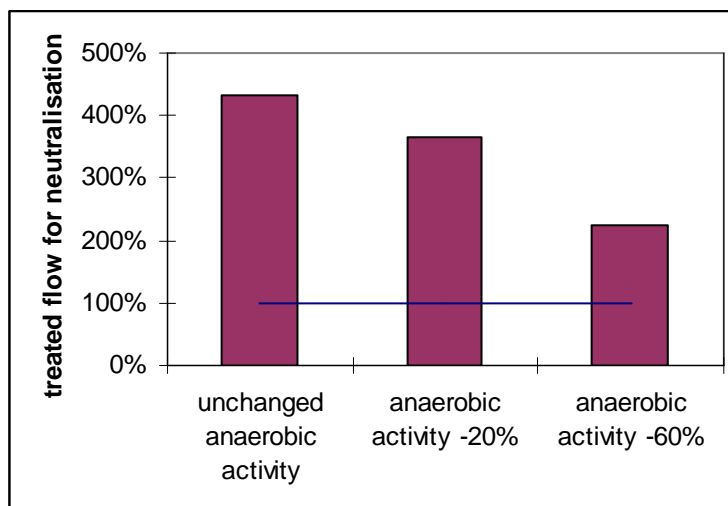
Figure 54. Required increase of the flow to be treated by the WWTP for neutralising dissolution of calcite filler in pulp preparation upon recirculation of the bio-treated effluent (reference treated flow without recirculation = 100%)

These simulations had highlighted the importance to determine the impact of the bio-effluent recycling on the bacterial activity. In the following, laboratory experiments are performed to evaluate this impact.

6.2.2. - Impact of effluent recycling on VFA producing bacteria

6.2.2.1. - Materials & Methods

The impact on bacterial activity which produce VFA when bio-treated effluent is recycled to process water have been studied through the impact on VFA production, the impact on pH decrease and the impact on Calcium release.

Method used: Different mixture of bio-treated effluent and process water coming from an industrial mill, with and without additional carbon source (glucose or paper), have been stored in bottle with lid (not completely airtight because of pH probe), in heated bath to maintain a constant temperature of 35°C. pH evolution has been followed in a continuous way (Figure 56). From time to time, measurement of VFA (as equivalent acetate in meq/L) has been made by a method of acid-base titration and Ca content was measured using Merck 100858 Calcium test.

The bio-treated effluent and process water quality has been first characterised and its saturation index has been calculated thanks to the interface SatIn, developed by CTP in previous project (Huber, Nivelon, Ottenio, *et al.* 2012). As already observed, the clarified water characteristics are the high content of calcium, the low inorganic carbon content and the high VFA content. All of them leading to an aggressive tendency with a negative saturation index versus the calcite. And the typical characteristics of bio-treated effluent are a high inorganic carbon content and low VFA content, leading to scaling tendency with high saturation index versus the calcite.

Using the interface SatIn, we can calculate the mixture ratio of both waters to reach equilibrium versus $CaCO_3$: a mixture of 20% of bio-treated effluent with 80% of clarified water leads to neutral water versus $CaCO_3$.

Figure 55   Method and materials used to study the impact of recycling bio-treated effluent on the anaerobic bacteria activity

Method of acid-base titration to measure Volatile fatty acid concentration (Degrémont method): acidification to pH=3.5 with sulphuric acid, then boiling for 3 min to strip the inorganic carbon, followed by cooling, the amount of VFA (meq/L) is then equal to the required amount of NaOH (meq/L) to dose the filtrate back from pH=4 to pH=7).

6.2.2.2. - Results & discussion

Analysis and measurement done during sCALe sampling campaigns showed that anaerobic microbial activity occurs during pulp and water storage. The first part of our experiments has been devoted to the understanding of impact of mixture on bacterial activity during water storage. The second part concerns pulp storage.

From a theoretical point of view, the anaerobic degradation transforms firstly the organic loads in acids, alcohols, then the acids and alcohols are degraded in CO_2 that is able to be stripped (Figure 56). In water circuits process only acids are present.

Anaerobic degradation involves 2 mechanisms that have opposed effect on the pH: a decrease with the production of acid and an increase with the CO_2 stripping.

Simulated kinetic rates:
• **Acetogenesis : $C_6H_{12}O_6 \rightarrow 3\ CH_3COOH$**
• **Mineralisation : $CH_3COOH + 2\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O$**
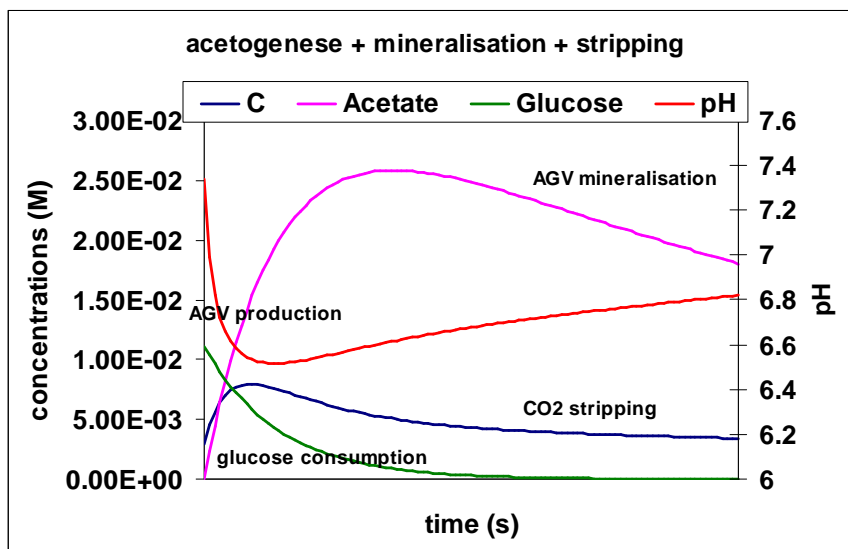• **Stripping : inorganic $C \rightarrow CO_2(g)$**

Figure 56   PHREEQC kinetic simulation: pH, VFA and CO_2 concentration evolution during glucose bacterial degradation

6.2.3. - Conclusions

Anaerobic degradation transforms firstly the organic loads into acids, then the acids are decomposed in CO_2 that is able to be stripped. I.e. anaerobic degradation involves 2 mechanisms that have opposed effect on the pH: a decrease with the production of acid and an increase with the CO_2 stripping. And other phenomena interfere when $CaCO_3$ solid is present, as the pH increases with dissolution of $CaCO_3$. That is the case during repulping of recovered paper:

From the numerous experiments, we can conclude that:

- bio-effluent is not a source of bacteria that produce VFA
- the main source of bacteria producing VFA is the recovered paper
- In process water storage tank, pH increases due to a low bacterial activity and CO_2 stripping
- Recycling bio-effluent to process water to dilute pulp can indeed limit $CaCO_3$ dissolution: with an initial pH higher than in process water, more time is needed to reach critical pH versus $CaCO_3$ dissolution. Also as the anaerobic bacterial activity is lower during the first hours of storage, the Ca release is lower.
- Storage consistency has an impact on the specific VFA production and Ca release, high consistency storage is better as less VFA is produced for a given amount of pulp.

7. - Conclusions and Prospects

In this report, existing and novel technologies were evaluated for the treatment and reuse of process water and WWTP effluents, in order to achieve industrial water quality in terms of suspended solids, colloids, salinity and total flora, and to replace fresh water usage for specific or general application (PM showers, additives dilution, pulp dilution…).

The main limitations addressed when recycling process water and effluents are the potential risk of organic, inorganic deposit in various locations of the process, nozzle clogging, process additives perturbation. These limitations can be successfully overcome by the various technologies tested or evaluated (ultrafiltration, deionization of alternative disinfection).

The needs for implementing new water treatment technologies and water recycling strategies highly depend on the situation of each paper mill regarding production grade, raw materials and chemical used, as well as water reduction objectives. The additional water treatment requirement in terms of quality and capacity will be examined in more details by modelling different scenario during WP3, on the basis of the two examples paper mills. The environmental and economic impact of the new water management strategies will be assessed and compared in parallel in WP5.

8. - References

- 69 -

9. - Annexes

Contribution of raw materials: Results analyses of different raw materials pulped in deionised water at laboratory scale
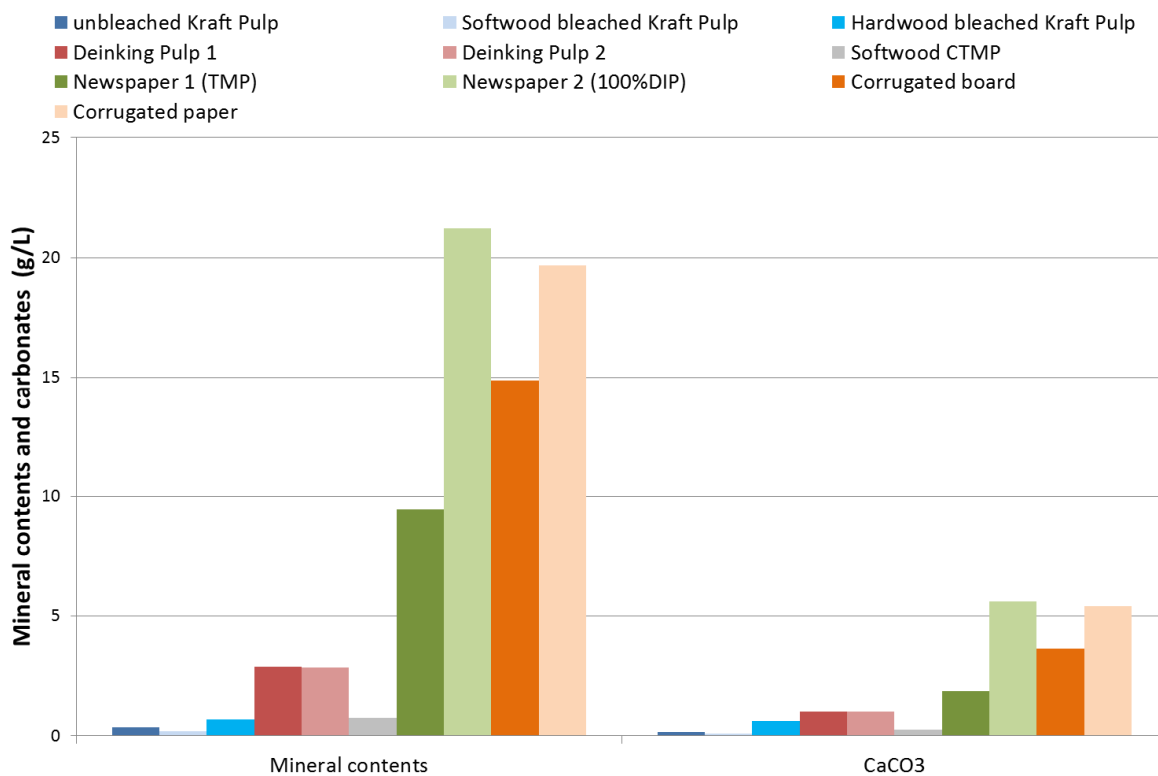
- Mineral content and carbonates in pulp fraction:

Figure 57: Mineral content and carbonates in pulp fractions
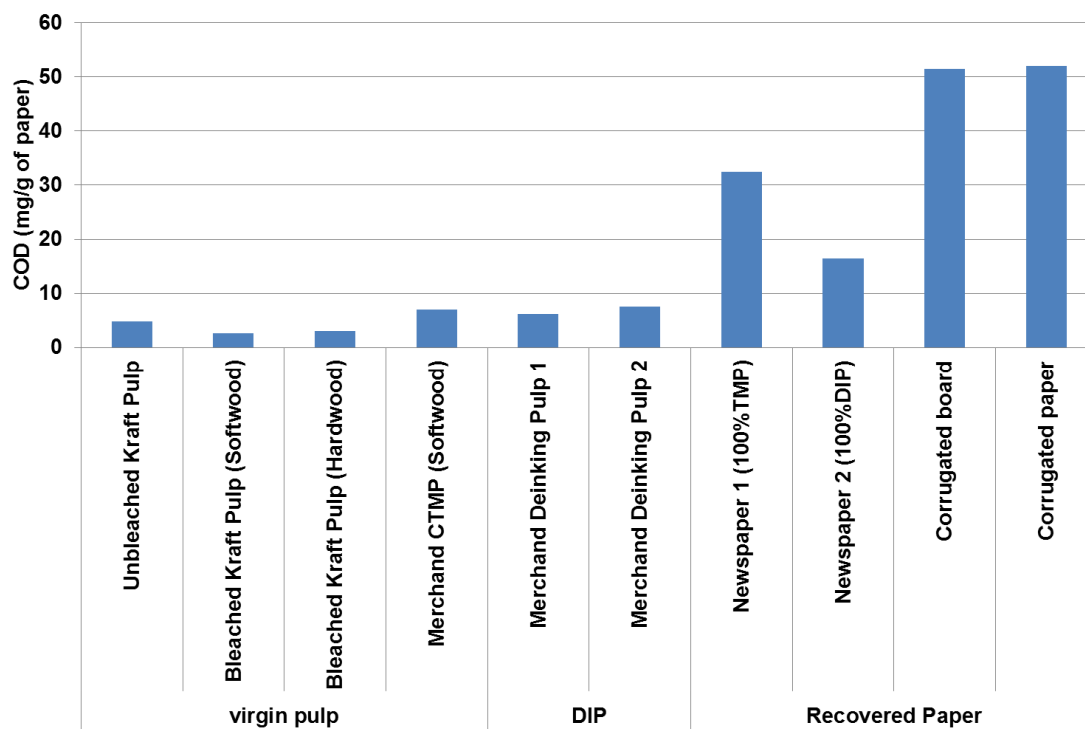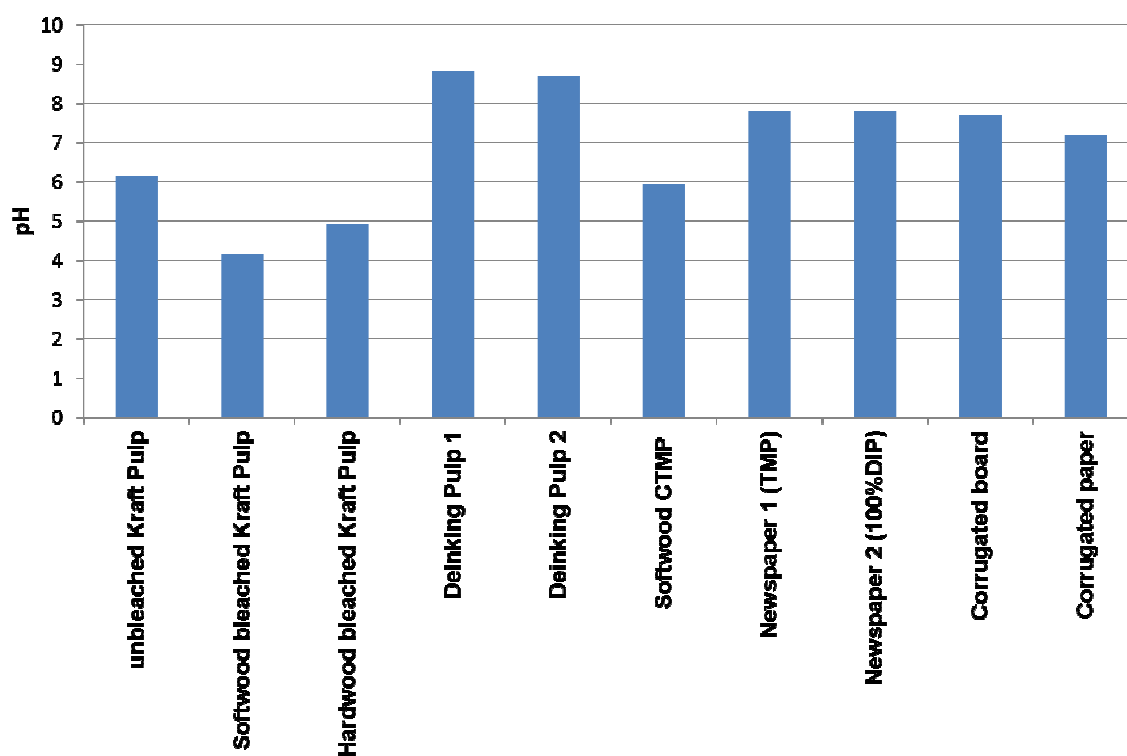
- COD and pH in water fraction:

Figure 58: COD in water fractions

Figure 59: pH of water fractions