

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY  
Faculty of Technology  
Department of Chemical Technology

*Konstantin Gabov*

**THE EFFECT OF PULP WASHING ON BLEACHING EFFICIENCY**

Examiners: Professor Kaj Henricson  
M.Sc. (Tech.) Tiina Nokkanen

Supervisors: Professor Kaj Henricson  
Senior Researcher Matti Ristolainen, PhD

## **ABSTRACT**

Lappeenranta University of Technology  
Faculty of Technology  
Degree Program of Chemical Technology

Konstantin Gabov

### **The effect of pulp washing on bleaching efficiency**

Master's thesis

2009

91 pages, 42 figures, 44 tables and 4 appendices

Examiners: Professor Kaj Henricson  
M.Sc. (Tech.) Tiina Nokkanen

Keywords: bleaching, bleaching efficiency, COD, concentrate, ultrafiltration, washing.

The main aim of this study was to inspect the influence of the ultrafiltration implementation on the washing and on bleaching efficiency. Four cases corresponding to four washing stages were observed: two with hardwood pulp and two with softwood pulp; each case had a reference and a trial experiment.

The experiments with hardwood pulp were arranged in a manner to explore predominantly the possibility of bleaching performance improvement by applying for washing instead of untreated filtrate (reference case) the same treated one (trial case). Despite that the ultrafiltration reduced the COD of the wash filtrates allowing the decreasing of COD carry-over to the bleaching stage it didn't affect the bleaching performance.

Another set was used in the experiments with softwood pulp. It implied the ultrafiltration and recirculation of the filtrate to the same washing stage with the purpose to reduce the volumes and pollution of the bleaching effluents. In one case the negative result was obtained which was expressed by worse parameters of the pulp after bleaching. Another case showed the opportunity to replace hot water with the filtrate and reduce the fresh water consumption.

## **ACKNOWLEDGEMENT**

At the beginning I would like to express my thanks to UPM Company for such interesting topic and for providing me with all meanings necessary to make this thesis. A great gratitude is addressed to my supervisors: professor Kaj Henricson, senior researcher Matti Ristolainen and Tiina Nokkanen for their aid to make proper decisions and for the advices which helped me to write the thesis. Separately, I want to thank portfolio manager Esa Hassinen and researcher Kati Eskelinen who have greatly participated in this work.

In addition, I express a deep appreciation to people, who provided me with the information necessary for my work and to those who answered on my questions and helped me to make out some points. Among them are Mr. Timo Tidenberg, Mr. Andreas Rönqvist, professor Esa Vakkilainen and Mr. Tervola Pekka. Special thanks to the laboratory technicians for their assistance with experiments and analysis.

Finally, I would like to express the best thanks to my parents and to my friends for their support and attention.

Lappeenranta, 2009

Konstantin Gabov

## TABLE OF CONTENTS

1 INTRODUCTION.....	9
LITERATURE REVIEW.....	11
2 PULP BLEACHING REAGENTS .....	11
2.1 Chlorine dioxide.....	11
2.1.1 Properties .....	11
2.1.2 Treatment with chlorine dioxide.....	12
2.1.3 Reactions of chlorine dioxide with lignin.....	14
2.2 Sodium hydroxide.....	21
2.2.1 Properties .....	21
2.2.2 Alkaline treatment.....	21
2.2.3 Reactions of lignin during alkaline extraction .....	22
2.2.4 Oxidant-reinforced treatment.....	26
2.3 Hydrogen peroxide.....	29
2.3.1 Properties .....	29
2.3.2 Treatment with hydrogen peroxide.....	30
2.3.3 Reactions of hydrogen peroxide with lignin.....	32
3 WASHING .....	36
3.1 Principles of washing .....	36
3.2 Washing parameters.....	38
3.3 Washing equipment .....	41
3.3.1 Vacuum drum washers.....	42
3.3.2 Pressure washers .....	44
3.3.3 Wash presses.....	46
4 MEMBRANE SEPARATION TECHNOLOGY.....	48
5 THE COMPOSITION OF BLEACHING FILTRATES.....	52

EXPERIMENTAL PART .....	57
6 LABORATORY EXPERIMENT .....	57
6.1 Sampling of pulps and filtrates .....	57
6.1.1 Hardwood line.....	57
6.1.2 Softwood line.....	57
6.2 Ultrafiltration .....	58
6.3 Washing and bleaching.....	60
6.3.1 Washing .....	61
6.3.2 Bleaching .....	62
6.4 Analysis of pulp .....	64
6.5 Analysis of filtrates .....	64
7 RESULTS AND DISCUSSIONS .....	66
7.1 Ultrafiltration .....	66
7.2 Washing .....	69
7.3 Analyses of pulps.....	71
7.3.1 Hardwood pulp .....	71
7.3.2 Softwood pulp.....	72
7.4 The effect of ultrafiltration on bleaching efficiency .....	73
7.4.1 Hardwood pulp .....	73
7.4.2 Softwood pulp.....	74
7.5 Analysis of filtrates .....	76
7.6 COD reduction of bleaching effluents .....	79
7.6.1 Hardwood line.....	79
7.6.2 Softwood line.....	80
7.7 Utilization of the concentrates .....	81
8 CONCLUSIONS .....	88
REFERENCES.....	89
APPENDICES .....	92

## LIST OF FIGURES

Figure 1. Sequences for the reaction of chlorine dioxide with phenolic rings in lignin	16
Figure 2. Reactions of chloride dioxide with non-phenolic rings in lignin .....	18
Figure 3. Reaction of chlorine dioxide with ring-conjugated ethylenic groups.....	20
Figure 4. Neutralization of lignin-derived acidic functional groups in prebleached pulps .....	23
Figure 5. Base-catalyzed elimination of organically bound chlorine .....	24
Figure 6. Base-catalyzed condensation of methoxy-p-benzoquinone.....	25
Figure 7. Kappa number and lignin content of bleached pulps .....	26
Figure 8. Brightness ceiling data comparing the different alkaline extraction conditions (the curves for the data are freehand made for visualization).....	27
Figure 9. Sequences for the oxidation of phenolic lignin units to oxirane (A), muconic acid (B) and carbonyl structures .....	28
Figure 10. Sequence for the reaction of oxygen with carbonyl-conjugated structures .	29
Figure 11. Effect of temperature and retention time on brightness in pressurized peroxide bleaching (Kvaerner).....	30
Figure 12. Phases in peroxide bleaching process.....	31
Figure 13. Reaction of hydroperoxide anions to quinoid structures and to side-chain enone structure .....	34
Figure 14. Dakin reaction at the C <sub>α</sub> -keto group of phenolic unit.....	35
Figure 15. Schematic diagram of dilution/extraction washing .....	36
Figure 16. Schematic diagram of displacement washing.....	37
Figure 17. Schematic representation of washer .....	38
Figure 18. Vacuum drum washer (Ingersoll-Rand) .....	43
Figure 19. GasFree Filter (Andritz) .....	44
Figure 20. Diagram of Compaction Baffle filter (Ingersoll-Rand).....	45
Figure 21. DD washer (Ahlstrom Kamyrr Inc) .....	46
Figure 22. The Metso TwinRoll press .....	46
Figure 23. Schematic representation of membrane.....	48
Figure 24. RI chromatogram for untreated bleach plant total alkaline and acid effluents.....	54
Figure 25. RI chromatogram for untreated bleach plant total alkaline effluent, EOP filtrate, E2 filtrate and permeate after ultrafiltration of total alkaline effluent .....	54

Figure 26. COD characterization .....	55
Figure 27. Cross-Rotational filter CR200 .....	58
Figure 28. The sketch of membrane installation.....	59
Figure 29. The sequence of experiments.....	60
Figure 30. Laboratory washing equipment. ....	62
Figure 31. Permeability and volume reduction factor during the ultrafiltration of EOP and EP filtrates .....	67
Figure 33. Permeability and volume reduction factor during the treatment of D <sub>1</sub> “dirty” filtrate .....	68
Figure 32. Permeability and volume reduction factor during the ultrafiltration of PO “dirty” filtrate.....	68
Figure 34. Average permeability of filtrates during the treatment.....	69
Figure 35. COD values of feeds, permeates and concentrates. ....	76
Figure 36. TOC values of feeds, permeates and concentrates. ....	76
Figure 37. Total chlorine values of feeds, permeates and concentrates.....	77
Figure 38. Dry solids content of the feeds, permeates and concentrates. ....	77
Figure 39. Gross calorific value of concentrates and average values for Nordic black hardwood and softwood liquors .....	82
Figure 40. Total chlorine content in concentrates and average values for black liquor from Scandinavian wood.....	83
Figure 41. Potassium content in the concentrates and the average values for black liquor from Scandinavian wood .....	85
Figure 42. Dry solids content of concentrates and average value for black liquor.....	85

## LIST OF TABLES

Table 1. Properties of chlorine dioxide .....	12
Table 2. Conditions of D <sub>0</sub> bleaching stage.....	13
Table 3. Conditions of D <sub>1</sub> and D <sub>2</sub> bleaching stages .....	14
Table 4. Concentration of sodium hydroxide in water at different temperatures .....	21
Table 5. Typical alkaline extraction stage conditions.....	22
Table 6. Typical conditions in pressurized peroxide bleaching (Sunds Defibrator) ....	32
Table 7. Typical washer loading factors and drum dimensions.....	42
Table 8. Driving forces of some membrane processes .....	49
Table 9. Comparison of micro-, ultra-, nanofiltration and reverse osmosis .....	50
Table 10. Results of analysis of bleach plant effluents before waste treatment .....	53
Table 11. Conversion factors used in the COD characterization.....	55
Table 12. Measured parameters of hardwood pulp samples .....	57
Table 13. Measured parameters of softwood pulp samples .....	57
Table 14. Conditions of the membrane treatment.....	59
Table 15. List of experiments with hardwood pulp .....	61
Table 16. List of experiments with softwood pulp .....	61
Table 17. Conditions of EOP stage (experiments 1 and 2).....	63
Table 18. Conditions of D <sub>1</sub> stage (experiments 3 and 4) .....	63
Table 19. Conditions of PO stage (experiments 5 and 6) .....	63
Table 20. Conditions of D <sub>2</sub> stage (experiments 7 and 8) .....	64
Table 21. Methods for pulp analysis .....	64
Table 22. Time and operating power of microwave oven during preparation of the samples for total chlorine analyses .....	65
Table 23. Volumes of feeds, permeates and concentrates, and volume reduction factors .....	66
Table 24. Average pure water permeability and flux reduction.....	67
Table 25. COD and volumes of liquid streams around the washer and average values of washing parameters.....	70
Table 26. Viscosity, kappa number and brightness of pulp in different points of experiments 1 and 2 .....	71
Table 27. Viscosity, kappa number and brightness of pulp in different points of experiments 3 and 4 .....	71

Table 28. Viscosity, kappa number and brightness of pulp in different points of experiments 5 and 6 .....	72
Table 29. Viscosity, Kappa number and brightness of pulp in different points of experiments 7 and 8 .....	73
Table 30. COD values of liquid in pulp suspension coming to bleaching and pulp parameters after bleaching, experiments 1 and 2 .....	73
Table 31. COD values of liquid in pulp suspension coming to bleaching and pulp parameters after bleaching, experiments 3 and 4 .....	74
Table 32. COD values of liquid in pulp suspension coming to bleaching and pulp parameters after bleaching, experiments 5 and 6 .....	75
Table 33. Metal content in D <sub>1</sub> “dirty” permeate and D <sub>2</sub> “dirty” filtrate.....	75
Table 34. COD values of liquid in pulp suspension coming to bleaching and pulp parameters after bleaching, experiments 7 and 8 .....	75
Table 35. Reduction of TOC, COD, total chlorine and dry solids content in the filtrates by the ultrafiltration; hardwood line .....	78
Table 36. Reduction of TOC, COD, total chlorine and dry solids content in the filtrates by the ultrafiltration; softwood line.....	78
Table 37. Reduction of COD load per ton of pulp when treating the effluent to the waste water treatment plant and the stream to the D <sub>0</sub> washer .....	80
Table 38. COD reduction by the treatment of the EP filtrate coming to the EOP washer .....	80
Table 39. Reduction of COD load of the bleaching effluents for softwood line .....	81
Table 40. Some non-process elements and their impact on pulp mill’s processes .....	81
Table 41. Volumes of the concentrates which can be fed to recovery boiler .....	84
Table 42. Molar ratio between sodium and chlorine.....	84
Table 43. Energy required for evaporation of concentrate-black liquor mixture to 80 % .....	86
Table 44. Increasing energy consumption for evaporation when decreasing the dry matter content of black liquor from 15 % .....	87

## LIST OF ABBREVIATIONS

### Abbreviations

AOX	Absorbable Organic Halogens
BOD	Biological Oxygen Demand
C	Chlorination stage
CBF	Compaction Baffle Filter
COD	Chemical Oxygen Demand
D (D <sub>0</sub> , D <sub>1</sub> and D <sub>2</sub> )	Chloride dioxide treatment (the numerals are related to position of the stage in bleaching sequence)
DCF	Discharge Correction Factor
DD washer	Drum Displacement washer
DF	Dilution Factor
DR	Displacement Ratio
E (E <sub>1</sub> and E <sub>2</sub> )	Alkaline extraction stage (positions in bleaching sequence)
ECF bleaching	Elemental Chlorine Free bleaching
EDR	Equivalent Displacement Ratio
EO	Alkaline extraction stage with addition of oxygen
EOP	Alkaline extraction stage with addition of oxygen and hydrogen peroxide
EP	Alkaline extraction stage with addition of hydrogen peroxide
F	Filtrate
FR	Flux Reduction
H	Hypochlorite treatment stage
HMWC	High Molecular Weight Compounds
HW	Hardwood
ICF	Inlet Correction Factor
LMWC	Low Molecular Weight Compounds
MWCO	Molecular Weight Cut-Off
O	Oxygen delignification stage
PCDD	Polychlorinated Dibenzo-p-Dioxins
PCDF	Polychlorinated Dibenzofurans

PVDF	Polyvinylidenedifluoride
PWP <sub>a</sub> , PWP <sub>b</sub>	Pure Water Permeability after and before ultrafiltration
SW	Softwood
TCF bleaching	Total Chlorine Free bleaching
VRF	Volume Reduction Factor
WL	Wash Liquor

### Latin letters

$c_F, c_{in}, c_{out}, c_{WL}$	Concentration of solutes in discharging filtrate, in liquid of entering pulp stream, in liquid of leaving pulp stream and wash liquor
$c_f, c_p$	Concentration of dissolved materials in feed and permeate
E	Norden efficiency factor
$L_{in}, L_{out}$	Amount of liquid in inlet and outlet pulp suspension
$N_{in}, N_{out}$	Inlet and outlet consistency of pulp suspension
P	Amount of oven-dry pulp
R	Wash liquor ratio
R	Rejection coefficient
$V_f$	Volume of feed
$V_p$	Volume of permeate
W	Weight liquor ratio
$x_A, x_B$	Concentration of components A and B in feed
Y	Wash yield
$y_A, y_B$	Concentration of components A and B in permeate

### Greek letters

$\alpha_{A/B}$	Separation factor for two components A and B
----------------	--

## 1 INTRODUCTION

Bleaching is an important process in bleached pulp manufacture. The main aim of this procedure is to increase the brightness of pulp by the destruction and removing of the coloured materials, mainly residual lignin and its chromophores. Since a cooking is no more selective process after certain time and the extensive degradation of carbohydrates begins to occur the chemicals with the high selectivity towards the wood components have to be applied to remove the rest of the non-carbohydrate components from pulp.

Until recent, molecular chlorine was used widely in bleaching sequences, due to its good selectivity and relatively low price [1]. Later it was found that the treatment with chlorine affords chlorinated organic materials which are harmful for environment, among them dioxins are especially dangerous for the biosphere. This was the reason of declining of the chlorine application in bleaching process. Mills tended to implement the new environmental friendly technologies of ECF (Elemental Chlorine Free) and TCF (Total Chlorine Free) bleaching sequences. In the TCF sequences oxygen-containing reagents such as oxygen, hydrogen peroxide, ozone, *etc.* are involved. The ECF schemes include also chlorine dioxide treatment.

Some other measures have been taken to reduce the negative impact of pulp and paper mills on the environment, among them the introduction of oxygen delignification, extended delignification in cooking, oxidant-reinforced alkaline treatment, the installation of more efficient washing facilities, *etc.* The higher reduction of kappa number of pulp in the closed part of the fiberline the lower BOD (Biological Oxygen Demand), COD (Chemical Oxygen Demand), colour and AOX (Absorbable Organic Halogens) of the effluents from open part [2]. For example, lower kappa number of the pulp fed to bleaching plant causes less pollution of the bleaching effluents.

Last decade new restrictions, legislations and also own needs pushed pulp and paper mills towards the decreasing of volume of discharged waste water, particularly from bleach plant, which led to closing up the mills and recirculation of process water. In case of bleaching the degree of closing affects the cleanness of wash liquor in bleach plant due to accumulation of inorganic and organic materials. The use of dirtier wash

water can influence the pulp properties or the higher consumption of the bleaching chemicals in the succeeding bleaching stage [3]. Therefore, some technique needs to be installed to improve the reuse of water within the mill and bleach plant.

A membrane technology can serve to that purpose; acting as a “kidney”, a membrane unit will remove the part of accumulated materials, possibly improving a bleaching performance. In addition, reducing the pollution and volume of the effluents it will be possible to decrease the load of the water treatment plant [4].

## LITERATURE REVIEW

### 2 PULP BLEACHING REAGENTS

#### 2.1 *Chlorine dioxide*

##### 2.1.1 *Properties*

Chlorine dioxide is unstable in the gaseous state, in the liquid state and as a concentrated water solution, it explodes under the heating; the explosion also can occur under the influence of light, electric spark or with the presence of some organic substances. Therefore, it must be manufactured on-site and stored as 1 % water solution. As the solution it can be kept for several months at the low temperature (5 °C) and in the dark place. [1, 5]

The concentration of chlorine dioxide in the gas phase must be controlled during its production, handling and storage. The partial pressure of chlorine dioxide in gas phase must be below 100 mmHg, for that the dilution with air or combination of steam and vacuum can be used to decrease the partial pressure. At the pressure of 100 mmHg and at the temperature of 40-70 °C (as a typical process temperature), chlorine dioxide is steady for approximately 5 seconds; it is enough for the transportation of chlorine dioxide from the generator to the absorber that takes 0.5 second. [1] The properties of chlorine dioxide are represented in Table 1.

**Table 1.** Properties of chlorine dioxide [1]

Chemical formula	ClO <sub>2</sub>
Molecular weight, g/mol	67.45
Colour	Greenish-yellow gas at the normal conditions, which is transferred in very explosive reddish-brown liquid under cooling;
Density, kg/m <sup>3</sup>	3
Solubility in water	About 10 g per litre (at 5 °C)
Temperature of – boiling, °C – melting, °C	9.7 -59
Stability	Decomposes to chlorine and oxygen with noise, heat, flame, and a minor pressure wave at low concentrations (puff). At partial pressure higher than 300 mmHg decomposes with explosion
Health Hazards	Concentration of 0.1 ppm is permissible during 8 hours Smell of chlorine dioxide is sensed in air at 17 ppm; At 45 ppm it irritates eyes and nose.

### ***2.1.2 Treatment with chlorine dioxide***

Chlorine dioxide began to be used as an industrial bleaching reagent after World War II with the availability of manufacturing process from sodium chlorate and the corrosion-resistant materials for implementation of that process. At the first time, chlorine dioxide was applied at the last or near the last stages of bleaching sequences, i.e. C-E-H-D, C-E-H-D-E-D or C-E-D-E-D. Then, when it was discovered that characteristics of final pulp can be improved by the partial substitution of chlorine with chlorine dioxide, the last started to be applied in the delignification stage. [6]

With the course of time, it was found that the using of molecular chlorine in pulp bleaching produces chlorinated compounds, including extremely dangerous polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF); and amount of these substances depends on the consumption of molecular chlorine in the first delignification stage. This became a cause for the introducing of the new regulations that limited the amount of chlorinated organic substances discharged from the bleaching plant. On the other hand, it had been proved that the treatment with chlorine dioxide affords fewer amounts of chlorinated compounds. Considering this environmental aspect, a good selectivity with respect to wood compounds, the quality

and strength properties of bleached pulp, chlorine dioxide had become a very popular bleaching chemical instead of molecular chlorine. [6]

Chlorine dioxide is used in the first stages as a delignifying reagent, decomposing lignin and reducing kappa number. The kappa number after chlorine dioxide treatment and alkaline extraction can be decreased from 12-18 to 3-5 for softwood kraft pulp undergone oxygen delignification and for non-oxygen delignified pulp from 22-28 to 4-6. The typical industrial conditions of D<sub>0</sub> stage are represented in Table 2. [7]

**Table 2.** Conditions of D<sub>0</sub> bleaching stage [7]

Final pH	1.5-2.5
Temperature, °C	40-60
Pulp consistency*, %	10-15
Time, min	30-80
Pressure	Atmospheric
Charge factor	1.0-2.0 times the kappa number, calculated as kg of active chlorine per ton of pulp

\*in old designed mills consistency is 3-4%.

Chlorine dioxide is also applied in the later stages. Typically, the treatment with chlorine dioxide divides into two parts, designated as D<sub>1</sub> and D<sub>2</sub>, with an intermediate alkaline extraction or washing. If two stages are consecutive without extraction the final pH at the end of the D<sub>1</sub> may be adjusted to alkaline. [7]

As it can be viewed from Table 3, the conditions of the D<sub>1</sub> and D<sub>2</sub> are almost the same; except that the temperature is usually slightly higher in the second stage and the retention time is slightly longer, but due to low lignin content at the end of bleaching the chemical charge is lower [7].

**Table 3.** Conditions of D<sub>1</sub> and D<sub>2</sub> bleaching stages [7]

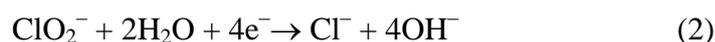
Parameter	Stage	
	D <sub>1</sub>	D <sub>2</sub>
Final pH	3.5-5	3.5-5
Temperature, °C	55-75	60-85
Pulp consistency, %	10-15	10-15
Time, min	120-240	120-240
Pressure	Atmospheric	Atmospheric
Charge	Usually 4-6 times the kappa number after the extraction stage, calculated as kg active chlorine per t of pulp charged to the D <sub>1</sub> and D <sub>2</sub> stages (D <sub>1</sub> / D <sub>2</sub> charge ratio is usually 2/1-3/1)	

### 2.1.3 Reactions of chlorine dioxide with lignin

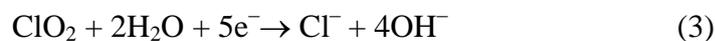
Chlorine dioxide has nine paired electrons and one unpaired, therefore it is considered as a free radical. The redox potential according to the reaction (1) is 0.954 V. it depends on the pH decreasing by -0.062 V if pH increases by one unit.



Another significant part of the reaction is



The redox potential is 0.76 V. So, the total reaction of chlorine dioxide reduction can be written as follows:



According to the reaction (3) the equivalent weight of chlorine dioxide is 13.5 (calculated as 67.5/5). The equivalent weight of chlorine can be calculated as 71/2 basing on the reaction:

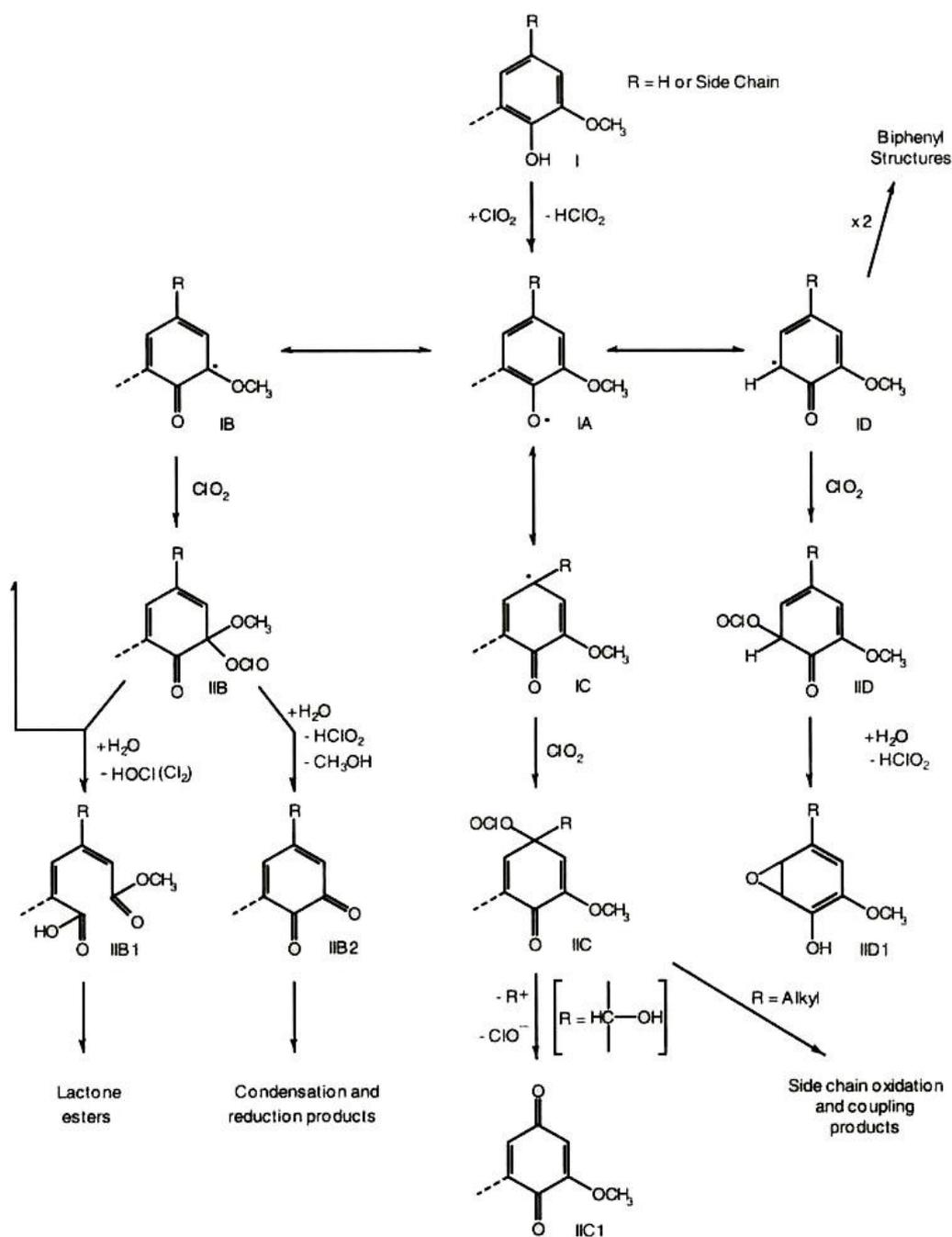


These figures are used for the conversion of chlorine dioxide into active chlorine equivalents considering the equal electron transferring. One weight unit of chlorine

dioxide is equivalent to 2.63 weight units of chlorine (35.5/13.5). This is considered during the calculation of chlorine substitution with chlorine dioxide. [1, 6]

Chlorine dioxide attacks the lignin sites with the high electron density, such as benzene ring of phenolic and non-phenolic units, and ring-conjugated ethylenic groups. There are two basic types of the reactions occurring during chlorine dioxide delignification – oxidation and aromatic chlorine substitution. [1]

**Reactions with phenolic units** (Figure 1). Chlorine dioxide in acid media oxidizes phenolic units with the formation of phenoxy radical (IA in Figure 1) and its resonance forms (IB-ID). The further reaction of chlorine dioxide with these forms produces chlorous acid esters which are converted through the reactions of the elimination to o-benzoquinones or the corresponding catechols, p-benzoquinones, muconic acid monomethyl esters or their lactone derivatives and oxirane structures. The structures IIB1 are oxidized further to dicarboxylic acid fragments. The reaction of o-benzoquinone structure (IIB2) generation or oxidative demethylation is the most prominent as it is explained by the high yields of methanol in the reactions of lignin model substances and lignin with chlorine dioxide. The reaction of p-benzoquinone structures (IIC1) formation has a low rate, since for that way of reaction the side chain has to contain benzyl alcohol groups which considerably decrease during pulping. If the side chain has an alkyl groups it can be oxidized to a benzyl alcohol or  $\alpha$ -carbonyl group. [1]



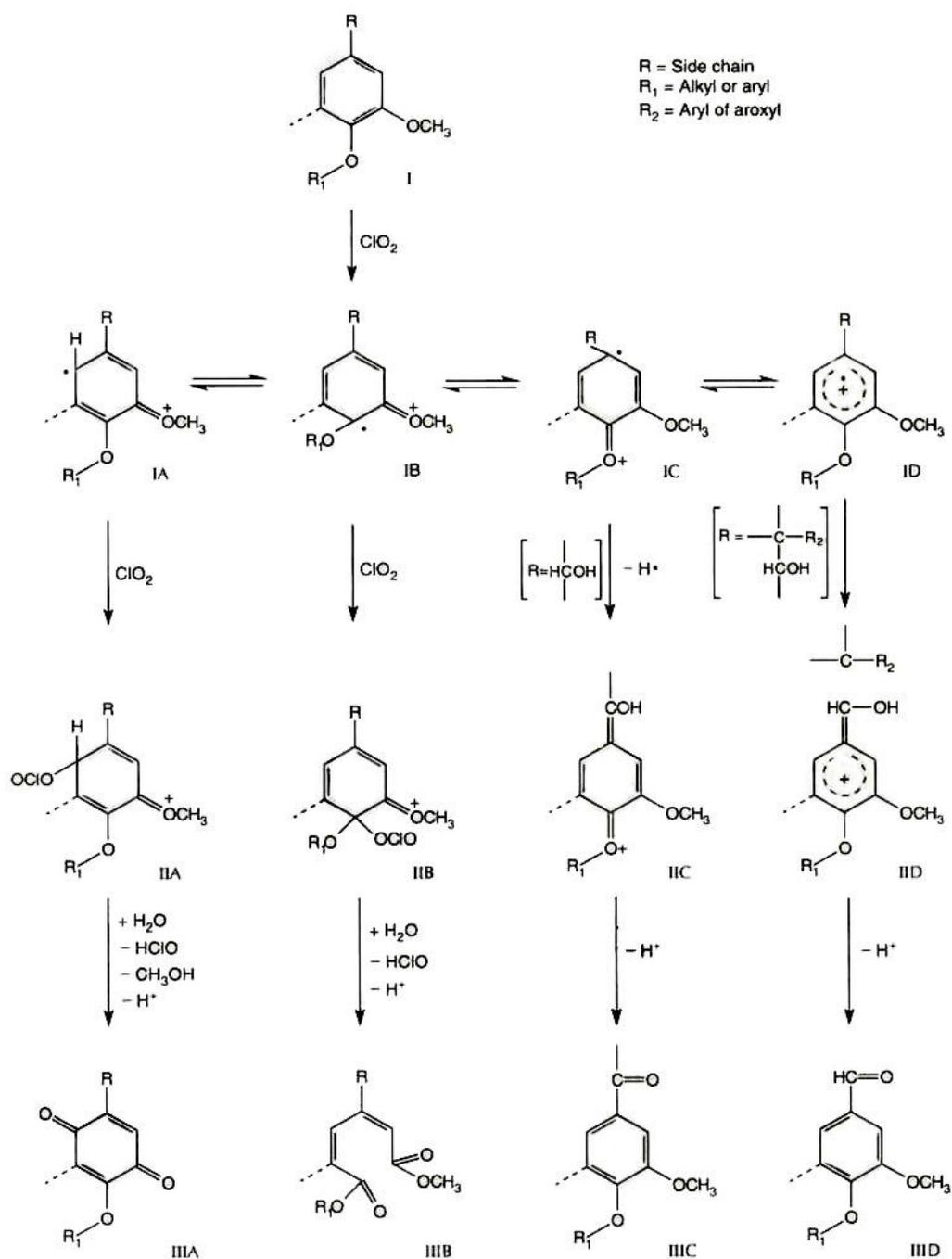
**Figure 1.** Sequences for the reaction of chlorine dioxide with phenolic rings in lignin [1].

**Reactions with non-phenolic groups** (Figure 2) occur with lower rate in contrast to phenolic units. Firstly, mesomeric radical cations (IA, IB, IC) are formed. IA and IB structures react with chlorine dioxide producing chlorous acid esters which undergo hydrolysis forming p-benzoquinone (IIIA) and muconic acid di-ester (IIIB) or lactone. Fourth branch (D) illustrates cleavage of  $C_{\alpha}$ - $C_{\beta}$  bond with formation of an aromatic aldehyde (Figure 2). [1]

The reaction of demethylation is also dominant in the case of non-phenolic units; it occurs during the hydrolysis of methyl aryl ether groups (IIA) and the muconic acid methyl esters [1].

As it was mentioned above chlorine dioxide reacts readily with phenolic units than with non-phenolic. But non-phenolic units can undergo conversion reactions under elemental chlorine or hypochlorous acid treatment and form phenolic units. [1]

In reactions of chlorine dioxide with both phenolic and non-phenolic structures chlorinated organic materials are appeared. The chlorination reactions occur under the impact of hypochlorous acid (as well as chlorine) generated through partial reduction of chloride dioxide. The substitution level is one chlorine atom per one aromatic ring. With the following oxidation by chlorine dioxide, the chlorine becomes a substituent of the oxidized product. [1]



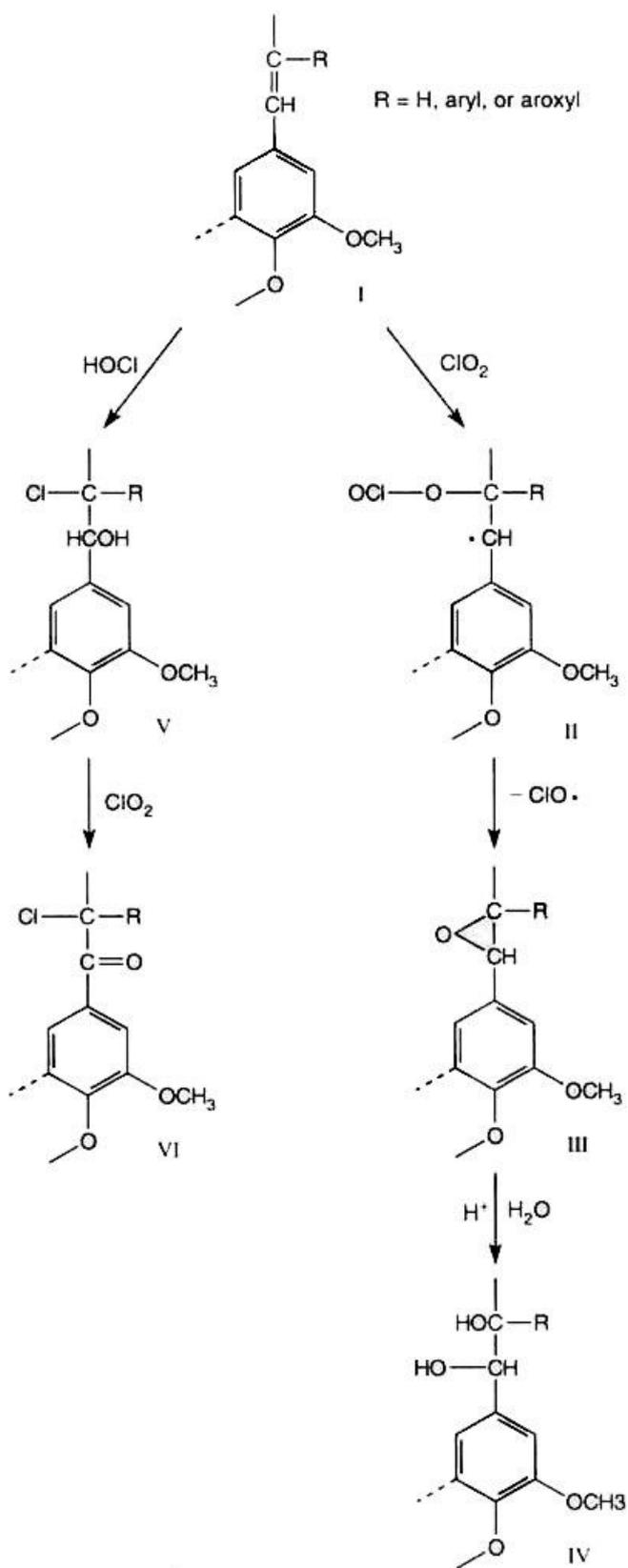
**Figure 2.** Reactions of chloride dioxide with non-phenolic rings in lignin [1].

**Reactions with ring-conjugated ethylenic groups** are shown in Figure 3. Such structures are presented in p-hydroxycinnamaldehyde and p-hydroxycinamyl alcohol units in native lignin and in styryl aryl ether and stilbenoid structures in chemically changed lignin. Chlorine dioxide attacks double bond forming structure II as shown in Figure 3, after removing of hypochlorite radical epoxide is generated. The epoxide is undergone hydrolysis in acid medium at pH 2 forming diol (IV), but at pH 6 the ring is relatively stable. [1]

The second way of reactions occurs with hypochlorite acid or elemental chlorine which are generated by the reaction of chlorine dioxide with hypochlorite radical:



Hypochlorite forms chlorohydrins (V). Oxidation of the latter leads to the generation of  $\alpha$ -chloro ketone (VI). These reactions have a small effect on lignin decomposition and promote forming of chlorinated organic materials which have a negative influence on the environment. [1]



**Figure 3.** Reaction of chlorine dioxide with ring-conjugated ethylenic groups [1].

## 2.2 Sodium hydroxide

### 2.2.1 Properties

Sodium hydroxide forms the colourless crystals with a rhombic crystal lattice. The density is  $2.13 \text{ g/cm}^3$ , the melting and boiling temperatures are  $320 \text{ }^\circ\text{C}$  and  $1378 \text{ }^\circ\text{C}$ , respectively. Industrial product is white non-transparent material. Sodium hydroxide is hygroscopic and well soluble in water (Table 4). The process of solubilization is exothermic accompanying with the release of heating. [1, 5]

**Table 4.** Concentration of sodium hydroxide in water at different temperatures [5]

Temperature, $^\circ\text{C}$	0	20	50	80	92
Concentration of NaOH, %	29.6	52.2	59.2	75.8	83.9

Absorption of carbon dioxide from air must be avoided during transportation and storage. It is recommended to use non-silicon containing alloys for the equipment considered to contact with sodium hydroxide. [1, 5]

Sodium hydroxide provokes burns and is especially dangerous for eyes. All works with sodium hydroxide solutions must be carried out with usage of protective goggles and gloves. [1, 5]

### 2.2.2 Alkaline treatment

An alkaline extraction stage denotes E. The role of it is to dissolve the organic materials oxidized on previous stage and reactivate lignin for the subsequent treatment by the generating new active groups. The degree of removal of organics influences on chemical consumption in the further stage and chemical reactivation ensures sufficient reaction speed in the subsequent stage. [1]

Forming sodium salts of oxidized organic materials increases the water solubility of the last. Degree of lignin molecules association and thus their hydrodynamic volume decreases in alkaline environment. [1] Alkaline medium also causes swelling of cellulose fibers. All these reasons promote the removal of lignin molecules.

Usually, the first extraction stage is reinforced with oxygen (EO) or hydrogen peroxide (EP), or both of them (EOP). In the second extraction stage only hydrogen peroxide is added as a bleaching booster, oxygen addition is not advantageous in that case, since oxygen is mostly a delignifying reagent. Conditions of alkaline treatment are shown in Table 5. [7]

**Table 5.** Typical alkaline extraction stage conditions [7]

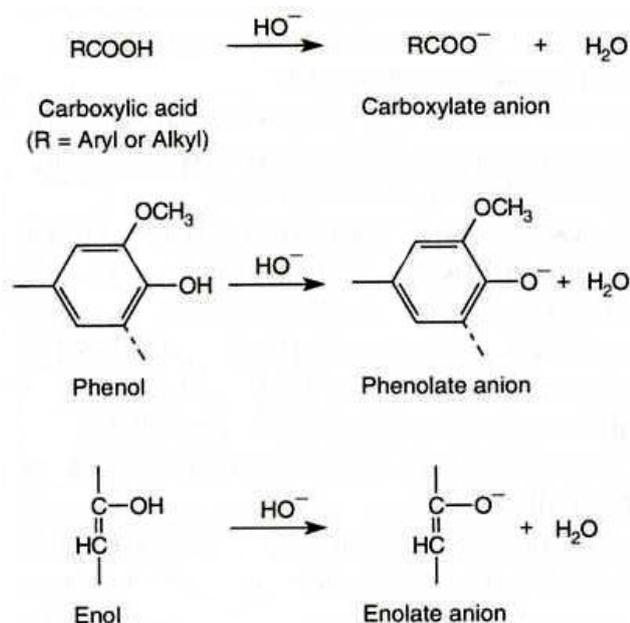
Parameter	Stage	
	first	second
Final pH	10-11.5	10-11.5
Temperature, °C	60-90	60-90
Pulp consistency, %	10-15	10-15
Time, min	60-90	60-90
Pressure, bar	2.5-5 in upward flow and atmospheric in downward flow	Atmospheric
NaOH charge	Usually 2-5 kg/t plus a charge equal to the kappa number coming to the D <sub>0</sub> stage calculated as kg NaOH/t	3-5 times the kappa number calculated as kg NaOH/t

### ***2.2.3 Reactions of lignin during alkaline extraction***

Several types of reactions occur during the extraction: neutralization of acidic groups, hydrolysis of chlorinated organic materials, condensation reactions and also reaction of rearrangement of o-quinonoid structures [1].

The first type of the reactions is the most important, since it increases the solubility of the lignin fragments containing those acidic groups (Figure 4). The typical acid groups of oxidized lignin are:

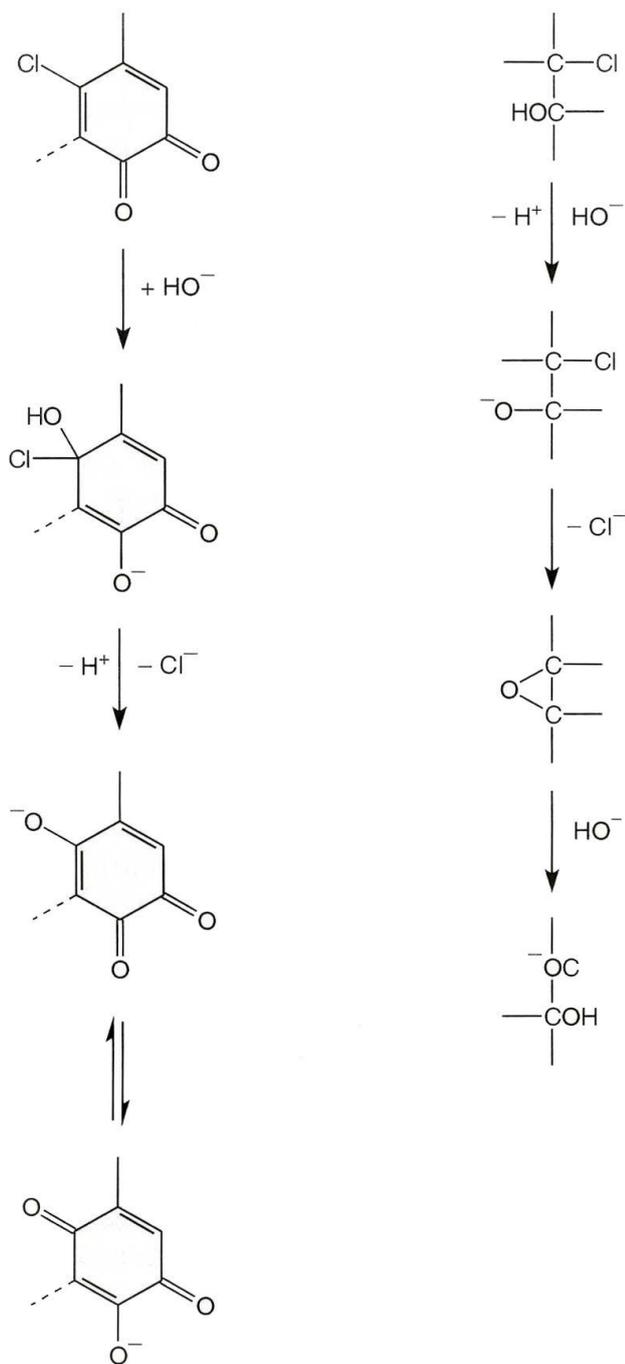
- carboxylic groups;
- phenolic hydroxyl groups (mainly presented by guaiacyl structures);
- enol groups. [1]



**Figure 4.** Neutralization of lignin-derived acidic functional groups in prebleached pulps [1].

The mechanism of the base-catalyzed hydrolysis of organically bound chlorine is nucleophilic displacement, when chlorine atom is substituted by hydroxyl group. Figure 5 shows two sequences of such reaction: the substitution of chlorine from the benzene ring and from the side chain. The hydrolysis reaction increases solubility of lignin fragments and thus has a positive impact on lignin elimination. [1]

The degree of chlorine removal and reaction rate depend on the structure of the fragment (aliphatic or aromatic) to which chlorine bound, the presence of substituents and position of chlorine relative to them; the conditions of extraction stage also affect chlorine removal. Chlorine easily splits off from aliphatic structures (for example, side chain of aromatic structures), from aromatic rings of oxidation products (o-benzoquinone derivatives) and from muconic acid derivatives (chlorine atoms in  $\alpha$  site to the carboxyl group undergo easier the alkaline hydrolysis than in  $\beta$  position). On the other hand, the loss of chlorine bound to aromatic ring (guaiacyl, veratryl, syringyl derivatives) except some catechols, is quite low. [8]



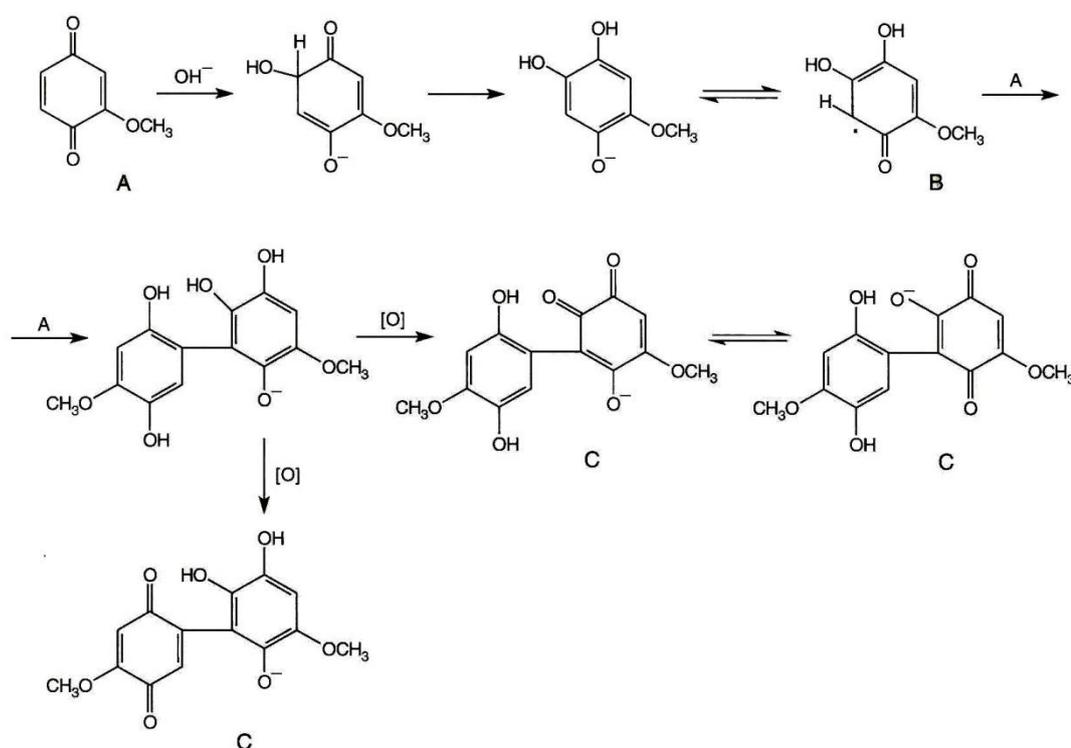
**Figure 5.** Base-catalyzed elimination of organically bound chlorine [1].

The most sensitive to base-catalyzed condensation lignin derivatives are o- and p-benzoquinones produced in the preceding bleaching stage. These structures are found to be quite unstable in aqueous media especially in alkaline and the degree of instability differs depending on type and number of ring substituents. Quinones are decomposed in alkali and this process is accompanying with darkening or “browning”. But this consequence is recovered during the following treatment with strong oxidizing reagents [1].

The next changes occur with o- and p-benzoquinones under alkaline conditions:

- the condensation with formation of biphenyl linkages;
- an increase of phenolic hydroxyl and decrease of carbonyl groups;
- o- and p-benzoquinones are converted into catechol and hydroquinone, respectively.

The reaction of methoxy-p-benzoquinone with alkali is showed in Figure 6. The resulting products are quinone substituted polyphenolic units (C) [1].



**Figure 6.** Base-catalyzed condensation of methoxy-p-benzoquinone [1].

The reactions of condensation cause the reduction of solubilization of lignin fragments, but this effect is partially compensated by forming phenolic hydroxyl groups, which, on the contrary, increase the solubility [1].

O-quinonoid may undergo a benzylic acid rearrangement forming cyclopentadiene  $\alpha$ -hydroxycarboxylic acid derivative, which enhances solubility of lignin fragments. But such rearrangement is not peculiar to o-quinonoid structures bound with lignin network. [1]

### 2.2.4 Oxidant-reinforced treatment

It was found before 1980 that the addition of oxygen to alkaline extraction stage allows decreasing charge of more expensive chlorine dioxide in the subsequent D<sub>1</sub> stage. But the realization of simple and economically beneficial oxygen-reinforced alkaline treatment was impossible until medium-consistency high-intensity mixing technology became available. From that time it was discovered that introduction of oxidants such as oxygen and hydrogen peroxide in extraction stage enables decreasing the molecular chlorine charge in the first stage; that in turn reduces the formation of chlorinated organic materials in pulp and in effluents. [1, 9]

Addition of oxygen allows higher kappa number decrease, while introduction of hydrogen peroxide increases the brightness of pulp [10]. This fact can be observed from data represented in diagrams shown in Figures 7 and 8.

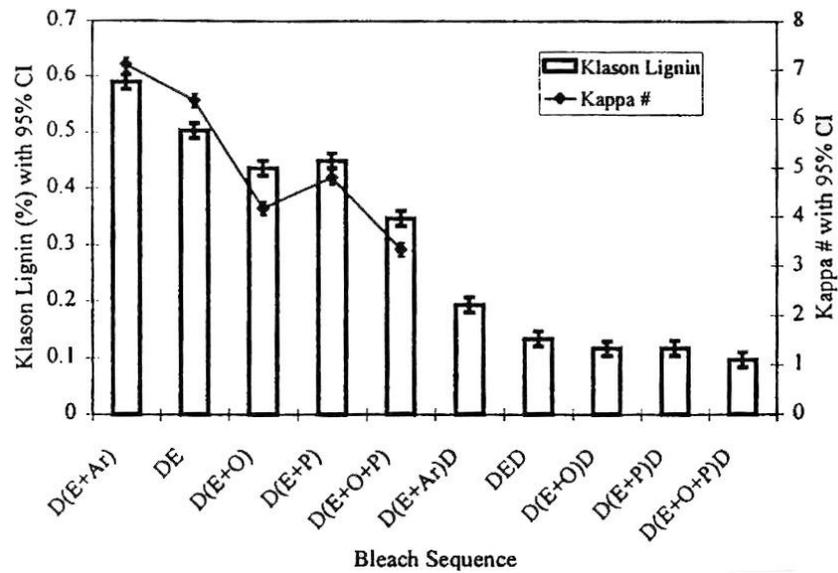
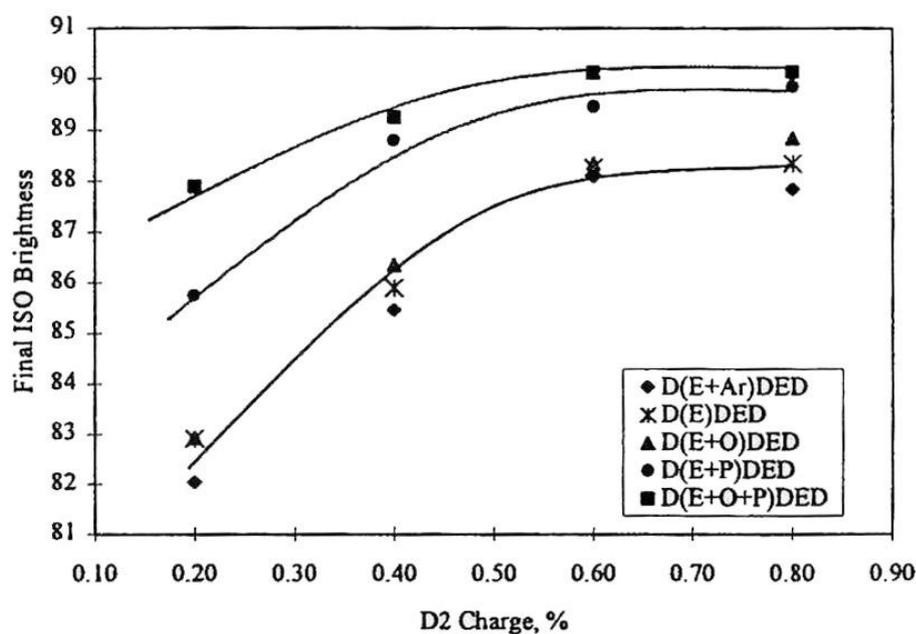


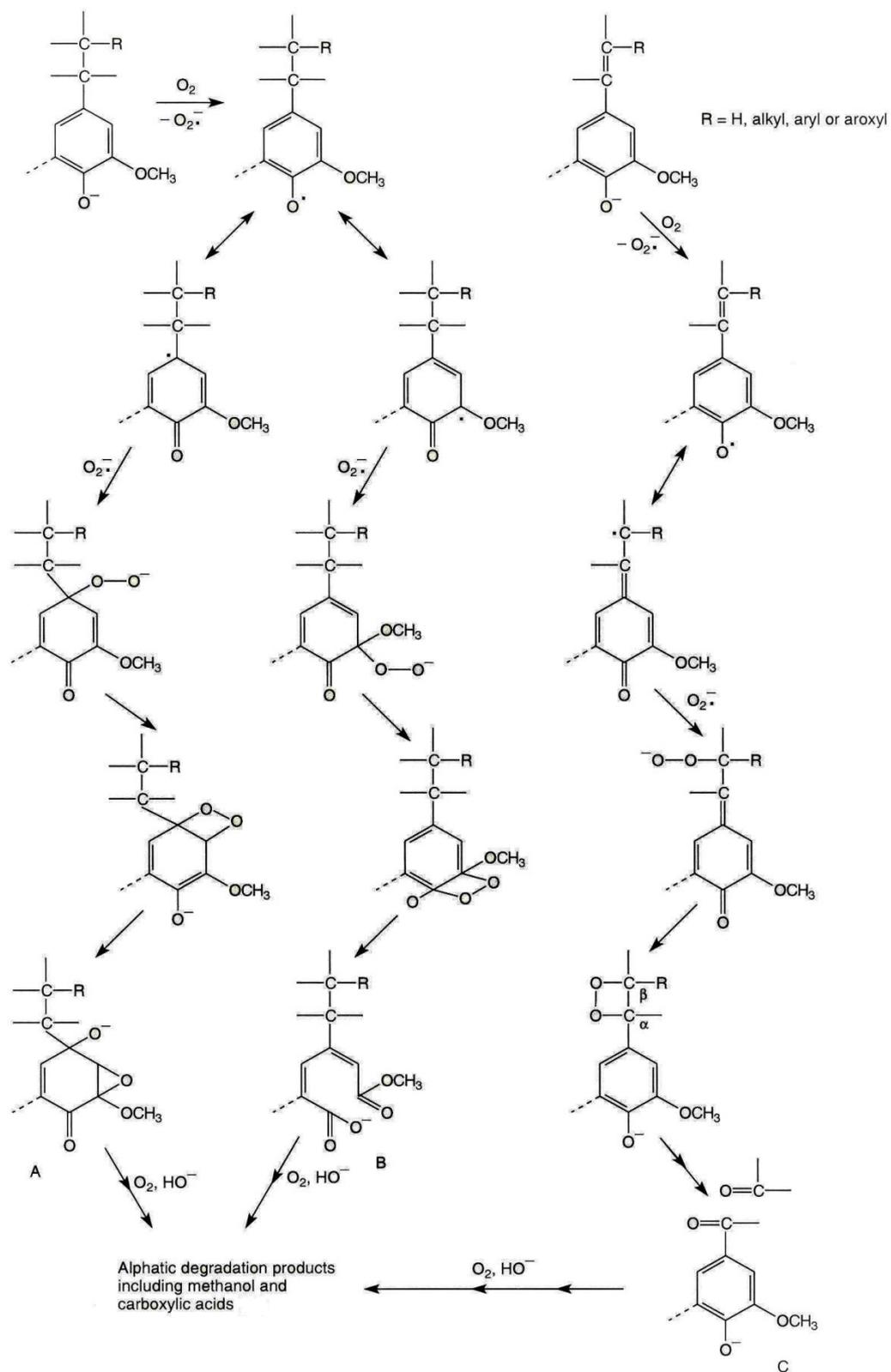
Figure 7. Kappa number and lignin content of bleached pulps [9].



**Figure 8.** Brightness ceiling data comparing the different alkaline extraction conditions (the curves for the data are freehand made for visualization) [9].

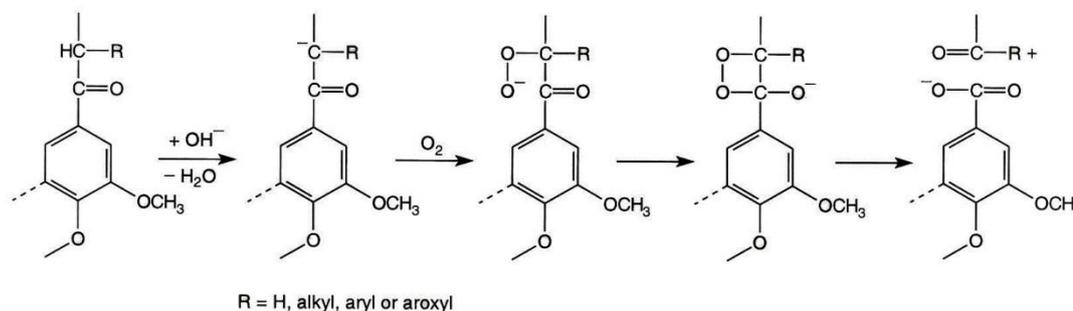
Auto-oxidation of phenolic units occurs under oxygen influence. Firstly, oxygen takes an electron producing superoxide ion radical  $O_2^{\cdot-}$  and phenoxy radical. The latter forms mesomeric structures which undergo oxygenation generating hydroperoxide radicals. Oxidizing phenolate ion these radicals are converted into the hydroperoxide anion structures which form dioxetanes through nucleophilic reaction. These structures are very reactive and undergo the reaction of rearrangement producing oxirane structures (A, Figure 9), muconic acid derivatives (B). Ring-conjugated ethylenic structures have the same reaction path, but in that case formed dioxetanes undergoes cleavage of  $C_\alpha-C_\beta$  bond affording  $\alpha$ -keto structure (C). [1, 10, 11, 12] Phenoxy radicals can combine with each other generating diaryl structures. In some cases oxygenation of the “para” site can lead to the side-chain removal and formation of p-quinonoid structures (for example, in the case of benzyl alcohol structures). [12]

Various oxygen-containing species appear during an oxygen treatment in alkali media. Hydroperoxide ions are generated from organic hydroperoxides and increase brightness of pulp. Hydroxyl radical formed under the thermal and transition metals influence can react with phenoxide ions and with other organic materials. [1]



**Figure 9.** Sequences for the oxidation of phenolic lignin units to oxirane (A), muconic acid (B) and carbonyl structures [1].

In the ring-conjugated carbonyl structures the cleavage of  $C_{\alpha}$ - $C_{\beta}$  bound occurs under the oxygen influence in alkaline media (Figure 10) [1].



**Figure 10.** Sequence for the reaction of oxygen with carbonyl-conjugated structures [1].

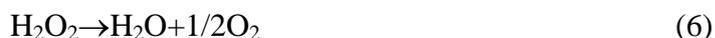
Hydrogen peroxide reacts with carbonyl structures of lignin forming organic hydroperoxide anions which undergo rearrangement with the splitting of C-C linkages. Disrupted aromatic rings can be further degraded to low molecular carboxyl acid derivatives. [9, 11] The reactions of hydrogen peroxide are shown later in the next chapter.

## 2.3 Hydrogen peroxide

### 2.3.1 Properties

Hydrogen peroxide is colourless transparent liquid at the normal conditions. The density is  $1450 \text{ kg/m}^3$  at the temperature of  $20 \text{ }^\circ\text{C}$  and  $1730 \text{ kg/m}^3$  at  $-20 \text{ }^\circ\text{C}$  (solid state). The boiling temperature is  $150.2 \text{ }^\circ\text{C}$  and melting one is  $-0.43 \text{ }^\circ\text{C}$ . Hydrogen peroxide can mix with water in any ratios. [5]

Pure hydrogen peroxide is quite stable (degree of decomposition is 30 % per year at the temperature of  $30 \text{ }^\circ\text{C}$ ), but with the presence of some metals and their ions (Cu, Fe, Mn, *etc.*), enzymes, different impurities, under influence of the radiation, electrical spark hydrogen peroxide decomposes according to the following exothermic reaction:

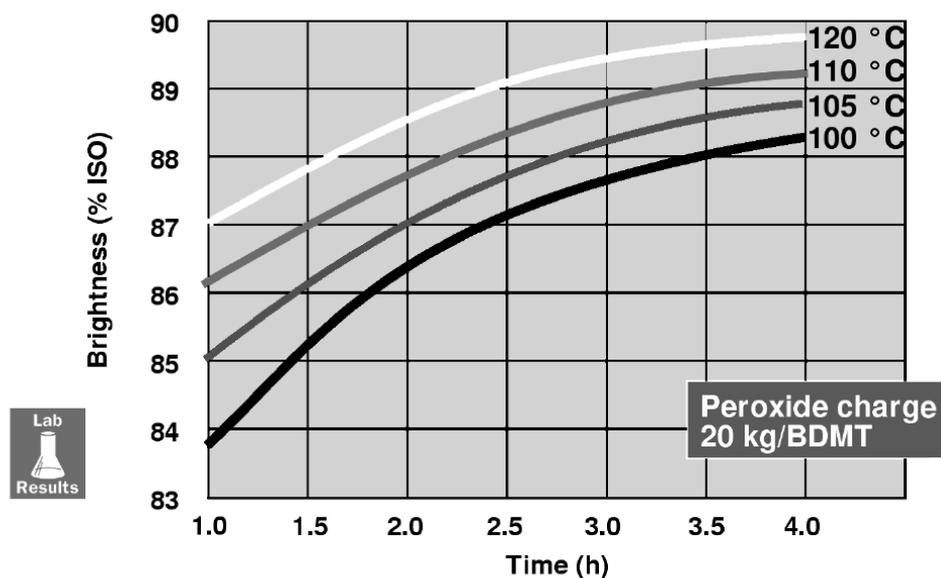


High temperature and pH accelerate the reaction (6). [5] Hydrogen peroxide is not flammable by itself, but can cause the ignition of organic materials during contact with the last. Titanium can undergo corrosion reactions at the high temperatures (>80 °C), pH (>11) and concentrations (>3 %), which should be considered in equipment designing. [1]

Handling of hydrogen peroxide (especially concentrated solutions) requires special measures to prevent serious burns and irritations of skin, eyes and mucous membranes [1].

### 2.3.2 Treatment with hydrogen peroxide

Before 1993 bleaching with hydrogen peroxide realized under the atmospheric pressure, since it was considered that the temperature higher than 100 °C affects the fast decomposition of hydrogen peroxide. Later, it was found that metal surfaces of equipment have a greater effect on hydrogen peroxide decomposition than high temperatures and it became possible to use high temperatures and made retention time shorter (Figure 11). [7]

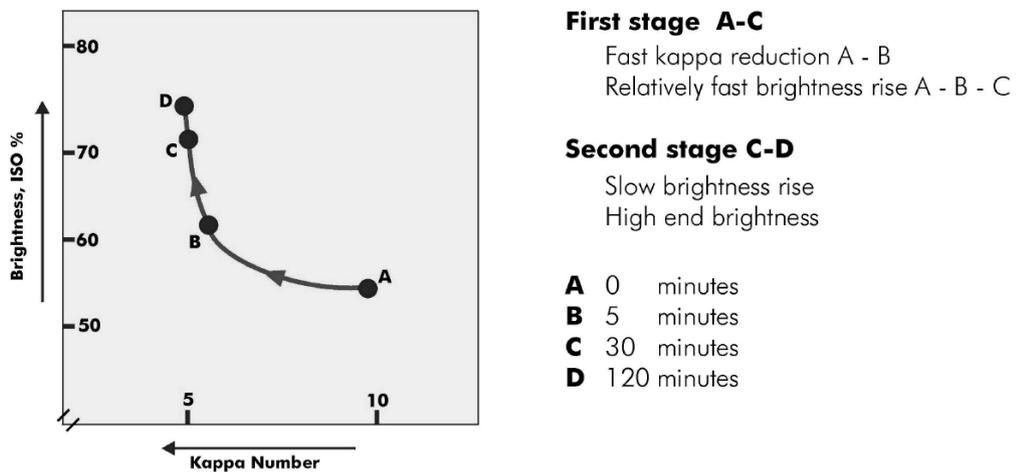


**Figure 11.** Effect of temperature and retention time on brightness in pressurized peroxide bleaching (Kvaerner) [7].

The pressurized process also gives some advantages:

- simpler process control and ,additionally, temperature can be used as an adjusting parameter;
- higher brightness can be achieved with the same consumption of the chemical. [7]

Two stages can be distinguished during hydrogen peroxide bleaching: the fast initial and secondary slow stages (Figure 12). The first stage lasts for 5-30 minutes consuming 50-80 % of charged amount and significantly reduces kappa number. The second stage can have duration of several hours depending on temperature and consumes the rest of hydrogen peroxide. [7]



**Figure 12.** Phases in peroxide bleaching process [7].

Pressurized hydrogen peroxide treatment is implemented in a two-stage system. The retention time in the first reactor is 5-30 minutes and in the second one is 45-120 minutes depending on the process conditions (temperature, chemical charges and kappa number of pulp before treatment). [7]

The charge of oxygen is low (Table 6), but oxygen released from decomposition of hydrogen peroxide can influence the process, therefore arrangement of oxygen removing system between reactors is necessary [7].

**Table 6.** Typical conditions in pressurized peroxide bleaching (Sunds Defibrator) [7]

Final pH	10.5-11
Temperature, °C	80-110
Pulp consistency, %	10-15
Time, min	30-180
Pressure, MPa	0.3-0.8
Charges, kg/t	
Oxygen	2-10
Hydrogen peroxide	2-40

### 2.3.3 Reactions of hydrogen peroxide with lignin

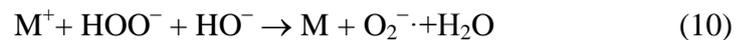
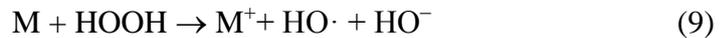
In alkaline media hydrogen peroxide acts mostly as a brighten pulp reagent which destructs lignin chromophores [6]. The main reactive particle during hydrogen peroxide treatment in alkali media is hydroperoxide anion (nucleophilic particle) generated through the following reaction [1]:



In addition, the reaction of decomposition occurs during the bleaching:



This reaction happens under the transition metals (manganese, copper, iron, cobalt, *etc.*) influence and it is accompanied with the formation of very reactive particles such as hydroxyl radical ( $\text{OH}\cdot$ ) and superoxide anion radical ( $\text{O}_2^{\cdot-}$ ):

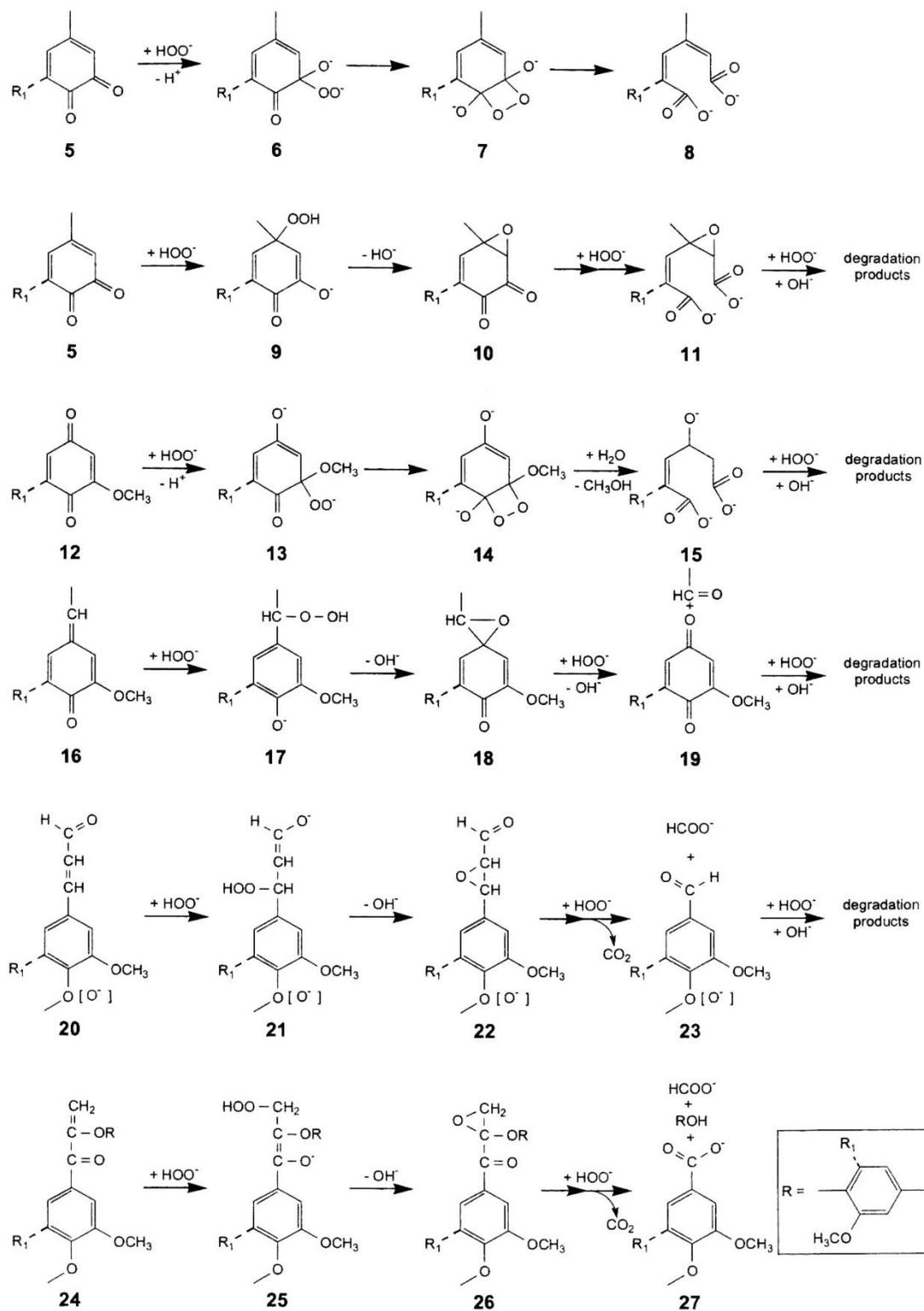


where M is transition metal. [13]

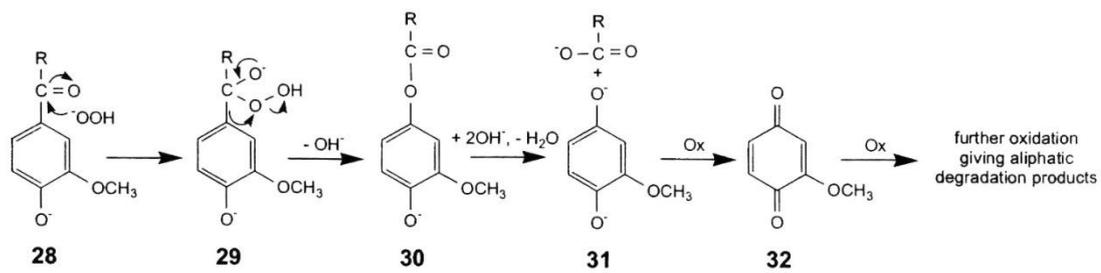
Generated radicals (hydroxyl, hydroperoxide and superoxide anion) react with both lignin and carbohydrates decomposing them and, basically, have a negative effect in the delignification process. Their formation must be avoided and therefore amount of the transition metals in pulp must be kept at the harmless level. [6] This can be done by chelating stage (Q), also, the metals are removed during the washing of pulp.

The reactions of hydrogen peroxide with quinoid and side-chain enone structures are shown in Figure 13. Hydrogen peroxide reacts with o- and p-quinone structures (5, 12) producing miconic acid derivatives (8, 11, 15) through the formation of hydroperoxides (6, 9, 13) in the first step and dioxetane (7, 14) or oxirane structures (10) in the second step. Arylalkane (quinone methide structures, 16) and enone structures (20, 24) also form hydroperoxides (17, 21, 25) which interfering with hydroxyl anion generate epoxide (18, 22, 26). Further rapture of  $C_{\alpha}$ - $C_{\beta}$  bound of 22, 26 structures leads to aldehyde (23) and carboxylic acid (27) formation. Structure 18 undergoes splitting off  $C_{\alpha}$  from benzene ring producing p-quinone (19). Structures 11, 15, 19, 23 can be further degraded by hydroperoxide and hydroxyl anion. [6]

The sequence of reactions of phenylpropanones (phenylpropanols react in the same way) with hydroperoxide anion is shown in Figure 14. Ester (30) formed from hydroperoxide structure (29) undergoes elimination reaction producing carboxylic acid and phenolate. The latter can be further oxidized to p-quinone which in turn also can be degraded under oxidation reaction. [6]



**Figure 13.** Reaction of hydroperoxide anions to quinoid structures and to side-chain enone structure [6].



**Figure 14.** Dakin reaction at the  $C_{\alpha}$ -keto group of phenolic unit [6].

### 3 WASHING

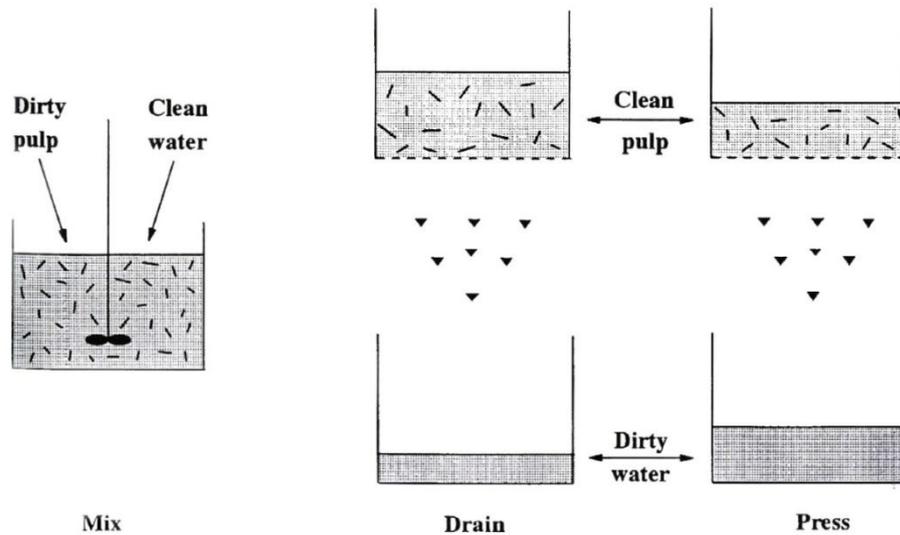
Washing in bleach plant is applied between bleaching stages. The main purpose of this procedure is to remove soluble organic (lignin fragments, hemicelluloses, *etc*) and inorganic substances (metals, salts, *etc.*). These dissolved materials can be harmful for the following bleaching stages and cause higher bleaching reagent consumption or lower level of brightness or lower strength properties of pulp. [1, 14] In addition, washing enables adjusting of pH, temperature and consistency for the ensuing bleaching stage [15].

#### 3.1 Principles of washing

There are two basic principles in pulp washing:

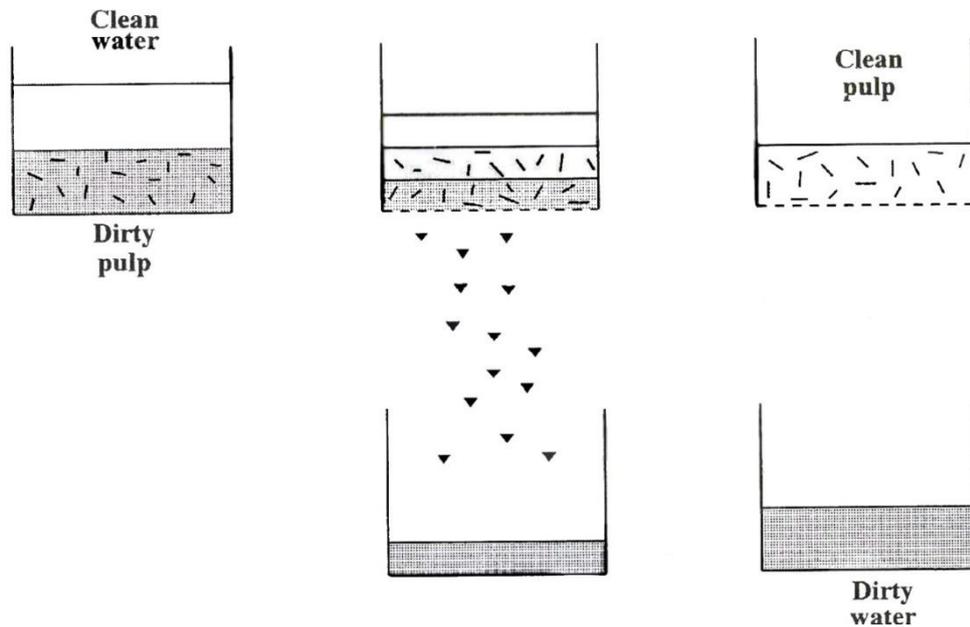
- dilution/extraction washing;
- displacement washing [1].

The principle of dilution/extraction washing is illustrated in Figure 15. Firstly, pulp suspension is diluted and mixed with wash liquor and then thickened by filtering or pressing. The efficiency of the washing is affected by the quality of wash water, consistency after dilution and thickening, and also depends on the degree of adsorption of dissolved substances by fibers and time needed for desorption [16].



**Figure 15.** Schematic diagram of dilution/extraction washing [1].

During the displacement washing, liquid from unwashed pulp is replaced with wash liquor “in piston-like manner” (Figure 16). In the ideal case mixing doesn’t occur between displaced liquid and wash liquor, and all solutes can be removed by displacing one volume of the liquor in pulp. In practice, a pure displacement washing cannot be achieved due to presence of some mixing between wash water and displaced liquor and also fibers absorb some dissolved substances. The efficiency of displacement washing depends on temperature, displacing velocity, pulp pad thickness and consistency. [1]



**Figure 16.** Schematic diagram of displacement washing [1].

Displacement washing is applicable to high freeness pulps such as chemical pulps, mat of which can be easily passed through by wash water. Contrariwise, low freeness pulps (mechanical pulps and recycled fibers) form thick mat and extraction/dilution washing is most suitable for them. [14]

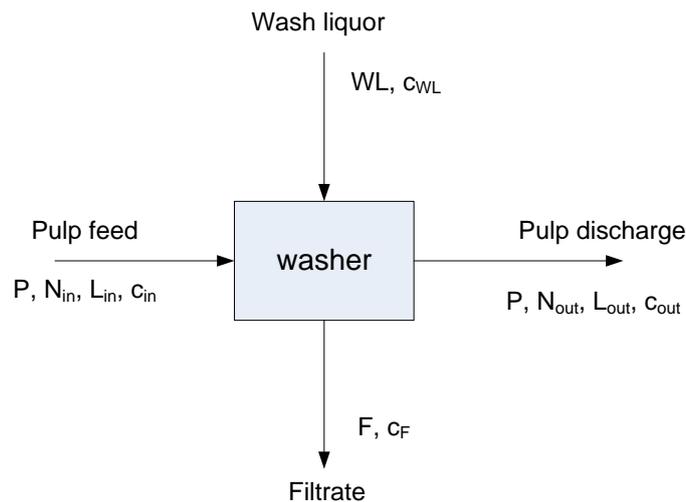
All pulp washing equipment apply one or both of these processes. Industrial washers that use dilution/extraction only are presses for chemical pulp washing and screw presses and twin-wire presses for washing of (chemi)-mechanical pulp. Washers which perform both the dilution/extraction and displacement washing in combination are pressure and atmospheric diffusion washers, vacuum drum filters, wash presses, and pressure washers such as Compaction Baffle filter (CBF) and Drum Displacement (DD) washer. [1]

### 3.2 Washing parameters

There are several variables affecting washing: dilution factor, inlet and outlet consistency, pH, temperature, entrained air. All these parameters relate to process conditions. Parameters such as mechanical pressure, fluid pressure (or vacuum) and particular travelling speed are considered as equipment specific parameters. Sheet formation, wash liquor distribution and its quality also have effect on the washing process. In addition to all above mentioned factors, pulp characteristics also have to be considered, especially drainage and sorption behaviour. Not all of these variables can be adjusted, since some of them are peculiar to special process step or piece of equipment. Most of these parameters interact with each other and an improvement of one can differently affects other. [17, 18]

The following terms are used to describe a washing performance: dilution factor, wash and weight liquor ratios, wash yield, displacement ratio, modified (or standardized) Norden efficiency factor and equivalent displacement ratio. [1, 17]

The sketch of washer so-called “black box” is represented in Figure 17, it will be used to describe washing performance.



**Figure 17.** Schematic representation of washer [17].

The inlet and outlet pulp streams are described with such parameters as the amount of oven-dry pulp ( $P$ ), consistency ( $N_{in}$  and  $N_{out}$ ), corresponding amount of liquid accompanying the pulp ( $L_{in}$  and  $L_{out}$ ) and concentration of solutes ( $c_{in}$  and  $c_{out}$ ). The

wash liquor and filtrate streams are characterized with the volumes (WL and F, respectively) and concentration of dissolved materials ( $c_{WL}$  and  $c_F$ ).

**Dilution factor** can be written in the following form:

$$DF = \frac{WL - L_{out}}{P} \quad (13)$$

This term shows how much liquid is added to the pulp slurry above existing amount. Basically, the higher the dilution factor the better washing. On the other hand, the high value of dilution factor causes higher evaporation load in the case of brownstock washing and effluent volumes concerning the washing in bleaching. [17] Dilution factor can be negative if amount of applied wash water is less than that of liquid leaving washer with the pulp. DF equal to 0 tells that liquid in the pulp is substituted with the same amount of wash liquor. [16]

**Wash liquor (R)** and **weight liquor (W)** ratios:

$$R = WL/L_{out} \quad (14)$$

$$W = F/L_{in} \quad (15)$$

If the R value equals to 1 for the displacement washing the liquor in pulp is substituted with an equal volume of wash water. R and W are approximately the same if consistency stays unchanged through the washer. [16]

The **wash yield (Y)** is a ratio between the amount of solutes leaving a washer with filtrate (or removed from pulp) and amount of solutes coming to the washer with pulp slurry. This parameter presumes absence of substances in wash liquor.

$$Y = 1 - \frac{L_{out} c_{out}}{L_{in} c_{in}} = \frac{Fc_F}{L_{in} c_{in}} \quad (16)$$

It could be used as a way to evaluate washing efficiency, but due to the assumption it is inapplicable for most of mill's cases. [17]

**Displacement ratio (DR)** shows the ratio between actual and maximum possible removal of the solutes assuming that pulp after washing can't be "cleaner" than wash liquor.

$$DR = \frac{c_{in} - c_{out}}{c_{in} - c_{wl}} \quad (17)$$

To compare different wash facilities with the term of displacement ratio dilution factor must be taken into account. [17]

The **Norden efficiency factor (E)** shows the number of ideal counter current mixing stages equivalent to a washer or washing system [1]. It can be calculated as follows:

$$E = \frac{\log\left(\frac{L_{in}}{L_{out}} \times \frac{c_{in} - c_F}{c_{out} - c_{wl}}\right)}{\log\frac{WL}{L_{out}}} \quad (18)$$

Standardized value considers the standard outlet consistency  $N_{std}$  and corresponding amount of liquid ( $L_{st}$ ) accompanying discharged pulp; thus this parameter is independent of discharge consistency. The most frequently used standardized outlet consistency is 10% and after modification the equation will have the following form [17]:

$$E_{10} = \frac{\log\left(\frac{L_{in}}{L_{out}} \times \frac{c_{in} - c_F}{c_{out} - c_{wl}}\right)}{\log\left(1 + \frac{DF}{9}\right)} \quad (19)$$

The total efficiency of washing system can be calculated by summing the  $E_{std}$  of each stage [1].

**Equivalent displacement ratio (EDR)** enables to calculate washing efficiency for the hypothetical washer which has the same loss as an actual washer and operates at the same dilution factor. The loss is considered as a difference between the amount of solutes leaving washer with pulp and amount of solutes entering with wash liquor.

$$(1 - \text{EDR}) = (1 - \text{DR})(\text{DCF})(\text{ICF}) \quad (20)$$

where DCF is discharge correction factor:

$$\text{DCF} = \frac{B_{\text{out}}}{7.33} \quad (21)$$

and ICF – inlet correction factor:

$$\text{ICF} = \frac{99(B_{\text{in}} + \text{DF})}{B_{\text{in}}(99 + \text{DF}) - B_{\text{out}}(99 - B_{\text{in}})(1 - \text{DR})} \quad (22)$$

$B_{\text{out}}$  and  $B_{\text{in}}$  – discharge and inlet ratios of liquor to pulp, kg of liquor/kg of pulp:

$$B_{\text{out}} = \frac{100 - N_{\text{out}}}{N_{\text{out}}} \quad (23)$$

$$B_{\text{in}} = \frac{100 - N_{\text{in}}}{N_{\text{in}}} \quad (24)$$

The equivalent displacement ratio doesn't depend on inlet and outlet consistencies. It shows a displacement ratio for the standard inlet consistency of 1 % and outlet consistency of 12 %. [19]

### ***3.3 Washing equipment***

A lot of types of wash equipment exist today and most of them have several design options. Loading factors, operating consistencies and drum dimensions for the washers commonly applied in industry (except belt filters and diffusers) are represented in Table 7.

**Table 7.** Typical washer loading factors and drum dimensions (design values for a modern greenfield softwood kraft mill producing 1000 admt of pulp per day) [1]

Washer type	Loading factor, admt/d/m <sup>2</sup>	Consistency		Drum dimensions
		Feed, % a.d.	Discharge, % a.d.	Diameter×Length, m×m
Vacuum drum washer	8.0-8.5	1.0-1.3	16-18	4.1×9.1
GasFree filter	<12	0.5-2.0	14-17	4.0×7.0
Compaction Baffle filter	25-30	3.5-4.0	13-15	3.0×4.0
Drum Displacement washer	<15	3.0-5.0 or 10.0-12.0	12-15	4.0×6.0
Wash press	<27	3.5-4.0	28-35	1.2×5.0 (×2 rolls)

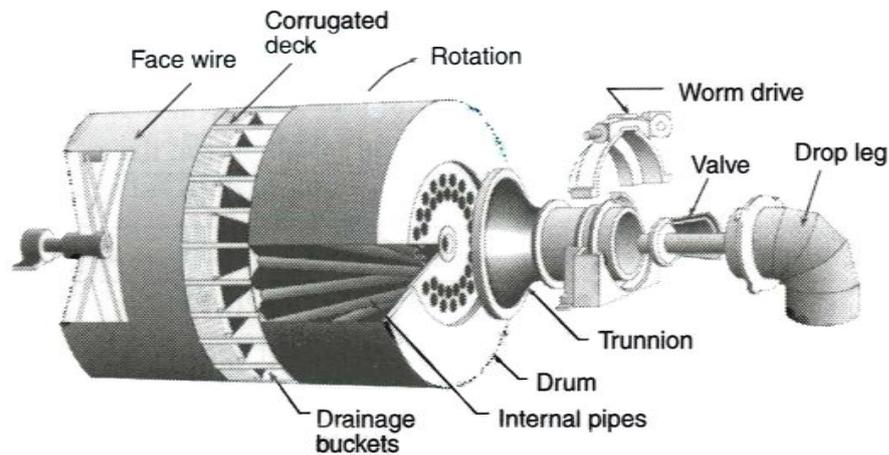
### 3.3.1 Vacuum drum washers

Rotary drum washer (Figure 18) is the type which has been used widely for the brownstock and bleach plant washing. It has been continuously developed and today exists in various designs. [16, 18] The E-factor for such type of washers varies from 1.5 to 3 [17].

The washing procedure includes several steps. Before entering the washer pulp slurry is diluted with recirculated filtrate from the tank to consistency of 1.0-1.5 % at normal operation conditions or higher consistency at overloading. The diluted pulp suspension overflows a weir into a vat. The vat has a rotating cylinder (typically diameter is 4.1 m and length is 9.1 m, see Table 7) on which a pulp mat is formed. [1] The cylinder or drum is covered with plastic or metal mesh called the “face” and has a vacuum inside created by a drop-lead. The pulp mat is dewatered further by pressure difference before it enters the displacement washing zone. Washing liquid is applied to the mat through the holes of horizontally placed pipes. [18] After the washing pulp is thickened and then discharged from the washer to a repulper. The outlet consistency depends on the process conditions and can vary from 8 % at the overloading or due to air entrainment problems to 18 % at optimal operation. [1, 17]

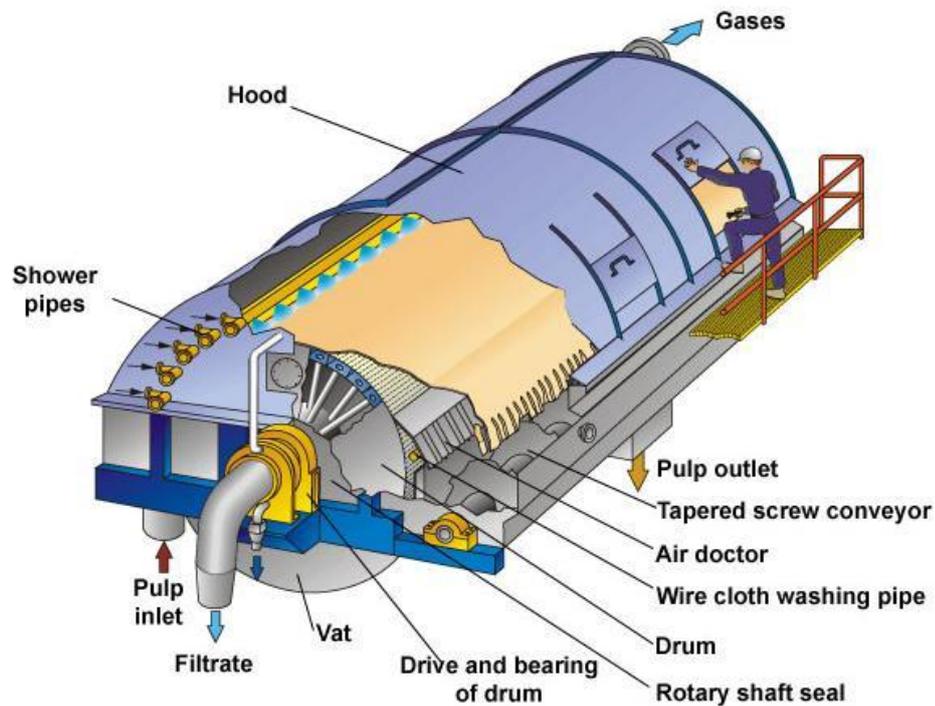
The length of the drop-leg depends on amount of air in leaving filtrate and has to be chosen enough to provide sufficient vacuum inside of the drum. In [18] the height of 9-10.7 meters is recommended for the drop-leg. This design of the washer causes its location at higher level than the filtrate tank; it also affects the temperature of the process which should not be higher than 80-85 °C, otherwise vapour pressure of water becomes harmful for vacuum [17].

Filtrates come to the filtrate tank where undergo air separation and then recirculated to dilute the pulp suspension before the washer or/and used as wash liquor to another washer [18].



**Figure 18.** Vacuum drum washer (Ingersoll-Rand) [1].

The GasFree filter (Figure 19) is vacuum drum washer modified with specifically designed rotary valve which separates air from discharged filtrates. Air is then vented back to the casing thus less emitting from the washer. Due to this improvement the drop-leg of GFF operates more efficiently providing higher outlet consistency of pulp. [1] The dimensions of GasFree filter are represented in Table 7.



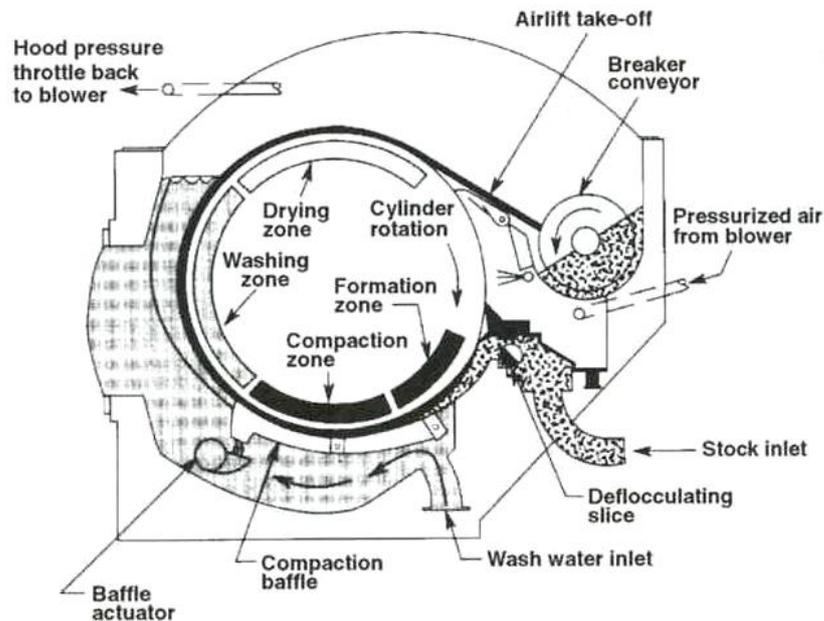
**Figure 19.** GasFree Filter (Andritz) [15].

### 3.3.2 Pressure washers

Pressure washers include the Compaction Baffle Filter (Ingersoll-Rand) and Drum Displacement washer (Ahlstrom Kamyr), these are shown in Figures 20 and 21, respectively. The pressure washers don't have a drop-leg and therefore can operate at higher temperatures than vacuum drum washers and be installed at any level. Due to sealed housing gas emissions are lower. [1]

The Compaction Baffle filter shown in Figure 20 operates at higher inlet pulp consistency of 3-5 %. This provides higher capacity per surface area and decreases the volume of discharged filtrates, which in turn allows the application of auxiliary equipment with smaller sizes than that for a conventional drum washer. The baffle separates feeding pulp suspension from the wash liquor pond and provides higher consistency (20 %) of formed pulp mat before it enters the washing zone. Washing is carried out in the wash liquor pond at the consistency of 10 %. The washing in such manner doesn't provoke foaming problems and minimizes air entrainment into pulp mat. The discharge consistency of pulp is typically of 13-15 %. [1]

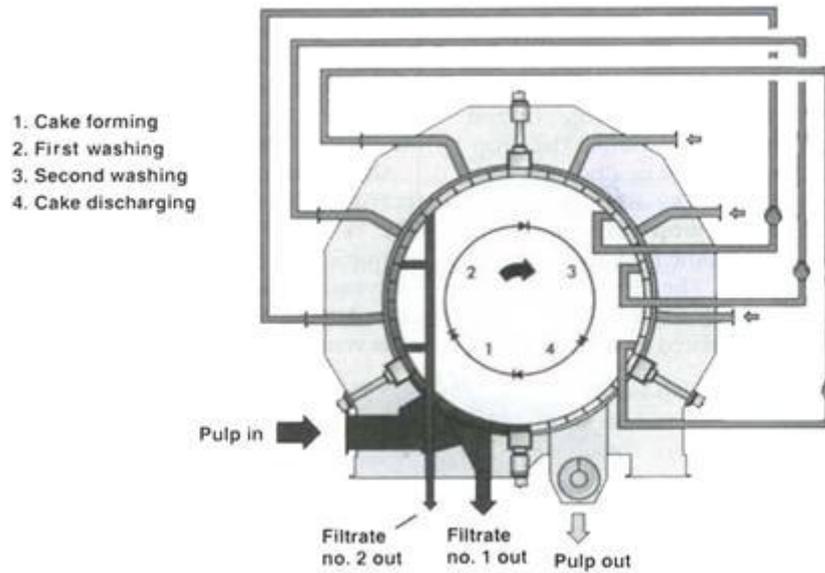
The pressure difference (driving force) through the pulp mat is created by the pressure of gas inside the hood which is vented back from the filtrate tank [17].



**Figure 20.** Diagram of Compaction Baffle filter (Ingersoll-Rand) [1].

The Drum Displacement washer (Figure 21) is also referred to the type of pressurized washers. It includes the formation zone, two to four washing stages and discharge zone and can be applied for the washing after the oxygen delignification (two stage unit) as well as for the brownstock washing (three or four stage unit). [1] Typical dimensions of Drum Displacement washer are represented in Table 7.

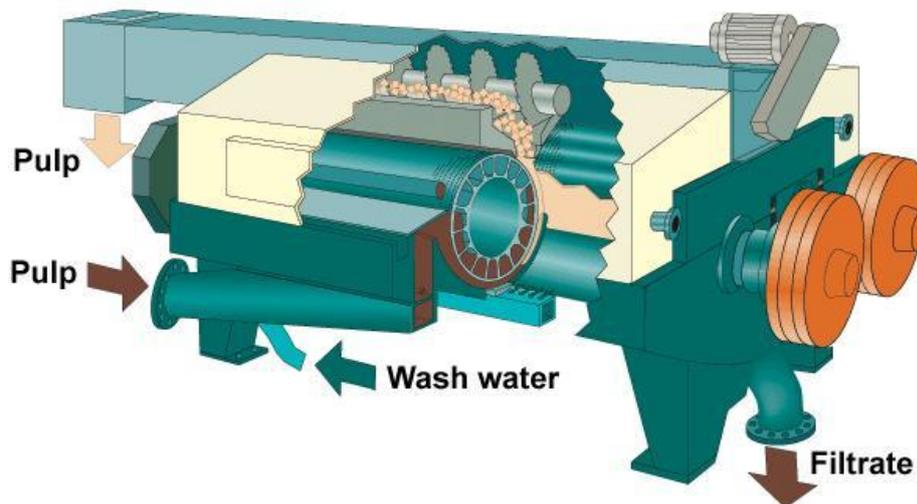
The hood is divided by sealing horizontal bars on the compartments. The inlet consistency of pulp is 3-5 % (low consistency displacement washer) or 10-12 % (medium consistency displacement washer). Before entering the washing zone the pulp forms a mat with the consistency of 10-12 %. The washing zone has several stages which are separated by the sealing bars creating wash pond in each stage. Pulp is washed countercurrently with wash liquor from the succeeding washing stage. After he washing zone pulp proceeds to the vacuum zone where the mat is dewatered with aid of a vacuum pump and finally discharges with the consistency of approximately 15 %. [1] The E-factors for two-, three- and four-stage DD washer are 6-9, 9-12 and 11-14, respectively [17].



**Figure 21.** DD washer (Ahlstrom Kamyr Inc) [1].

### 3.3.3 Wash presses

Wash press designed by Metso is shown in Figure 22.



**Figure 22.** The Metso TwinRoll press [15].

It can operate either at low of 3-5 % or medium (6-10 %) inlet consistency. A pulp mat with consistency of 8-12 % is formed in the dewatering zone between the rolls and fixed baffles; liquor from pulp is forced out through the halls inside the rolls. After the dewatering zone the pulp mat proceeds to the displacement zone where wash liquor is applied and displaces liquid from pulp inside the rolls. Filtrates are removed from the

press through the openings at the end of the rolls. Pulp comes through the nip to the shredder conveyer located above the rolls. The discharge consistency of pulp after the nip is approximately 30-35 %. [17]

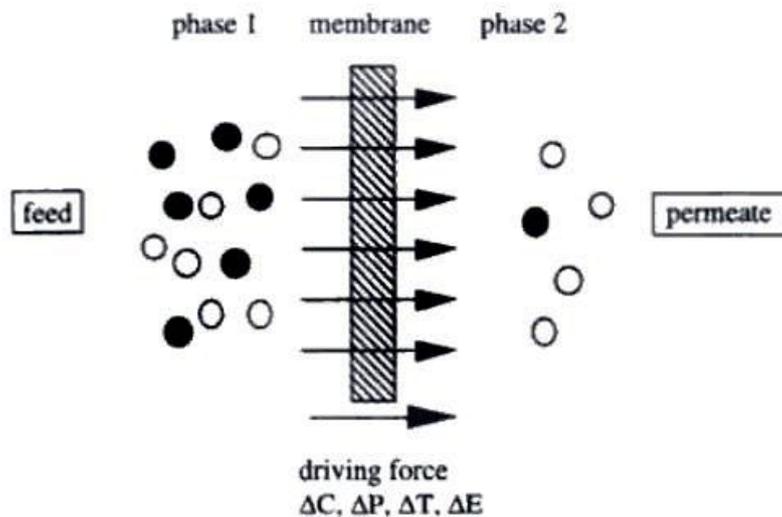
The E factor for a wash press is about 1, and  $E_{10}$  value varies from 3 to 5. The advantage of such washer type is the high outlet consistency and thus small amount of accompanying liquid in discharged pulp. This feature makes easier pH and temperature adjustment in the following dilution. [17]

#### 4 MEMBRANE SEPARATION TECHNOLOGY

Membrane processes have been known since the middle of 18<sup>th</sup> century when the osmosis phenomena was observed by Abbe Nollet. Despite that fact, the commercialization of membrane processes occurred only in 20<sup>th</sup> century. The big step promoted an implementation of membranes into industry was the discovering of asymmetric membranes by Loeb and Sourirajan in the beginning of 1950s. Nowadays, the membrane processes are widely used in various fields and the range of application becomes wider. [20, 21]

The membrane processes include microfiltration, ultrafiltration, nanofiltration, reverse osmosis, electrodialysis, dialysis, gas separation, pervaporation, membrane distillation and separation with liquid membranes. These processes run under different driving forces and deal with the objectives of various dimensions (from molecules to particles), but all of them have a membrane as a tool of separation. [20]

A membrane is defined as a selective barrier between two phases – feed and permeate (Figure 23). Separation occurs due to different speed of the permeation of components through the membrane. The rest after the filtration is concentrated feed called retentate. [20]



**Figure 23.** Schematic representation of membrane [20].

Membranes can be thick or thin, natural or synthetic, neutral or charged; structure of membrane can be homogeneous or heterogeneous, transportation through membrane can be active or passive. Membranes also divide on symmetrical and asymmetrical. The thickness of symmetrical membranes varies from 10 to 200  $\mu\text{m}$  and the resistance to mass transferring depends on the total thickness. An asymmetrical membrane consists of thin layer (0.1–5  $\mu\text{m}$ ) arranged on the substrate or bottom layer with thickness of 50–150  $\mu\text{m}$ . These membranes have high selectivity like thick membrane and high transport speed corresponding to thin membrane, since resistance to mass transferring is determined by thin layer. [20]

The transfer of certain component through the membrane occurs under the driving force which exists as gradient of pressure, concentration, temperature or electrical potential. Table 8 shows the driving forces for some membrane processes. [20]

**Table 8.** Driving forces of some membrane processes [20]

Membrane process	Phase 1/Phase 2	Driving force*
Microfiltration	Liquid/Liquid	$\Delta P$
Ultrafiltration	Liquid/Liquid	$\Delta P$
Nanofiltration	Liquid/Liquid	$\Delta P$
Reverse osmosis	Liquid/Liquid	$\Delta P$
Piezodialysis	Liquid/Liquid	$\Delta P$
Gas separation	Gas/Gas	$\Delta P$
Vapour permeation	Gas/Gas	$\Delta P$
Pervaporation	Liquid/Gas	$\Delta P$
Electrodialysis	Liquid/Liquid	$\Delta E$
Membrane electrolysis	Liquid/Liquid	$\Delta E$
Dialysis	Liquid/Liquid	$\Delta c$
Diffusion dialysis	Liquid/Liquid	$\Delta c$
Membrane contactors	Liquid/Liquid	$\Delta c$
	Liquid/Gas	$\Delta c/\Delta P$
	Gas/Liquid	$\Delta c/\Delta P$
Thermoosmosis	Liquid/Liquid	$\Delta T/\Delta P$
Membrane distillation	Liquid/Liquid	$\Delta T/\Delta P$

\*where  $\Delta P$ ,  $\Delta c$ ,  $\Delta E$ ,  $\Delta T$  – pressure, concentration, electrical potential and temperature gradients, respectively

A membrane itself (its nature, structure and material) also defines the field of its application. Depending on the pore size the membrane filtration processes divide on micro-, ultra-, nanofiltration and reverse osmosis (Table 9). The pore dimensions can

be indirectly characterized by molecular weight cut-off value (MWCO). This value shows the lowest molecular weight (in Daltons or g/mol) of materials which are rejected by membrane at least by 90 % [22].

**Table 9.** Comparison of micro-, ultra-, nanofiltration and reverse osmosis [22, 23]

	Microfiltration	Ultrafiltration	Nanofiltration	Reverse osmosis
Membrane	Symmetrical/ Asymmetrical	Asymmetrical	Asymmetrical	Asymmetrical
Thickness, $\mu\text{m}$ Thin layer, $\mu\text{m}$	10-150	150-250 0.1-5	150 0.1-5	150 0.1-5
Approx pore size, $\mu\text{m}$	4-0.02	0.1-0.002	< 0.002	< 0.002
Rejection of	Sand, silt, clays, <i>Giardia lamblia</i> and <i>Cryptosporidium</i> cysts, algae, and some bacterial species	Materials removed by microfiltration, plus polysaccharides, proteins, macromolecules some species of bacteria and viruses, humic materials	Almost all cysts, bacteria, viruses and humic materials; HMWC*, mono-, di-, oligosaccharides,	HMWC, LMWC**, sodium chloride, glucose, amino acids; radium, pesticides, cysts, bacteria, viruses
Approx. MWCO value***, Da	> 100000	1000-100000	200-10000	< 200
Membrane materials	Ceramic, polysulfone, PVDF****, polypropylene	Ceramic, cellulose acetate, PVDF, polysulfone (thin film)	Cellulose acetate (thin film)	Cellulose acetate (thin film)
Applied pressure, MPa	0.1-0.4	0.2-0.7	0.6-1.0	1.0-10.0

\*HMWC – high molecular weight compounds;

\*\*LMWC – low molecular weight compounds;

\*\*\*Data vary in different sources;

\*\*\*\*PVDF – polyvinylidenedifluoride.

The separation efficiency of certain membrane can be evaluated with meanings of flux and selectivity. Flux shows the volume of feed passing through the certain membrane area for the fixed time and expresses as  $\text{l}/(\text{m}^2 \cdot \text{h})$  or generally units of volume divided by multiplication of time and area units. Mass and molar units can be used instead of volume ones. [20]

A selectivity is expressed either by rejection coefficient (R) or separation factor ( $\alpha$ ). In cases of solvent-solute systems the rejection coefficient with respect to dissolved substances is widely used to express selectivity. It can be estimated in accordance to equation (25).

$$R = \frac{c_f - c_p}{c_f} = 1 - \frac{c_p}{c_f} \quad (25)$$

where  $c_f$  and  $c_p$  are the concentrations of solute in the feed and in the permeate. If the rejection coefficient equals to 1 the all amount of solute remains in concentrate and it would be the ideal separation case; if R is 0 both solute and solvent penetrate through membrane. [20]

The separation factor is applied for mixtures of gases or organic liquids and can be calculated as follows:

$$\alpha_{A/B} = \frac{y_A/y_B}{x_A/x_B} \quad (26)$$

where  $y_A$  and  $y_B$  are concentrations of components A and B in permeate;  $x_A$  and  $x_B$  – concentrations of the components in the feed. The separation factor  $\alpha$  is chosen to be greater than 1. If component A passes through the membrane in shorter time than B separation factor is defined as  $\alpha_{A/B}$  and *vice versa* if B permeates faster separation factor is  $\alpha_{B/A}$ . Separation does not occur in the case of  $\alpha_{A/B} = \alpha_{B/A}$ . [20]

## 5 THE COMPOSITION OF BLEACHING FILTRATES

The materials presenting in the filtrates are composed of:

- substances entering bleaching stage with pulp or liquor accompanying the pulp;
- substances generated through various reactions (oxidation, degradation, chlorination, *etc.*) in the bleaching stage and released into liquid;
- residual chemicals used in bleaching;
- compounds coming into filtrate with wash water.

Therefore, the composition of filtrates depends on pulp being bleached (or wood raw material), bleaching sequence, conditions in the bleaching stage and composition of liquor used for washing [24].

In the bleaching plant two kinds of filtrates can be distinguished: acidic and alkaline ones [24]. Generally, acid and alkaline filtrates differ in amounts of COD, TOC, AOX, content of inorganic materials and also vary in molar mass distribution of dissolved components.

Table 10 shows the results of bleach plant effluent analysis on composition. The samples were taken from a Scandinavian softwood kraft pulp mill employing OD(EOP)DE<sub>2</sub>D bleaching sequence. The mean kappa number of pulp after oxygen delignification is 13. The acid filtrate represents a mixture of the filtrates from chlorine dioxide treatment stages and alkaline filtrate consists of equal amounts of the EOP and E<sub>2</sub> filtrates. [25]

**Table 10.** Results of analysis of bleach plant effluents before waste treatment [25]

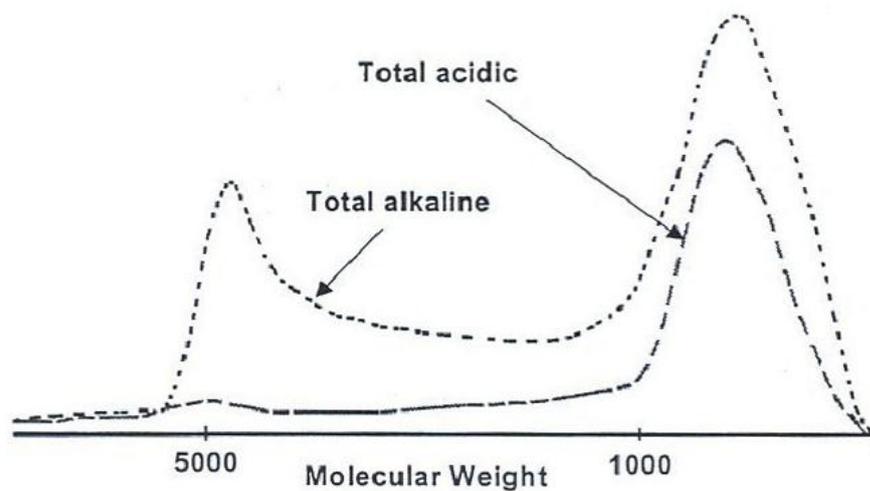
Parameters and units	Acid filtrate	Alkaline filtrate
Flow, m <sup>3</sup> /t	15.9	14.2
Dissolved solids, %	0.25	0.37
LOI*, % of dry solids	39	32
AOX, kg/t	0.47	0.16
COD, kg/t	8.9	20.5
TOC, kg/t	3.8	7.4
Colour (Pt-Co), kg/t	5.0	10.7
Lignin, kg/t	1.8	6.3
Carbohydrates, kg/t	1.1	1.0
Extractives, kg/t	0.66	1.3
Fatty acids, g/t	6.2	47.2
Resin acids**, g/t	0.88	9.5
Sterols**, g/t	0.33	3.92
Na, kg/t	6.1	12.8
K, kg/t	0.18	0.07
Ca, kg/t	0.80	0.17
Mg, kg/t	0.40	0.10
Mn, kg/t	0.030	0.006
Cl (total), kg/t	6.1	4.9
SO <sub>4</sub> <sup>2-</sup> , kg/t	24	9.2
CO <sub>3</sub> <sup>2-</sup> , kg/t	< 0.36	3.4
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	0.19	0.82

\*Loss of ignition

\*\*The composition of the resin acids and sterols in the different effluents are represented in Figures 1 and 2 of Appendix I.

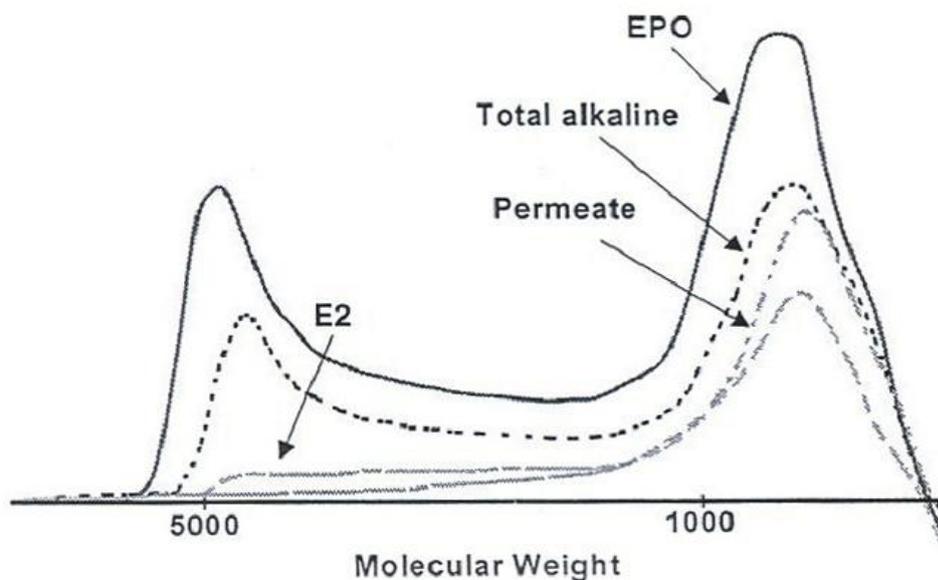
Basing on the data from Table 10 it can be concluded that the alkaline filtrates are rich in TOC, COD, lignin, resin and fatty acids, and sterols while the acidic filtrates have greater quantity of AOX and most of undesired nonprocess elements such as calcium, potassium and manganese. The same results can be found in various literature sources (*e.g.* [1], p 751-762).

Molecular weight distributions of organic and inorganic materials in the filtrates were measured also [25]. The data are reflected in Figures 24 and 25.



**Figure 24.** RI chromatogram for untreated bleach plant total alkaline and acid effluents [25].

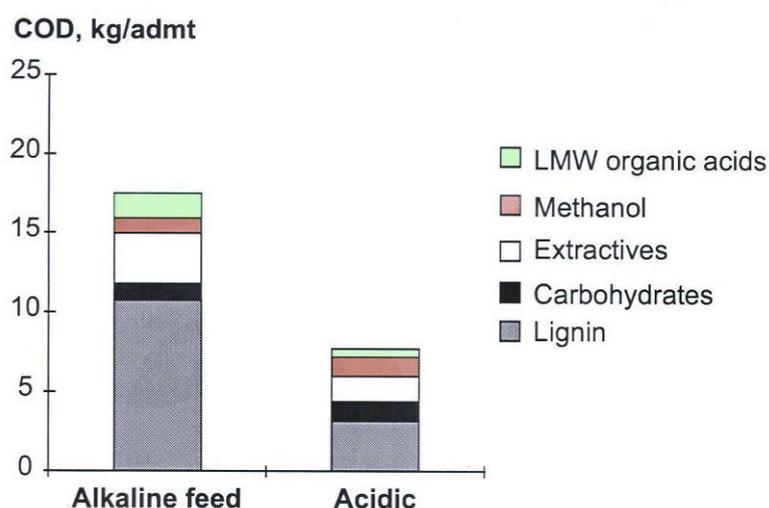
As it can be seen from Figure 24 the total alkaline effluent has a considerable quantity of substances with high molecular mass in contrast to the acid effluent which consists mostly of low molecular weight compounds. Thus, lignin in the alkaline effluent is composed of large fragments as compared with acid filtrates, lignin of which is represented by the low molecular weight fragments. [1, 25]



**Figure 25.** RI chromatogram for untreated bleach plant total alkaline effluent, EOP filtrate, E2 filtrate and permeate after ultrafiltration of total alkaline effluent [25].

The difference between the EOP and E<sub>2</sub> alkaline filtrates can be observed from Figure 25. The substances of the E<sub>2</sub> filtrate similarly to acid effluent are represented with low molecular weight compounds as opposed to the EOP filtrate [25].

The contribution in COD value of low-molecular organic acids, methanol, extractives, carbohydrates and lignin is shown in Figure 26. As it can be seen from the diagram the lignin constitutes the biggest share in oxygen consuming materials in alkaline filtrate [25].



**Figure 26.** COD characterization [26].

The conversion factors from the amount of substance to COD value for main oxygen consuming materials are represented in Table 11. These values can be used to calculate COD value of filtrate by multiplying the mass of individual component on the factor and summing obtained figures [26]. As [26] reports the accuracy of calculated value is 10 % of measured one.

**Table 11.** Conversion factors used in the COD characterization [26]

Compounds	Factors from substance to COD
Lignin	1.9
Carbohydrates	1.2
Extractives	2.7
Methanol	1.5
Low molecular weight acids:	
Acetic acid	1.1
Formic acid	0.4
Glycolic acid	0.6
Lactic acid	1.1
Oxalic acid	0.2

Washing liquor also affects filtrate composition since it can bring additional specific materials to the filtrate and to the water circulation system of bleach plant. For example, as wash water the black liquor evaporation condensate can be applied; it contains various contaminants in concentrations from trace amounts up to 1 % by weight. Among them are low molecular organic compounds such as alcohols (methanol, ethanol, propanols, *etc.*), sulfur containing odorous substances (methyl mercaptan, thiophene, *etc.*), terpenes (pinenes, camphene, *etc.*), ketones (acetone, 2-butanone, *etc.*), dissolved gases (methane, ethene, *etc.*), phenolics (phenol, guaiacol, *etc.*), various acids (formic, resin, fatty, *etc.*). The methanol alcohol is dominant organic presented in the condensate. [27, 28]

## EXPERIMENTAL PART

### 6 LABORATORY EXPERIMENT

#### 6.1 Sampling of pulps and filtrates

##### 6.1.1 Hardwood line

From hardwood line pulp was taken after D<sub>0</sub> and EOP bleaching stages from the drum before washing and after dilution. The properties of pulp are represented in Table 12. Filtrates were gathered from D<sub>1</sub>, EOP and EP washers (Figure 1 of Appendix II).

**Table 12.** Measured parameters of hardwood pulp samples

Pulp	Consistency, %	Brightness, %	Kappa no	Viscosity, dm <sup>3</sup> /kg
After D <sub>0</sub>	2.2	56	6.6	1000
After EOP	2.4	65.8	4.2	970

##### 6.1.2 Softwood line

From softwood line pulp was taken after D<sub>1</sub> and PO bleaching stages before washing. The properties of pulp are reflected in Table 13. The following filtrates were taken for the experiments: D<sub>1</sub> “dirty”, D<sub>2</sub> “dirty”, D<sub>2</sub> “clean”, PO “dirty”, PO “clean” (Figure 2 of Appendix II). The “dirty” and “clean” terms refer to discharging streams from the DD washer.

**Table 13.** Measured parameters of softwood pulp samples

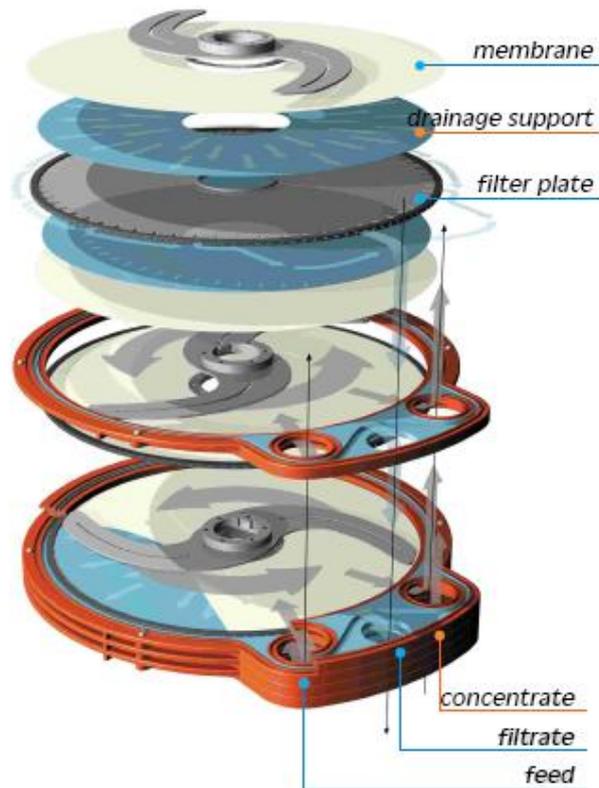
Pulp	Consistency, %	Brightness, %	Kappa no	Viscosity, dm <sup>3</sup> /kg
After D <sub>1</sub>	9.8	48.1	7.5	970
After PO	8.9	81.7	1.7	930

All hardwood and softwood samples were stored in cool place in order to keep them as unchanging as possible.

## 6.2 Ultrafiltration

The EOP and EP filtrates from hardwood line, the D<sub>1</sub> and PO filtrates from softwood line were treated with ultrafiltration.

The ultrafiltration was done in the Centre of Separation Technologies of Lappeenranta University of Technology by Alfa Laval UFX5 polysulfone membrane (cut-off value of 5000 g/mol). All membranes before the ultrafiltration were cleaned with the alkaline 0.2 % Ultrasil 110 cleaning agent (Henkel Ecolabs) in a decanter for 1 hour. After the cleaning the membranes were washed and placed in the cross-rotational filter CR200 (Figure 27). [29]



**Figure 27.** Cross-Rotational filter CR200 [30].

The conditions of the ultrafiltration procedure are represented in Table 14.

**Table 14.** Conditions of the membrane treatment [29]

Parameter	Value
The membrane area, m <sup>2</sup>	0.012
Temperature, °C	40-60
Pressure, bar	3
approx. VRF*	5
Speed of rotor, m/s	9

\*VRF – volume reduction factor. It can be calculated as follow:

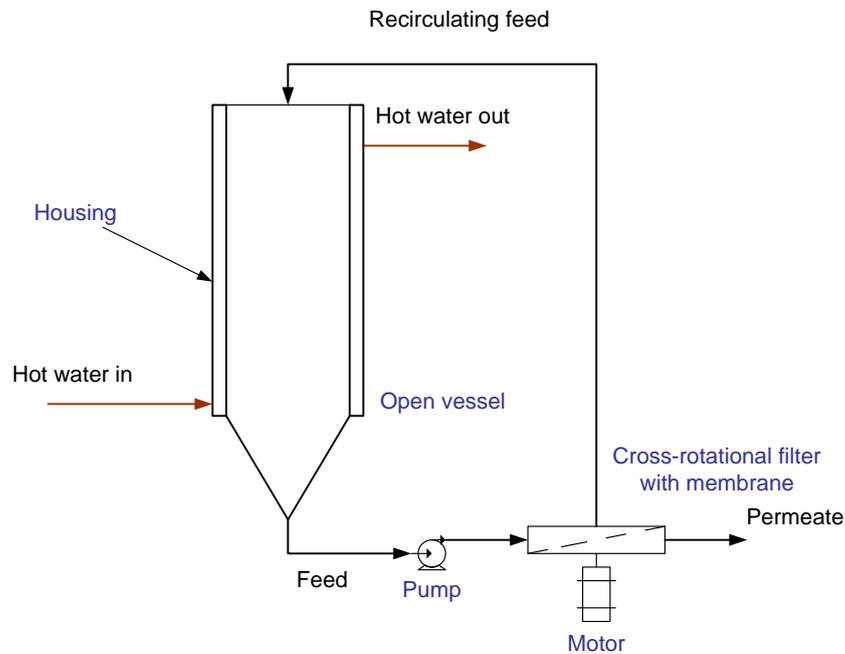
$$VRF = \frac{V_f}{V_f - V_p}, \quad (27)$$

where

$V_f$  – volume of filtrate fed to treatment, l;

$V_p$  – volume of the permeate, l.

The pure water permeability was measured before and after the ultrafiltration in order to explore a membrane contamination. The measurements were performed at the temperature of 40 °C and pressure of 2.5 bars. [29]



**Figure 28.** The sketch of membrane installation.

Figure 28 shows the schematic drawing of the membrane installation. The feed was preheated in open vessel and then pumped to the cross-rotational filter. The

temperature was supported by hot water fed into the housing of the vessel. In the cross-rotational filter the feed divided into two parts: the first part passed the membrane (permeate) was collected into a container and the second one retained on the membrane was recirculated back into the vessel until achieving of desired VRF. The rest of the feed after the treatment representing a concentrate was gathered for further analysis. Permeates were used for washing in trial experiments and also underwent some measurements.

### **6.3 Washing and bleaching**

Washing and bleaching were done in UPM research centre in Lappeenranta. The experiments were based on the mill's bleaching processes represented in Figure 1 (hardwood) and Figure 2 (softwood) of Appendix II. The first two washing stages with the following bleaching were simulated in both cases with hardwood and softwood pulps.

The sequence of all experiments in this work is shown in Figure 29. The amount of sample used for the experiments was 250 g of oven dry pulp. The washing and bleaching procedures are described in detail in further chapters. After the bleaching pulp was thickened and washed two times with 1.25 litres of hot water.



**Figure 29.** The sequence of experiments.

Four cases were studied (according to pulp samples) – two with hardwood and two with softwood pulp (Tables 15 and 16). Each case had a reference (odd number) and trial experiments (even number). All experiments were executed two times in order to get reliable results.

In the reference experiments with hardwood pulp the washing was performed only with the untreated filtrates. In trial experiments the same acid filtrate was used while alkaline untreated filtrates were replaced with the corresponding treated ones (Table 15). Such experimental setting enabled exploring the possibility to improve performance in a subsequent bleaching stage.

**Table 15.** List of experiments with hardwood pulp

Experiment		Pulp	Washing filtrates	Bleaching conditions
1 (reference)	a	after D <sub>0</sub> stage	<u>D<sub>1</sub> untreated and EOP untreated</u>	EOP stage
	b			
2 (trial)	a		<u>D<sub>1</sub> untreated and EOP treated</u>	EOP stage
	b			
3 (reference.)	a	after EOP stage	<u>EP untreated</u> and D <sub>1</sub> untreated	D <sub>1</sub> stage
	b			
4 (trial)	a		<u>EP treated</u> and D <sub>1</sub> untreated	D <sub>1</sub> stage
	b			

The experiments with softwood pulp were set in another way in contrast to hardwood pulp (Table 16). The replacement of the untreated filtrates with treated ones considered the case of filtrate recirculation with the aim to reduce the amount of effluents. Also it has to be noted that the order of filtrates used for washing was changed in the experiments 7 and 8.

**Table 16.** List of experiments with softwood pulp

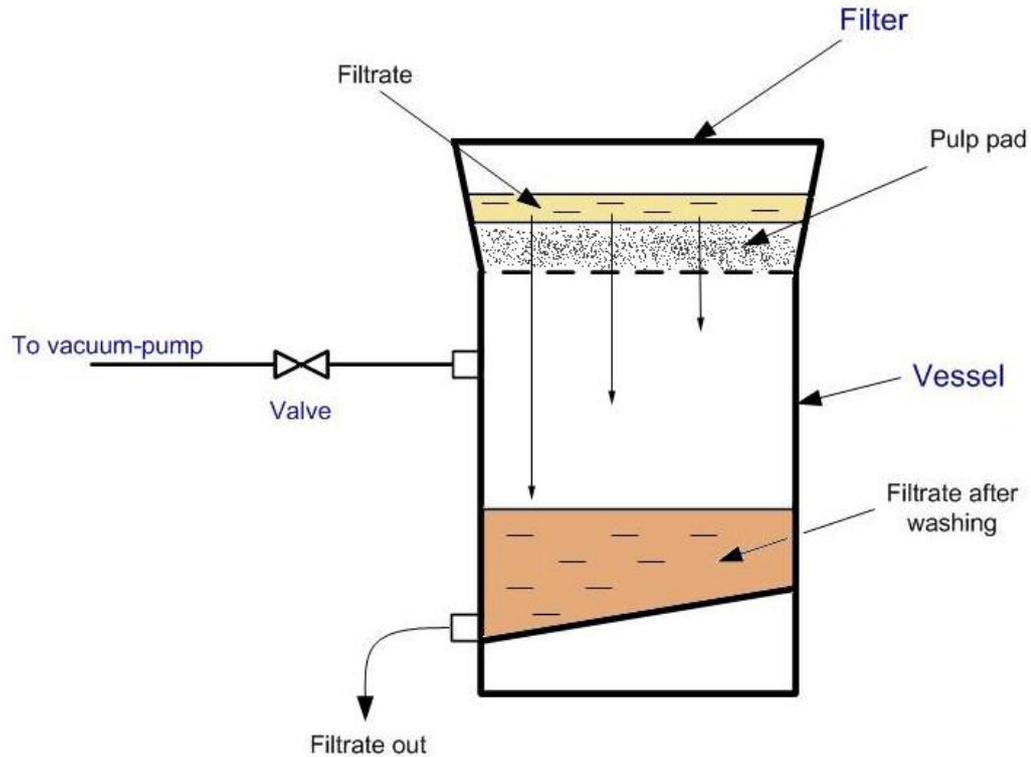
Experiment		Pulp	Washing filtrates	Bleaching conditions
5 (reference)	a	Pulp after D <sub>1</sub> stage	<u>D<sub>2</sub> "dirty" untreated</u> and PO "clean" untreated	PO stage
	b			
6 (trial)	a		<u>D<sub>1</sub> "dirty" treated</u> and PO "clean" untreated	PO stage
	b			
7 (reference)	a	Pulp after PO stage	D <sub>2</sub> "clean" untreated filtrate and <u>hot water</u>	D <sub>2</sub> stage
	b			
8 (trial)	a		<u>PO "dirty" treated</u> and D <sub>2</sub> "clean" untreated	D <sub>2</sub> stage
	b			

The schemes of the experiments can be found in Figures 1-8 of Appendix III.

### 6.3.1 Washing

Before washing the filtrates and pulp slurry warmed up in the microwave oven to the temperature of 60-75 °C according to the experimental set. Washing was done on a big ceramic filter similar to Buchner funnel fixed on a vessel (Figure 30). Pulp suspension poured out onto the funnel and thickened at the vacuum. First time collected liquor

recycled back to the funnel in order to avoid the loss of fines, and then pulp underwent thickening again. After that it was washed two times with 1.25 litres of each filtrate (the total amount of wash liquor is 2.5 litres). Filtrate evenly spread on pulp with a ladle passed through the pulp pad under the vacuum inside of the vessel.



**Figure 30.** Laboratory washing equipment.

### **6.3.2 Bleaching**

For the chlorine dioxide bleaching a fibreglass vessel with the volume of 15 litres was used. The vessel is disposed in the thermostatic box and rotates the treatment. The temperature inside the box is adjusted manually.

A pressurized alkaline treatment was performed in special rotating digester of Haato-tuote Oy. The temperature rise rate and final temperature are set manually. Pressure inside the digester is measured by manometer and can be adjusted manually by closing or opening the valve.

The amount of oven dried pulp used for the bleaching was 200-240 g. Pulp was heated into microwave oven and mixed with required amount of chemicals. The proper consistency was obtained by the addition of water. Chemical charges and conditions were set as on the mill for the corresponding stages (Tables 17-20).

**Table 17.** Conditions of EOP stage (experiments 1 and 2)

Chemicals	Consumption, %	Conditions				
		Temperature, °C	Retention time, min	Pressure**, MPa	pH	Consistency, %
NaOH	0.88	60-65	105	0.5	11	10
H <sub>2</sub> O <sub>2</sub>	0.24					
O <sub>2</sub> *	-					

\*Consumption of oxygen was considered according to pressure inside of digester;

\*\*Treatment was done at the pressure of 0.5 MPa during first 15 minutes then degassing occurred and treatment continued at the pressure of 0.1 MPa for the rest of time.

**Table 18.** Conditions of D<sub>1</sub> stage (experiments 3 and 4)

Chemicals	Consumption, %	Conditions				
		Temperature, °C	Retention time, min	Pressure, MPa	pH	Consistency, %
ClO <sub>2</sub>	1.33	60-65	150	0.1	3.5-4.0	10

**Table 19.** Conditions of PO stage (experiments 5 and 6)

Stage*	Chemicals	Consumption, %	Conditions				
			Temperature, °C	Retention time, min	Pressure, MPa	pH	Consistency, %
1	MgSO <sub>4</sub>	0.06	75	45	0.1	10.5- 11.0	10
	NaOH	1.00					
	H <sub>2</sub> O <sub>2</sub>	0.28					
	O <sub>2</sub> **	-					
2	NaOH	0.5	75	45	0.1	10.5- 11.0	10
	H <sub>2</sub> O <sub>2</sub>	0.28					
	O <sub>2</sub>	-					

\*Treatment was done in two steps without intermediate washing;

\*\*Consumption of oxygen was considered according to pressure;

**Table 20.** Conditions of D<sub>2</sub> stage (experiments 7 and 8)

Chemicals	Consumption, %	Conditions				
		Temperature, °C	Retention time, min	Pressure, MPa	pH	Consistency, %
ClO <sub>2</sub>	0.44	60-65	90	0.1	4.0-5.5	10

Chlorine dioxide and hydrogen peroxide used for bleaching were analyzed before the experiments in order to verify concentrations.

#### 6.4 Analysis of pulp

Initial pulp from the mill, after bleaching and washing with hot water was analyzed on viscosity, kappa number and brightness. Pulp after washing with filtrates (or permeates) was analyzed only on brightness. The methods and their description are represented in Table 21.

**Table 21.** Methods for pulp analysis

Analyses	Standard / Description
Consistency	ISO 4119: 1995 (E)
Viscosity	ISO 5351-2004(E)
Kappa number	SCAN-C 1:00
Brightness	Laboratory determination which is simplified version of ISO method. Certain amount of pulp was disintegrated in water. This pulp suspension was used to make three samples on Buchner funnel with diameter of 70 mm. Formed wet sheets were dried in a drying device at the temperature of 95 °C and vacuum of 950 mbar for 7 minutes. Brightness of the sheets was measured on “L and W Elrepho SE 070/070R” spectrophotometer

#### 6.5 Analysis of filtrates

Filtrates fed to the ultrafiltration and permeates were analyzed on COD, TOC, dry solids and chlorine contents. The same analyses and additionally gross calorific value and metal content were done for the concentrates. Metal content also was measured for D<sub>1</sub> “dirty” permeate and D<sub>2</sub> “dirty” filtrate.

COD measurements were done photometrically with accordance to ISO 15705 standard.

TOC was determined on TOC-5000 A Shimadzu basing on SFS-EN 1484 standard.

Dry solids content was measured gravimetrically: certain amount of liquid was evaporated at the temperature of 105°C for several days, residue after evaporation was weighted. Dry solids content was calculated as a ratio between the masses of residue after evaporation and of liquid before evaporation.

Chlorine content was evaluated by ion chromatography according to SFS-EN ISO-10304-1 standard. Before the measurements samples underwent the special preparation: 5 ml of the sample was mixed with 5 ml of 30% hydrogen peroxide and 4 ml of water and treated for 23 minutes into microwave oven. This time split in the manner shown in Table 22.

**Table 22.** Time and operating power of microwave oven during preparation of the samples for total chlorine analyses

Step	Time, min	Power, W
1	1	250
2	2	0
3	8	250
4	7	430
5	5	500

Gross calorific value was determined according to standard ISO 1928.

Metal content was determined on atomic adsorption spectroscope basing on standard SFS 3044. Before the analysis sample was treated in the following way: 3 ml of hydrogen peroxide (30 % concentration) and 5 ml of nitrogen acid (65 % concentration) were added to 5 ml of the sample; this mixture was placed into microwave oven for 23 minutes, the time and power were set in the same manner as it was done in the preparation for the total chlorine determination (Table 22).

## 7 RESULTS AND DISCUSSIONS

### 7.1 Ultrafiltration

During the ultrafiltration the volume reduction factor was about 5 depending on filtrate, which means that one fifth part of fed filtrate was rejected as a concentrate (Table 23).

**Table 23.** Volumes of feeds, permeates and concentrates, and volume reduction factors [29]

Filtrate	Feed, l	Permeate, l	Retentate, l	VRF
EOP	22.7	17.4	5.4	4.3
EP	24.9	21.2	3.8	6.7
PO “dirty”	22.0	17.6	2.3	5.0
D <sub>1</sub> “dirty”	25.0	19.1	2.4	4.2

The discrepancy of mass balances for PO “dirty” and D<sub>1</sub> ”dirty” is due to the evaporation of the feed [29].

The fouling of a membrane can be observed from difference of pure water permeability before and after treatment. The measure of fouling is flux reduction which is calculated by the following equation:

$$FR = \left(1 - \frac{PWP_a}{PWP_b}\right) \cdot 100\% \quad (28)$$

where:

PWP<sub>a</sub> – pure water permeability after the ultrafiltration, kg/m<sup>2</sup>h bar;

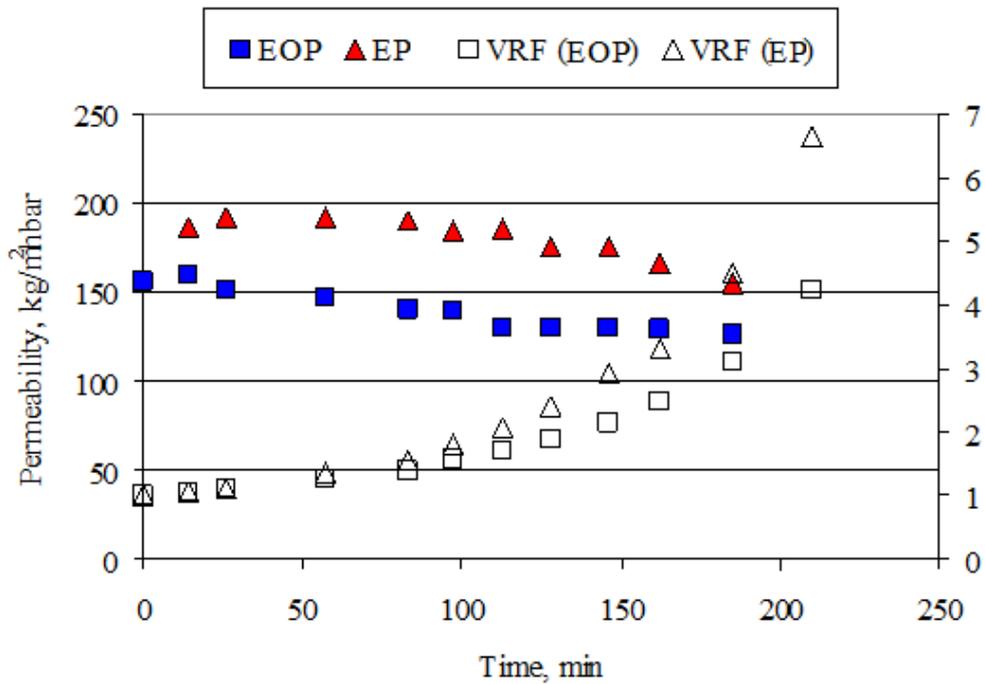
PWP<sub>b</sub> – pure water permeability before the ultrafiltration, kg/m<sup>2</sup>h bar. [29]

As can be viewed from Table 24, the alkaline filtrates have the negative values of flux reduction, which means that after the treatment flux became higher. Such result could be affected by a membrane impairing; in order to find the precise reasons for that phenomenon additional measurements (for example, rejection coefficient) have to be provided. From another side, the acid filtrate D<sub>1</sub> “dirty” has the positive value of flux reduction which says about the fouling of membrane.

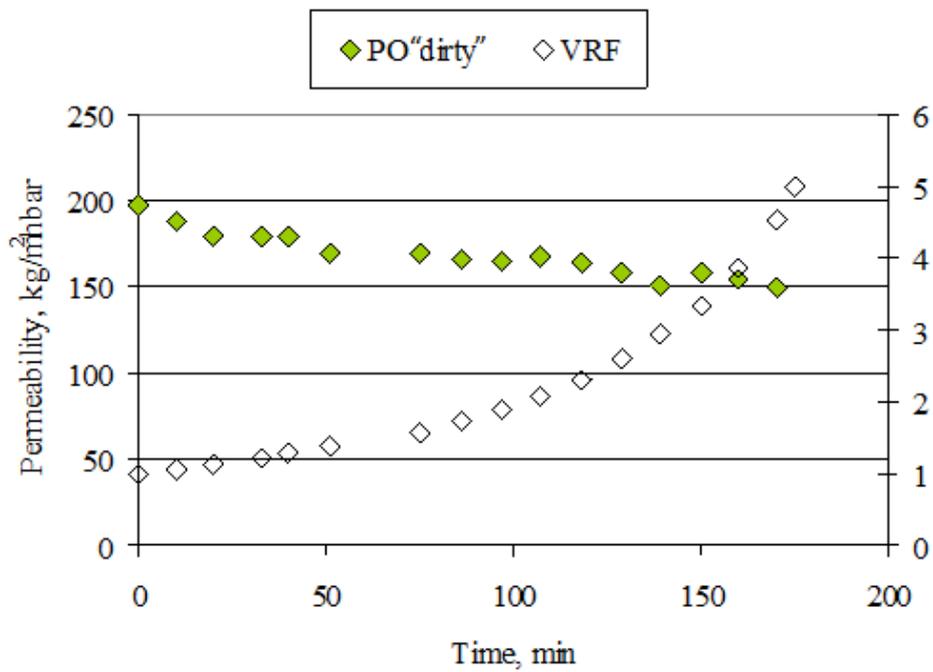
**Table 24.** Average pure water permeability and flux reduction [29]

Filtrate	PWP <sub>b</sub> , kg/m <sup>2</sup> h bar	PWP <sub>a</sub> , kg/m <sup>2</sup> h bar	FR, %
EOP	142	155	-9
EP	155	166	-7
PO “dirty”	139	172	-24
D <sub>1</sub> “dirty”	138	95	31

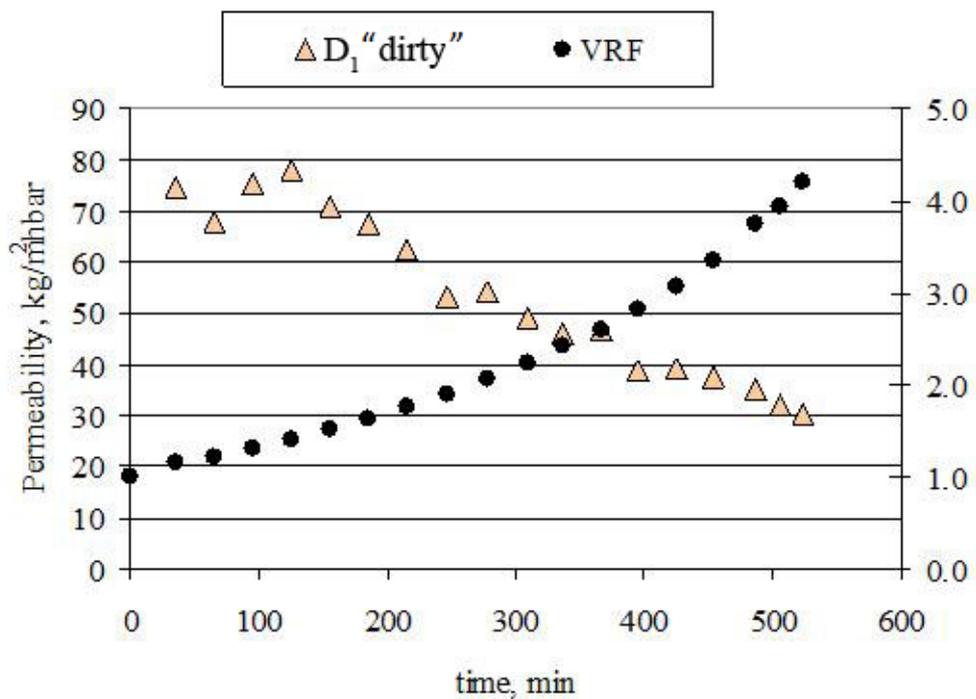
The permeability and volume flux reduction are represented in Figures 31-33. Basing on data from these diagrams it can be conclude that in case of the acid filtrate significant flux reduction occurred (permeability decreased from 80 kg/m<sup>2</sup>h bar to 30 kg/m<sup>2</sup>h bar) during the treatment as compared to alkaline ones which had a slight decrease of permeability. Also it is noticeable that more time was needed to treat the acid filtrate.



**Figure 31.** Permeability and volume reduction factor during the ultrafiltration of EOP and EP filtrates [29].

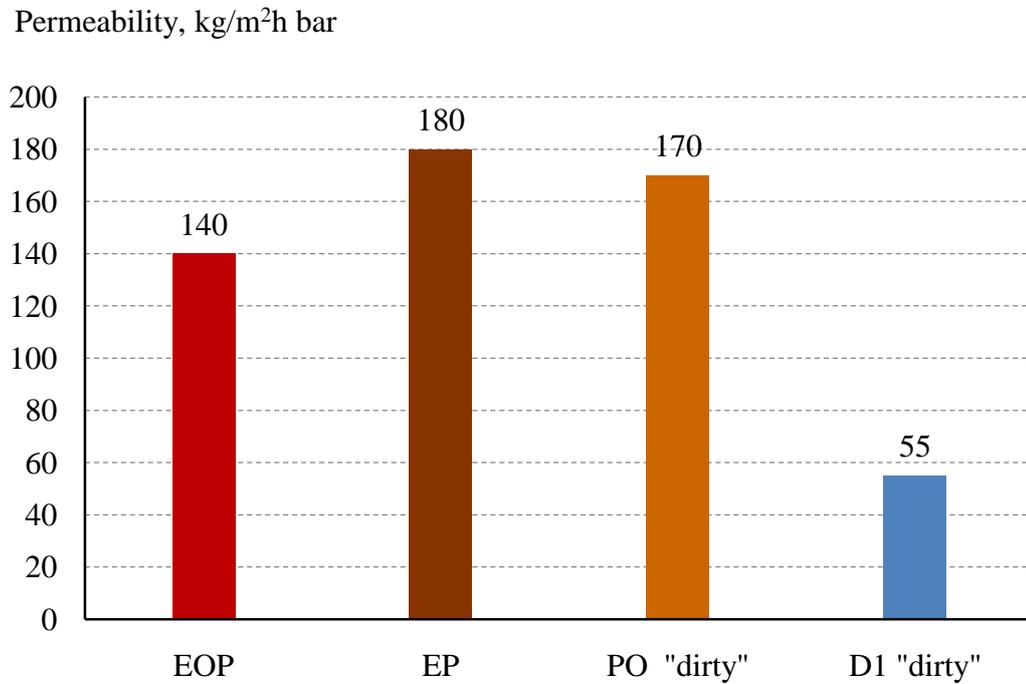


**Figure 32.** Permeability and volume reduction factor during the ultrafiltration of PO “dirty” filtrate [29].



**Figure 33.** Permeability and volume reduction factor during the treatment of D<sub>1</sub> “dirty” filtrate [29].

Average permeability of treated filtrates is shown in Figure 34: D<sub>1</sub> “dirty” has the lower permeability than the alkaline filtrates; therefore duration of the acid filtrate treatment was longer as comparing with the alkaline filtrates.



**Figure 34.** Average permeability of filtrates during the treatment.

Basing on the results from ultrafiltration procedure it can be said that UFX 5 membrane better suits to treat alkaline filtrates rather than acid ones.

## 7.2 Washing

Such parameters as dilution factor, displacement ratio and standardized Norden efficiency factor were calculated to evaluate the washing performance (Table 25, next page). For calculations COD values were considered as dissolved substances or carry-over and average COD values of wash filtrates were used to simplify the estimation.

**Table 25.** COD and volumes of liquid streams around the washer and average values of washing parameters

Experiment	Wash liquor		Discharging filtrate		Liquid accompanying pulp before washing		Liquid accompanying pulp after washing		Dilution factor, m <sup>3</sup> /t	Displacement ratio, %	Standardized Norden efficiency factor
	COD (average), mg/l	Volume (total), ml	COD, mg/l	Volume, ml	COD, mg/l	Volume, ml	COD, mg/l	Volume, ml			
1 (ref.)	1540	2500	1180	12120	1080	11010	3580	890	6.4	> 100	-
2 (test)	820	2500	1080	12020	1080	11010	2130	950	6.2	< 0	-
3 (ref.)	1030	2500	2145	11460	2280	10300	1150	815	6.7	90.4	4.7
4 (test)	730	2500	2080	11380	2280	10300	890	920	6.3	89.0	4.8
5 (ref.)	2240	2500	2810	3540	2630	2290	4170	890	6.4	< 0	-
6 (test)	2870	2500	2690	3460	2630	2290	5280	830	6.7	< 0	-
7 (ref.)	310	2500	2950	3590	4430	2560	670	950	6.2	91.3	4.6
8 (test)	1400	2500	3460	3550	4430	2560	1280	1040	5.8	> 100	-

“-” means that figure could not be obtained due to negative value under the logarithm (see equation 6 in chapter 2.2)

### 7.3 Analyses of pulps

#### 7.3.1 Hardwood pulp

Concerning hardwood pulp the applying of treated filtrates as it was done in experiment doesn't affect bleaching efficiency in the following stage as can be conclude basing on pulp parameters after bleaching (Tables 26 and 27, respectively).

**Table 26.** Viscosity, kappa number and brightness of pulp in different points of experiments 1 and 2

Point in the experiment	Measurement	Experiment	
		1 (reference)	2 (trial)
Initial pulp from the mill	Brightness, %	56	
	Kappa number	6.5	
	Viscosity, dm <sup>3</sup> /kg	1000	
Pulp after washing	Brightness, %	55.2	55.6
Pulp after washing and bleaching	Brightness, %	68.5	69
	Kappa number	3.6	3.8
	Viscosity, dm <sup>3</sup> /kg	970	960
Spent bleaching liquor	Residual H <sub>2</sub> O <sub>2</sub> , %	0	0

**Table 27.** Viscosity, kappa number and brightness of pulp in different points of experiments 3 and 4

Point in the experiment	Measurement	Experiment	
		3 (reference)	4 (trial)
Initial pulp from the mill	Brightness, %	65.8	
	Kappa number	4.2	
	Viscosity, dm <sup>3</sup> /kg	970	
Pulp after washing	Brightness, %	68	68.7
Pulp after washing and bleaching	Brightness, %	82.3	82.1
	Kappa number	2.2	2.2
	Viscosity, dm <sup>3</sup> /kg	970	970
Spent bleaching liquor	Residual ClO <sub>2</sub> , %	0	0

### 7.3.2 Softwood pulp

Comparing the final parameters of pulp from the experiments 5 and 6 (Table 28) it can be said that the substitution of D<sub>2</sub> “dirty” filtrate with D<sub>1</sub> “dirty” treated one or permeate has a strong negative effect on a bleaching efficiency in the following PO stage, since all parameters of pulp after the bleaching in the trial experiment are worse than that of pulp in the reference case.

**Table 28.** Viscosity, kappa number and brightness of pulp in different points of experiments 5 and 6

Point in the experiment	Measurement	Experiment	
		5 (reference)	6 (trial)
Initial pulp from the mill	Brightness, %	48.1	
	Kappa number	7.5	
	Viscosity, dm <sup>3</sup> /kg	930	
Pulp after washing	Brightness, %	46.8	46.9
Pulp after washing and bleaching	Brightness, %	71.9	68.6
	Kappa number	2.2	2.4
	Viscosity, dm <sup>3</sup> /kg	920	770
Spent bleaching liquor	Residual H <sub>2</sub> O <sub>2</sub> , %	0.18	0.01

The experiments 7 and 8 (Table 29) showed the possibility of the hot water substitution with PO “dirty” treated filtrate and thus decrease the consumption of fresh water, since the properties of pulp after the bleaching are almost the same. According to the process data from the softwood bleach plant flowsheet showed in Figure 2 of Appendix II the approximate amount of saved water equals to 3.1 m<sup>3</sup> per ton of oven-dry pulp.

**Table 29.** Viscosity, Kappa number and brightness of pulp in different points of experiments 7 and 8

Point in the experiment	Measurement	Experiment	
		7 (reference)	8 (trial)
Initial pulp from the mill	Brightness, %	81.7	
	Kappa number	1.7	
	Viscosity, dm <sup>3</sup> /kg	930	
Pulp after washing	Brightness, %	81.9	82
Pulp after washing and bleaching	Brightness, %	86.6	86
	Kappa number	1.3	1.3
	Viscosity, dm <sup>3</sup> /kg	910	910
Spent bleaching solution	Residual ClO <sub>2</sub> , %	0.04	0.07

#### 7.4 The effect of ultrafiltration on bleaching efficiency

##### 7.4.1 Hardwood pulp

It was assumed that the usage of treated filtrates or permeates instead of untreated ones would increase the washing efficiency and would improve the bleaching performance in ensuing stage. As can be seen from Tables 30 and 31 in the experiments with treated filtrates the wash loss or COD carry-over to the succeeding bleaching stage is lower as compared with the reference experiments. But, lower COD values didn't have a positive effect on bleaching procedure as results showed.

**Table 30.** COD values of liquid in pulp suspension coming to bleaching and pulp parameters after bleaching, experiments 1 and 2

Experiment	Amount of pulp coming to bleaching, odg	Parameters of liquor accompanying the pulp*			Parameters of pulp after bleaching**		
		Amount, ml	COD, mg/l	Total COD, mg	Brightness, %	Kappa number	Viscosity, dm <sup>3</sup> /kg
1 (ref.)	200	715	3580	2560	68.5	3.6	970
2 (trial)	200	760	2130	1620	69	3.8	960

\*Parameters of liquor accompanying the pulp are not average values, but these of experiments "a" or "b";

\*\* Parameters of pulp after bleaching are average values from two repeating.

**Table 31.** COD values of liquid in pulp suspension coming to bleaching and pulp parameters after bleaching, experiments 3 and 4

Experiment	Amount of pulp coming to bleaching, odg	Parameters of liquor accompanying the pulp			Parameters of pulp after bleaching		
		Amount, ml	COD, mg/l	Total COD, mg	Brightness, %	Kappa number	Viscosity, dm <sup>3</sup> /kg
3 (ref.)	200	670	1150	770	82.3	2.2	970
4 (trial)	200	735	885	650	82.1	2.2	970

Several possible reasons can be suggested to explain the results:

- The difference of wash liquors in respect to COD is small especially considering experiments 3 and 4, and it doesn't have significant influence on bleaching performance;
- Bleaching performance is affected by other materials (for example transition metals) which have greater effect on bleaching and which couldn't be rejected to a great extend by the ultrafiltration. This can serve as a reason in case of the experiments 1 and 2 where pulp after washing undergoes EOP treatment;
- As it is written in [31, 32] the COD is not suitable measure of wash loss, since some substances (for example methanol, carboxylic acids, *etc.*) significantly contributing to COD don't have an impact on bleaching and authors suggest using lignin content as a tool to identify reasonable carry-over compounds.

#### **7.4.2 Softwood pulp**

In the case of the softwood pulp experiments the COD was also considered as a carry-over in the estimation of washing efficiency. Tables 32 and 34 show the COD load of liquid in pulp suspension after washing and parameters of the pulp after bleaching. The outcomes for both cases can be explained in the same manner as it was done for hardwood pulp experiments.

**Table 32.** COD values of liquid in pulp suspension coming to bleaching and pulp parameters after bleaching, experiments 5 and 6

Experiment	Amount of pulp coming to bleaching, odg	Parameters of liquor accompanying the pulp			Parameters of pulp after bleaching*		
		Amount, ml	COD, mg/l	Total COD, mg	Brightness, %	Kappa number	Viscosity, dm <sup>3</sup> /kg
5 (ref.)	240	840	4170	3500	71.9	2.2	920
6 (trial)	240	800	5280	4220	68.9	2.4	770

\*The amount of residual hydrogen peroxide is 0.18% and 0.01% for the reference and trial experiments, respectively.

The results of the experiments 5 and 6 are affected by transition metals rather than by COD carry-over. D<sub>1</sub> “dirty” permeate contains higher amount of Mn, Fe and considerably greater of Cu as compared to D<sub>2</sub> “dirty” (Table 33). As it is well known transition metals are harmful for bleaching with oxygen containing reagents, including hydrogen peroxide, since they initiate formation of the extremely reactive particles, such as HO· and O<sub>2</sub><sup>·-</sup>, which decompose both lignin and carbohydrates that in turn causes lower brightness and viscosity of pulp.

**Table 33.** Metal content in D<sub>1</sub> “dirty” permeate and D<sub>2</sub> “dirty” filtrate

Analysed liquor	Metal, mg/l			
	Cobalt, Co	Copper, Cu	Iron, Fe	Manganese, Mn
D <sub>1</sub> "dirty" permeate	0.002	7.110	0.750	0.705
D <sub>2</sub> "dirty" filtrate	0.002	0.002	0.015	0.060

For the interpretation of experiments 7 and 8 the arguments which were listed in previous chapter can be added (see 6.4.1).

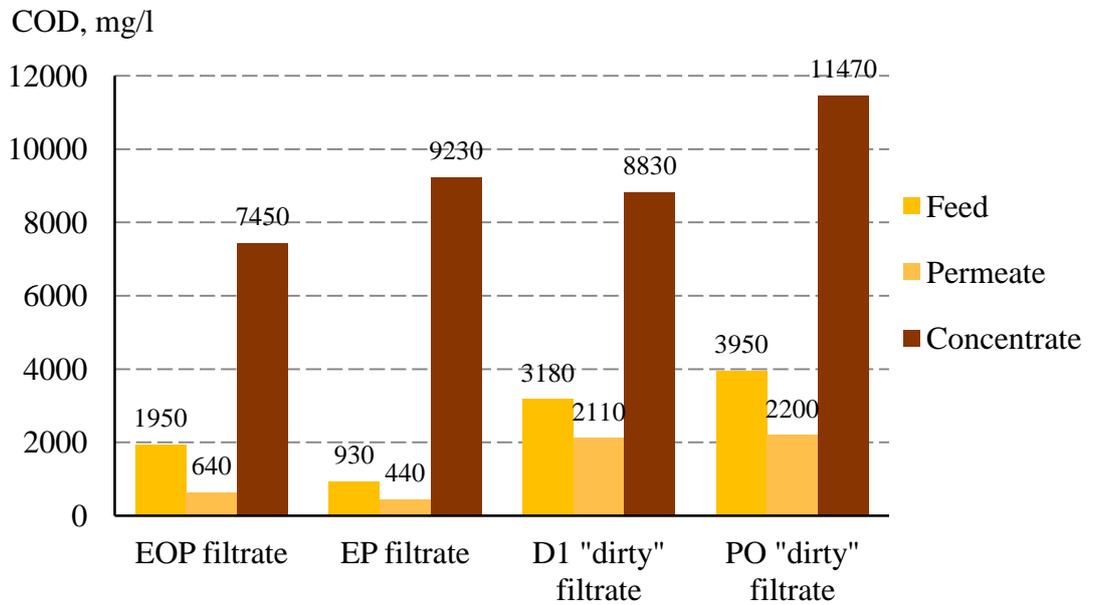
**Table 34.** COD values of liquid in pulp suspension coming to bleaching and pulp parameters after bleaching, experiments 7 and 8

Experiment	Amount of pulp coming to bleaching, odg	Parameters of liquor accompanying the pulp			Parameters of pulp after bleaching*		
		Amount, ml	COD, mg/l	Total COD, mg	Brightness, %	Kappa number	Viscosity, dm <sup>3</sup> /kg
7 (ref.)	230	880	670	590	86.6	1.3	910
8 (trial)	230	960	1280	1230	86	1.3	910

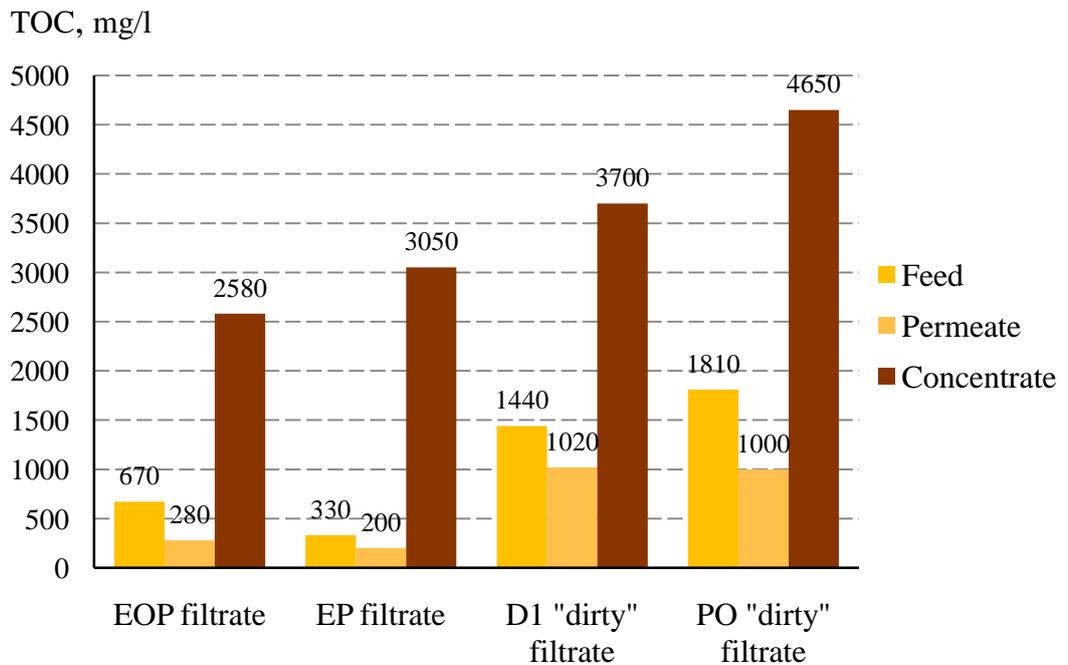
\*The amount of residual chlorine dioxide is 0.04 and 0.07 for the reference and trial experiments, respectively.

### 7.5 Analysis of filtrates

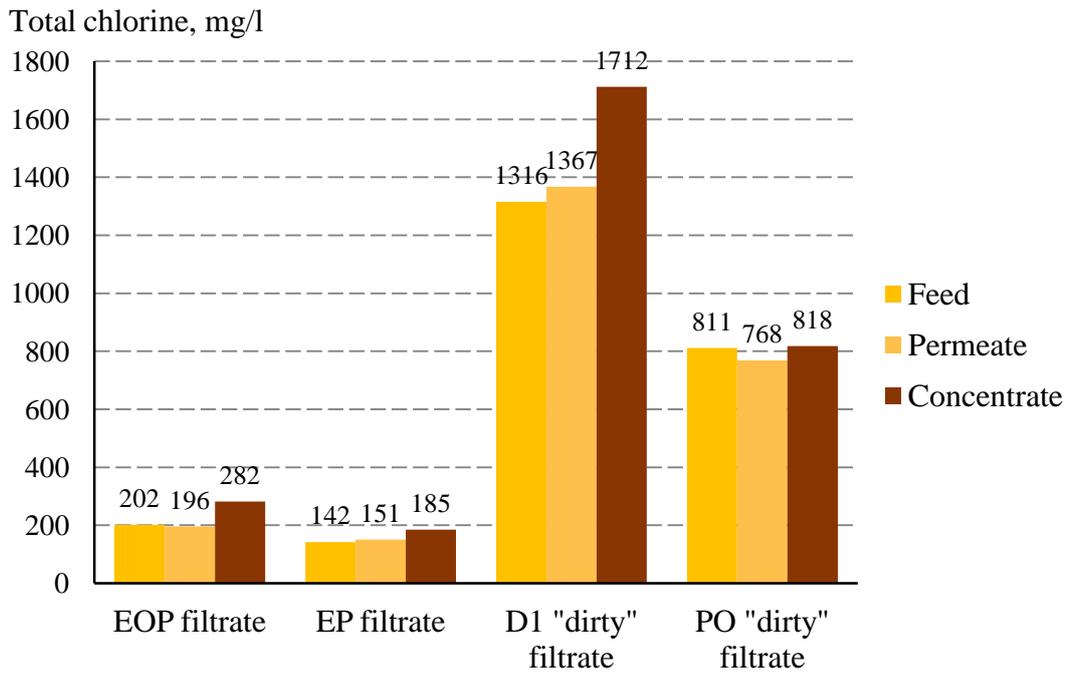
The results from the analyses of the feeds, permeates and retentates are illustrated by diagrams shown in Figures 35-38.



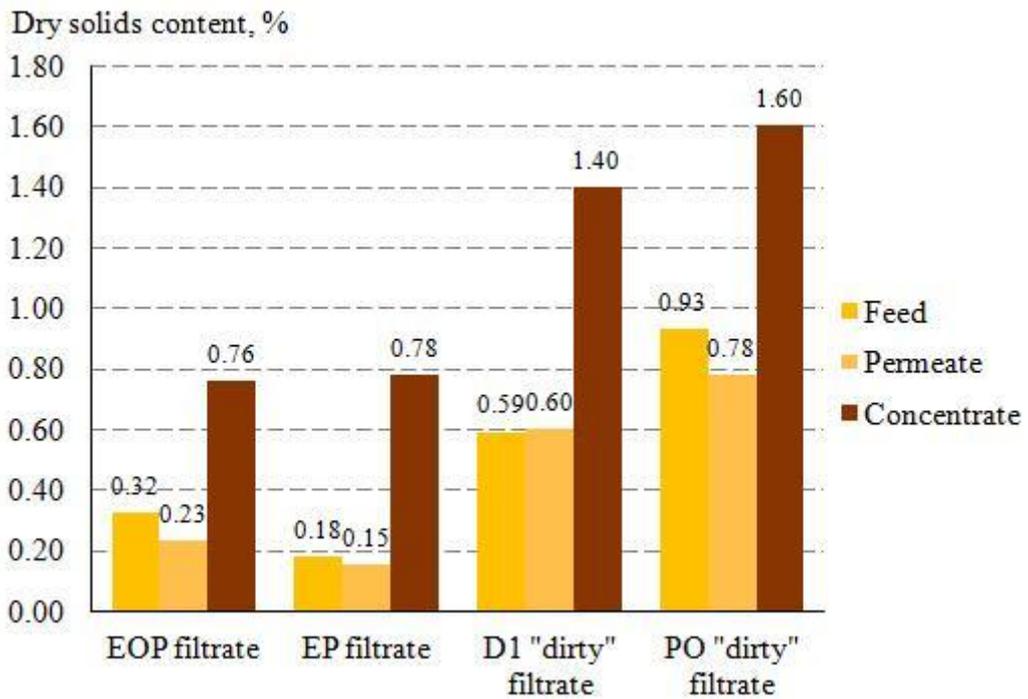
**Figure 35.** COD values of feeds, permeates and concentrates.



**Figure 36.** TOC values of feeds, permeates and concentrates.



**Figure 37.** Total chlorine values of feeds, permeates and concentrates.



**Figure 38.** Dry solids content of the feeds, permeates and concentrates.

Basing on the diagrams represented above the reduction of corresponding parameters by the ultrafiltration was calculated. The results for filtrates from hardwood and softwood streams are represented in Tables 35 and 36, respectively.

**Table 35.** Reduction of TOC, COD, total chlorine and dry solids content in the filtrates by the ultrafiltration; hardwood line

Parameters	EOP			EP		
	feed	permeate	reduction, %	feed	permeate	reduction, %
COD, mg/l	1950	640	67	930	440	54
TOC, mg/l	670	280	58	330	200	39
Total chlorine, mg/l	202	196	3	142	151	(-6)
Dry solids content, %	0.32	0.23	28	0.18	0.15	17

**Table 36.** Reduction of TOC, COD, total chlorine and dry solids content in the filtrates by the ultrafiltration; softwood line

Parameters	PO “dirty”			D <sub>1</sub> “dirty”		
	feed	permeate	reduction, %	feed	permeate	reduction, %
COD,mg/l	3950	2200	44	3180	2110	34
TOC, mg/l	1810	1000	45	1440	1020	29
Total chlorine, mg/l	811	768	5	1316	1367	(-4)
Dry solids content, %	0.93	0.78	16	0.59	0.6	(-2)

The ultrafiltration reduced COD and TOC and in the case of the alkaline filtrates the rejection was more pronounced as comparing with the acid filtrate. These results can be explained by the fact that alkaline filtrates contain greater amount of high molecular weight compounds contributing to COD and TOC as compared to D<sub>1</sub> “dirty” one.

The ultrafiltration doesn't have a separation effect regarding chlorine. The possible reason is that part of chlorine presents in inorganic state and part bound to low molecular weight organic compounds which can't be retained by membrane and split in a ratio according to VRF.

The dry solids content decrease is observed only for the alkaline filtrates and the reduction is lower than for COD and TOC. This means that alkaline filtrates consist mostly of substances with the molecular weight lower than 5000 Da (the cut-off value of the membrane).

The result of dry solids rejection in the case of the acid filtrate might be explained by some errors in analysis and by the evaporation occurred during the ultrafiltration, since the concentrate has increased quantity of dry solids (Figure 38), also the TOC and COD values are different for the feed and permeate.

## ***7.6 COD reduction of bleaching effluents***

In this chapter an approximate estimation of COD reduction of the bleaching effluents and various streams are represented.

### ***7.6.1 Hardwood line***

Basing on the flowsheet (Figure 1 of Appendix II), the part of the filtrates from D<sub>0</sub> and EOP washers come to the waste water treatment plant. According to development manager of the mill the total amount of effluents from hardwood bleaching line is 17 m<sup>3</sup>/ADt or approximately 19 m<sup>3</sup>/odt. 35-40 % of that volume comes from the EOP washer or approximately 7 m<sup>3</sup>/odt and the rest is discharged from the D<sub>0</sub> washer or 12 m<sup>3</sup>/odt.

Let's consider the ultrafiltration of the EOP filtrate. As it can be seen from the flowsheet (Figure 1 of Appendix II) a part of discharged EOP filtrate is applied as wash liquor in the D<sub>0</sub> washer, the second (the biggest) part is used for the dilution of pulp suspension before the EOP washer and the rest comes to sewage. A membrane can be installed to treat any of these streams, but larger volumes of feed require greater area of a membrane unit.

The calculations were performed considering the ultrafiltration of the streams coming to sewage and recirculating to the D<sub>0</sub> washer, since the first stream is interesting from environmental point of view and the second one is related to the experiments. The results are represented in Table 37.

**Table 37.** Reduction of COD load per ton of pulp when treating the effluent to the waste water treatment plant and the stream to the D<sub>0</sub> washer

Parameters	Filtrate to sewage			Filtrate to D <sub>0</sub> washer		
	Before ultrafiltration	After ultrafiltration	Reduction	Before ultrafiltration	After ultrafiltration	Reduction
Volume, m <sup>3</sup> /odt	7	5.6*	1.4	2.3	1.8	0.5
COD value, g/m <sup>3</sup>	1950	640	1310	1950	640	1310
COD load of effluent, kg/odt	13.6	3.6	10	4.9	1.2	3.7

\*Volume decreases according to VRF which equals to 5 in the experiment

The ultrafiltration of the EP filtrate also allows removing of COD from the system. The EP washing is close stage which means that whole EP filtrate is recirculated back to the bleach plant. As the flowsheet shows a part of the EP effluent is used for the dilution of pulp before the EP washing stage and two parts are recirculated to the EOP and D<sub>1</sub> washers (Figure 2 of Appendix II).

The following estimation can be made considering the ultrafiltration of the filtrate recirculated to the EOP washer (Table 38).

**Table 38.** COD reduction by the treatment of the EP filtrate coming to the EOP washer

Parameters	Stream to EOP washer		
	Before ultrafiltration	After ultrafiltration	Reduction
Volume, m <sup>3</sup> /odt	2.4	1.9	1.5
COD value, g/m <sup>3</sup>	930	440	490
COD load of effluent, kg/odt	2.2	0.8	1.4

### 7.6.2 Softwood line

There are two open stages in softwood bleaching line D<sub>1</sub> and PO (Figure 2 of Appendix II). From discussion with the development manager from the mill the total

volume of the effluents is 13 m<sup>3</sup>/ADt that corresponds to 14.5 m<sup>3</sup>/odt. Nearly 60 % of the total volume is discharged from the D<sub>0</sub> washer and the rest from the PO washer.

During the estimation the ultrafiltration of effluents to the water treatment plant was considered. Results of the calculations are represented in Table 39.

**Table 39.** Reduction of COD load of the bleaching effluents for softwood line

Filtrate/ washer	Before the ultrafiltration			After the ultrafiltration			Reduction, kg/odt
	Volume, m <sup>3</sup> /odt	COD value, g/m <sup>3</sup>	COD load of effluent, kg/odt	Volume, m <sup>3</sup> /odt	COD value, g/m <sup>3</sup>	COD load of effluent, kg/odt	
D <sub>1</sub>	8.7	3200	27.8	7	2110	14.8	13
PO	5.8	3950	23	4.6	2200	10.1	12.9

### 7.7 Utilization of the concentrates

A possible way to handle the concentrates is to send them to the brownstock area and subsequently to the recovery cycle. In that case non-process elements, which would enter recovery cycle with the concentrates, have to be considered (Table 40). Most of these substances have a negative influence on mill's operations and can accumulate in the recovery cycle; therefore their content must be monitored and must be kept on an appropriate level.

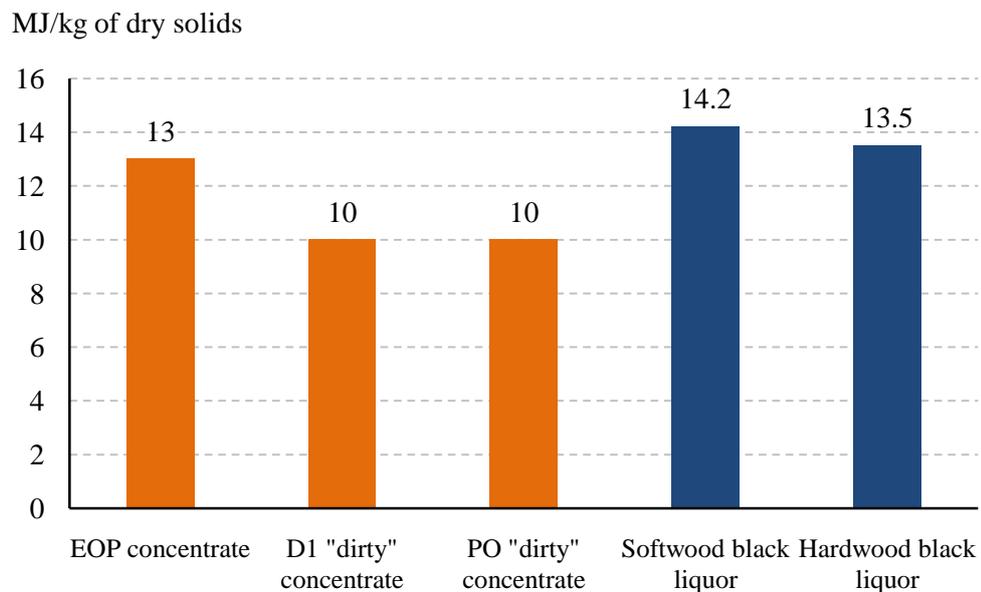
**Table 40.** Some non-process elements and their impact on pulp mill's processes [33]

Elements	Influence on different processes
Mn, Fe, Cu, Co	Decomposition of oxygen-containing reagents in bleaching and oxygen delignification
Ca, Al, Si, Ba, Mg, Mn	Scaling of evaporator's heat transfer surfaces
Cl, K, S	Corrosion and plugging of heat transfer surfaces in recovery boiler

The EOP, EP from hardwood and PO "dirty" from softwood line concentrates could be used in the brownstock washing area as supplementary wash water in the point, where liquor in pulp has the same or higher content of dry solids.

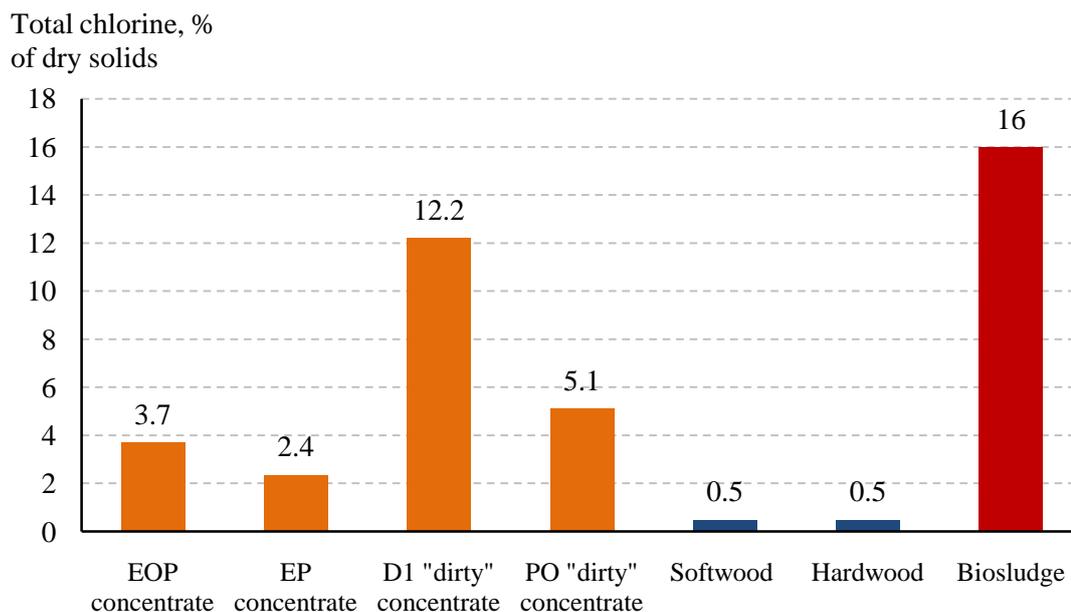
All concentrates including D<sub>1</sub> “dirty” can be admixed with black liquor and directed to the recovery boiler for incineration. The following properties of the concentrates are necessary to be considered in that case: gross calorific value, dry solids content, chlorine and potassium content.

**Gross calorific value** affects energy releases during burning. Figure 39 shows data from measurements for the concentrates (orange columns); also, for comparison the average values for black liquors are represented (blue columns). The EP concentrate wasn’t measured on gross calorific value due to an insufficient amount of the sample. As it can be seen from the diagram the value for the EOP concentrate is close to that of hardwood black liquor, the D<sub>1</sub> “dirty” and PO “dirty” concentrates have lower values.



**Figure 39.** Gross calorific value of concentrates and average values for Nordic black hardwood and softwood liquors (values for black liquor are taken from [34]).

**Total chlorine** and **potassium contents** of the concentrates were recalculated from in mg/l (measured values) to percents or gram per gram of dry solids (Figures 40 and 41, respectively).



**Figure 40.** Total chlorine content in concentrates and average values for black liquor from Scandinavian wood (values for black liquor are taken from [34]).

The concentrates, especially D<sub>1</sub> “dirty”, have a higher level of chlorine in comparison with the average values of Nordic black liquor. Addition of the concentrates to the black liquor will increase chlorine content of the last and the increment depends on the ratio between the concentrate and black liquor.

Chlorine causes the corrosion and fouling problems of a recovery boiler and other equipment used in the recovery cycle, and gravity depends on the amount of chlorine in black liquor. The content of chlorine less than 0.3 % of dry solids provokes little fouling; with the level of 0.3-0.8 % of dry solids an increased fouling can be observed and the high content of chlorine (> 0.8 %) causes serious fouling and corrosion problems. [35] The incineration of fuel with increased chlorine level also can lead to the formation of chlorinated organic compounds, although in insignificant quantities, which can emit from furnace with the gas and solid products of burning [36].

Nowadays in Finland the typical level of chloride in black liquor is less than 0.2 % of dry solids. On the other hand, recovery boilers can be designed to incinerate black liquor with any chlorine content. For example, in Brazil and Indonesia there are some boilers which operate at chlorine level above 2 % of dry solids in black liquor. [35]

Additionally, there is a practice of biosludge combustion in one Finnish pulp and paper mill. The dry solids content of the biosludge is 10% and the chlorine level is 16 % of dry solids (Figure 40, red column). The biosludge is mixed with black liquor and fed to the end of the evaporation plant. The amount of biosludge burnt daily is 7.2 t (as dry solids) and as it was reported the mill doesn't have any problems related to the recovery boiler operation. Basing on this case it was calculated how much of each concentrate can be fed to recovery boiler per day (Table 41).

**Table 41.** Volumes of the concentrates which can be fed to recovery boiler

Concentrate	Dry solids content, %	Chlorine content, % of dry solids	Concentrate fed to the boiler, t/d		
			as chlorine	as dry components	as liquid
EOP	0.8	3.7	1.15	31.08	3885
EP	0.8	2.4	1.15	47.92	5990
D <sub>1</sub> "dirty"	1.4	12.2	1.15	9.43	673
PO "dirty"	1.6	5.1	1.15	22.55	1409

A significant point concerning the incineration of the concentrates is the molar ratio of sodium and chlorine (Table 42). This proportion affects the ratio of NaCl and HCl generating through the various reactions during combustion. The excessive amount of sodium provokes the formation mostly of NaCl, thus preventing chlorine from being bound to organic compounds and *vice versa* big quantity of chlorine favours for HCl generation. [36]

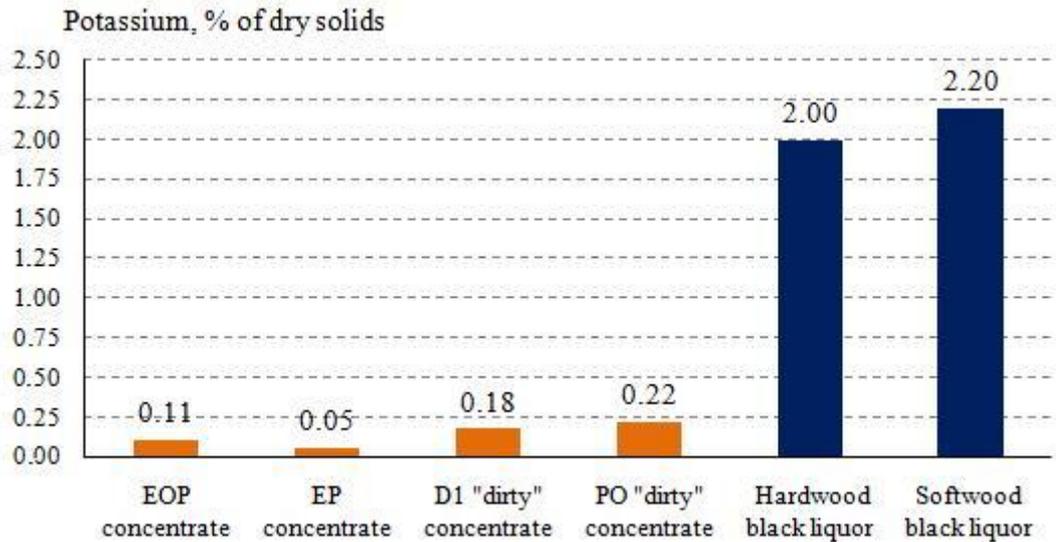
**Table 42.** Molar ratio between sodium and chlorine

Concentrate	Sodium		Chlorine		Sodium/chlorine
	mg/l	mmol/l	mg/l	mmol/l	
EOP	204	8.9	282	7.9	1.10
EP	177	7.7	185	5.2	1.50
D <sub>1</sub> "dirty"	187	8.1	1712	48.2	0.17
PO "dirty"	496	21.6	818	23.0	0.94

As it can be concluded from the calculated values during the combustion of the EOP and EP concentrates all chlorine most likely will be discharged from the boiler bound to sodium. The burning of the D<sub>1</sub> "dirty" filtrate will produce mostly HCl that gives a certain probability for the generation and emission of chlorinated organic materials.

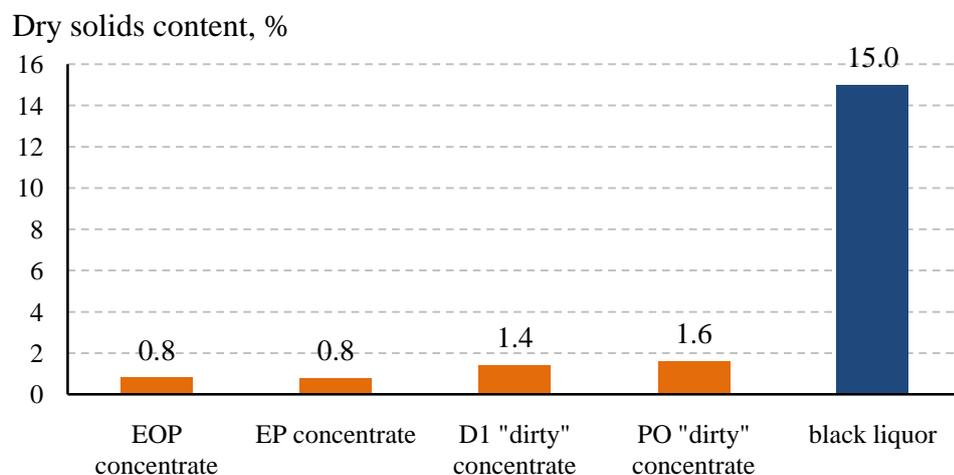
The PO “dirty” concentrate being burnt will generate significantly lower quantity of HCl as compared to D<sub>1</sub> “dirty”.

Potassium like chlorine causes fouling of recovery furnace tubes by decreasing the sticky temperature of ash. As Figure 41 shows the retentates have lower quantities of potassium in comparison with black liquor.



**Figure 41.** Potassium content in the concentrates and the average values for black liquor from Scandinavian wood (figures for black liquor are taken from [34]).

**Dry solids content** in the concentrates is significantly lower than that of black liquor (Figure 42).



**Figure 42.** Dry solids content of concentrates and average value for black liquor.

An introduction of the concentrates to black liquor would reflect on reduced dry solids content of the last and additional energy would be required the evaporation of the mixture to suitable for burning concentration as compared to original black liquor. Using the values of specific heat consumption for black liquor represented in Table 1 of Appendix IV some calculations were performed to estimate energy spent per dry solids to evaporate the mixture from certain concentration to 80%. The results of the calculations are represented in Table 43.

**Table 43.** Energy required for evaporation of concentrate-black liquor mixture to 80 %

Number of evaporation stages (n)	4	5	6	7
Specific heat consumption, kJ/kg water	640	560	470	400
Concentration before evaporation, %	Heat required for evaporation, MJ/kg dry solids			
20.0	2.40	2.10	1.76	1.50
19.0	2.57	2.25	1.89	1.61
18.0	2.76	2.41	2.02	1.72
17.0	2.96	2.59	2.18	1.85
16.0	3.20	2.80	2.35	2.00
15.0	3.47	3.03	2.55	2.17
14.0	3.77	3.30	2.77	2.36
13.0	4.12	3.61	3.03	2.58
12.0	4.53	3.97	3.33	2.83
11.0	5.02	4.39	3.69	3.14
10.0	5.60	4.90	4.11	3.50
9.0	6.31	5.52	4.63	3.94
8.0	7.20	6.30	5.29	4.50
7.0	8.34	7.30	6.13	5.21
6.0	9.87	8.63	7.25	6.17
5.0	12.00	10.50	8.81	7.50
4.0	15.20	13.30	11.16	9.50

The increasing of energy consumption for the evaporation when the dry matter content of black liquor decreases below 15 % by the dilution with the concentrates was also estimated (Table 44).

**Table 44.** Increasing energy consumption for evaporation when decreasing the dry matter content of black liquor from 15 %

Number of evaporation stages (n)	4	5	6	7
Concentration before evaporation, %	Additional heat spent for the evaporation, MJ/kg dry solids			
15.0	0.00	0.00	0.00	0.00
14.0	0.30	0.27	0.22	0.19
13.0	0.66	0.57	0.48	0.41
12.0	1.07	0.93	0.78	0.67
11.0	1.55	1.36	1.14	0.97
10.0	2.13	1.87	1.57	1.33
9.0	2.84	2.49	2.09	1.78
8.0	3.73	3.27	2.74	2.33
7.0	4.88	4.27	3.58	3.05
6.0	6.40	5.60	4.70	4.00
5.0	8.53	7.47	6.27	5.33
4.0	11.73	10.27	8.62	7.33

## 8 CONCLUSIONS

The main purpose of the experiments with hardwood pulp was to inspect the possibility of the bleaching performance improvement by the implementation of the ultrafiltration. And as it was shown the using of the treated filtrates according to the experimental set doesn't have an effect on the bleaching, since the parameters of pulp were the same for the reference and trial experiments.

The experiments with softwood pulp aimed to explore the possibility of volume decreasing of discharging effluents and also the possibility to reduce the fresh water consumption. This study showed that the substitution of the D<sub>2</sub> "dirty" untreated filtrate with the D<sub>1</sub> "dirty" permeate in the D<sub>1</sub> washing stage has a negative influence on the ensuing bleaching stage (PO). Another result revealed the opportunity for the fresh water replacement with the PO "dirty" treated filtrate without negative effect on the subsequent bleaching stage performance; the amount of saved water is approximately 3 m<sup>3</sup> per oven-dry ton of pulp.

Data from filtrate analysis and performed calculations showed that the ultrafiltration enables the reduction of the volumes and COD of the bleaching effluents, thus decreasing the load of the waste water treatment plant. Considering the treatment of the streams coming to sewage the following figures of COD diminution per ton of pulp were obtained: 10 kg/odt for hardwood and nearly 26 kg/odt for softwood line.

The possible way of the utilization of the concentrates is the recirculation to the brownstock area. The alkaline concentrates can be applied as wash water in the brownstock washing at the point where dry matter content of liquor in the pulp at the same or higher level. Another way to handle the retentates including the acid one is direct mixing with black liquor and further incineration in the recovery boiler. The last option would require additional evaporation capacity, since dry solids content of the concentrates is significantly lower. In addition, chlorine content of the mixture must be monitored and kept at harmless level.

## REFERENCES

- 1 Dence, C.W., Reeve, D.W., Pulp bleaching: Principles and Practice, Atlanta, Georgia, Tappi, 1996, 867 p.
- 2 Stal, C. M., Sunds Defibrator on the road to the closed bleach plant, IPPTA, 1994, p. I-VIII.
- 3 Sillanpää, M., Ala-Kaila, K., Tervola, P., Dahl, O., A view of pulp washing in bleaching, *Paperi ja Puu* 83(2001):1, 45-49.
- 4 Fälth, F., Jönsson, A., Wimmerstedt, R., Ultrafiltration of effluents from chlorine-free, kraft pulp bleach plants, *Desalination* 133(2001):2, p. 155-165, Elsevier.
- 5 Pazukhina, G. A., Avvakumova A. V., Reagents for pulp bleaching. SPb., 2002, 110 p.
- 6 Sixta, H., Süß, H-U., Potthast, A., Schwanninger, M., Krotscheck A. W, Pulp Bleaching, *Handbook of Pulp*, 2 volume, Sixta, H., Austria, 2006, p. 609-965.
- 7 Vakkilainen, E., Chemical recovery, *Chemical pulping, Papermaking Science and Technology*, Book 6B, Gullichsen, J., Fogelholm, C-J., Oy, Helsinki, 1999, p. 7-34.
- 8 Braddon, S.A., Dence, C.W., Structure and Reactivity of Chlorolignin, *Tappi* 51(1968):6, p. 249-256.
- 9 Runge, T., Ragauskas A., Comparison of oxidative alkaline extraction reaction's impact on pulp properties and the environment, *International pulp bleaching conference*, Helsinki, Finland, June 1-5, 1998, Book 2, p 613-618.
- 10 Gierer, J., Imsgaard, F., The reactions of lignins with oxygen and hydrogen peroxide in alkaline media, *Svensk papperstidning* (1977):16, p. 510-518.
- 11 Runge T.M., Ragauskas A.J., McDonough T.J., Lignin structural changes by oxidative alkaline extraction, *Pulping conference*, Montreal, Quebec, Canada, October 25-29, 1998, p 1541-1549.
- 12 Gierer, J., Mechanisms of bleaching with oxygen-containing species, *ISWPC*, 1987, p. 279-288.
- 13 Colodette, J.L., Rothenberg, S., Dence., C.W., *J. Pulp Paper Sci.* 14(1988):6, p. 126-132.
- 14 Peter, B., Pulp washing – key to more efficient process, *Fiber spectrum* 568(1998)2, p. 8-9.
- 15 Knowpulp database.

- 16 Crotogino, R.H., Poirier, N.A., Trinh, D.T., The principles of pulp washing, *Tappi J.* 70(1987):6, p. 95-103.
- 17 Krotscheck, A. W., Pulp Washing, *Handbook of Pulp*, 1 volume, Sixta, H., Austria, 2006, p. 511-559.
- 18 Shackford, L., Bleach washer performance, *Proceedings of the 1992 Bleach Plant Operations Short Course Notes*, Atlanta, p. 147-161.
- 19 Luthi, O., Equivalent displacement ratio-evaluating washer efficiency by comparison, *Tappi J.* 66(1983):4, p. 82-84.
- 20 Mulder, M., *Basic principles of membrane technology*, second edition, Kluwer Academic, 1996, 547 p.
- 21 Noble, R. D., Stern, S. A., *Membrane separations technology: principles and applications*, 1995, 739 p.
- 22 Wagner, J., *Membrane Filtration Handbook, Practical Tips and Hints*, second edition, Osmonics, Inc., 2001, 127 p.
- 23 National Drinking Water Clearinghouse, *Membrane Filtration*, *Water Encyclopedia*, vol. 1, Lehr, J., Keeley, J., Lehr, J., John Wiley & Sons, Inc., 2005, p. 331-337.
- 24 Sillanpää, M., *Studies on washing in kraft pulp bleaching*, Academic Dissertation, Faculty of Technology, Oulu University, 2005
- 25 Bryant, P.S., Sundström, G., Jour, P., and Johansson, N.G., Ultrafiltration of alkaline filtrates to maximize partial closure of ECF bleach plants, *International Pulp Bleaching Conference*, Helsinki, Finland, June 1-5, 1998, p. 229-237, *Proceedings from book 1*.
- 26 Herstad-Svärd, S., Jour, P., Bryant, P.S., et al., Increasing the biotreatability of ECF bleaching effluents by ultrafiltration and partial closure of alkaline filtrates, *proceedings from the TAPPI Pulping Conference*, Montreal, QC, 1998, p. 1165-1176.
- 27 Blackwell, B.R., Mackay, M.B., Myrray. F.E., et al., *Tappi* 62(1979):10, p. 33-37.
- 28 Fälth, F., Jönsson, A-S., Brinck, J. and Wimmerstedt. R., Ultrafiltration of bleach plant filtrate when using evaporation condensate as a wash liquor. *Tappi Journal* 83 (2000):5, p 1 – 7.
- 29 Laasonen, H., Mänttari, M., *Research report: Cleaning of alkaline filtrates using ultrafiltration*, Center of Separation Technology (Lappeenranta University of Technology), 2009.

- 30 CR-Filter Applications, Ultrafiltration in chemical industries, [http://www.membransysteme.de/pdfs/CR-Filter\\_Brochure.pdf](http://www.membransysteme.de/pdfs/CR-Filter_Brochure.pdf), [24.07.09].
- 31 Sillanpää, M. K., Sankari, M.I., Dahl, O.P. and Ala-Kaila., real wash loss compounds in peroxide bleaching of softwood kraft pulp, *Appita Journal* 56 (2003):5, p. 397-400.
- 32 Viirimaa, M., Perämäki, P., Niinimäki, J., Ala-Kaila, K. and Dahl, O., Identification of the wash loss compounds affecting the ECF bleaching of softwood kraft pulp, *Appita Journal* 55(2002):6, p. 484-488.
- 33 Kaj Henricson, Non process elements, Lecture materials, 2008.
- 34 Pikka, O., Vesala, R., Vilpponen, A., Dahlläuf, H., Germgård, U., Norden, S., Bokström, M., Steffes, F., Gullichsen, J., Bleaching applications, *Chemical pulping, Papermaking Science and Technology, Book 6A*, Gullichsen, J., Fogelholm, C-J., Fapet Oy, Helsinki, 1999, p. 616-665.
- 35 Esa Vakkilainen, Private discussion, 2009.
- 36 Nichols, K. M., The feasibility of thermal destruction of chlorine-containing concentrated streams from closed cycle processes, 1991 Environmental Conference, San Antonio, April 7-10, 1991, TAPPI PRESS, Atlanta, 1991, Book 1, p. 59-72.
- 37 Holmlund, K., Parviainen, K., Evaporation of black liquor, *Chemical pulping, Papermaking Science and Technology, Book 6B*, Gullichsen, J., Fogelholm, C-J., Fapet Oy, Helsinki, 1999, p. 37-93.

APPENDICES

Appendix I

1(1)

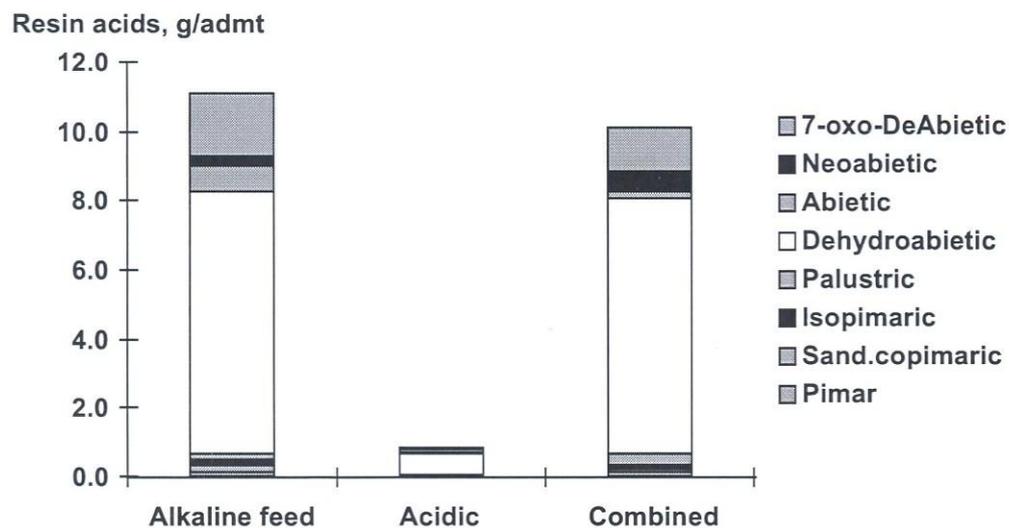


Figure 1. Resin acids in alkaline, acidic and combined effluents [26].

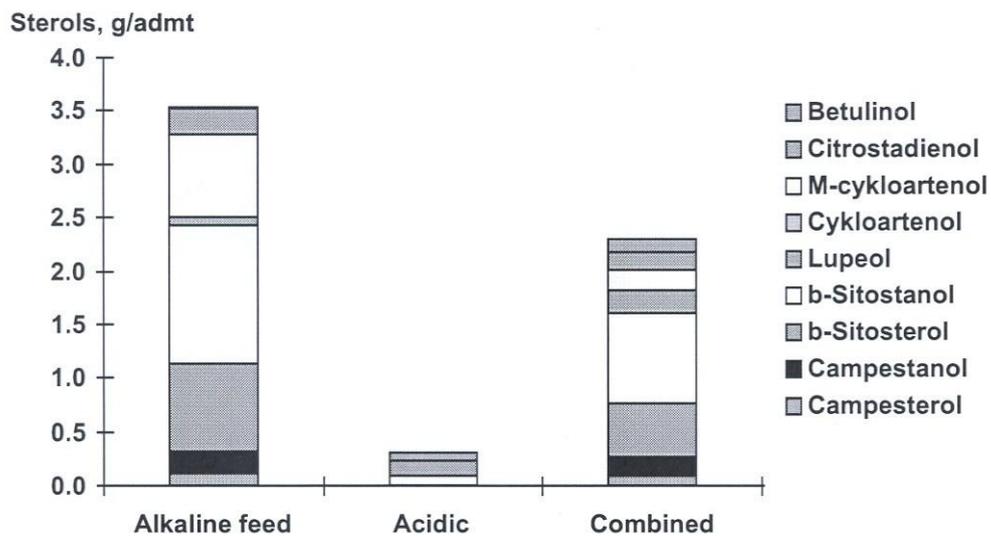


Figure 2. Sterols in alkaline, acidic and combined effluents [26].

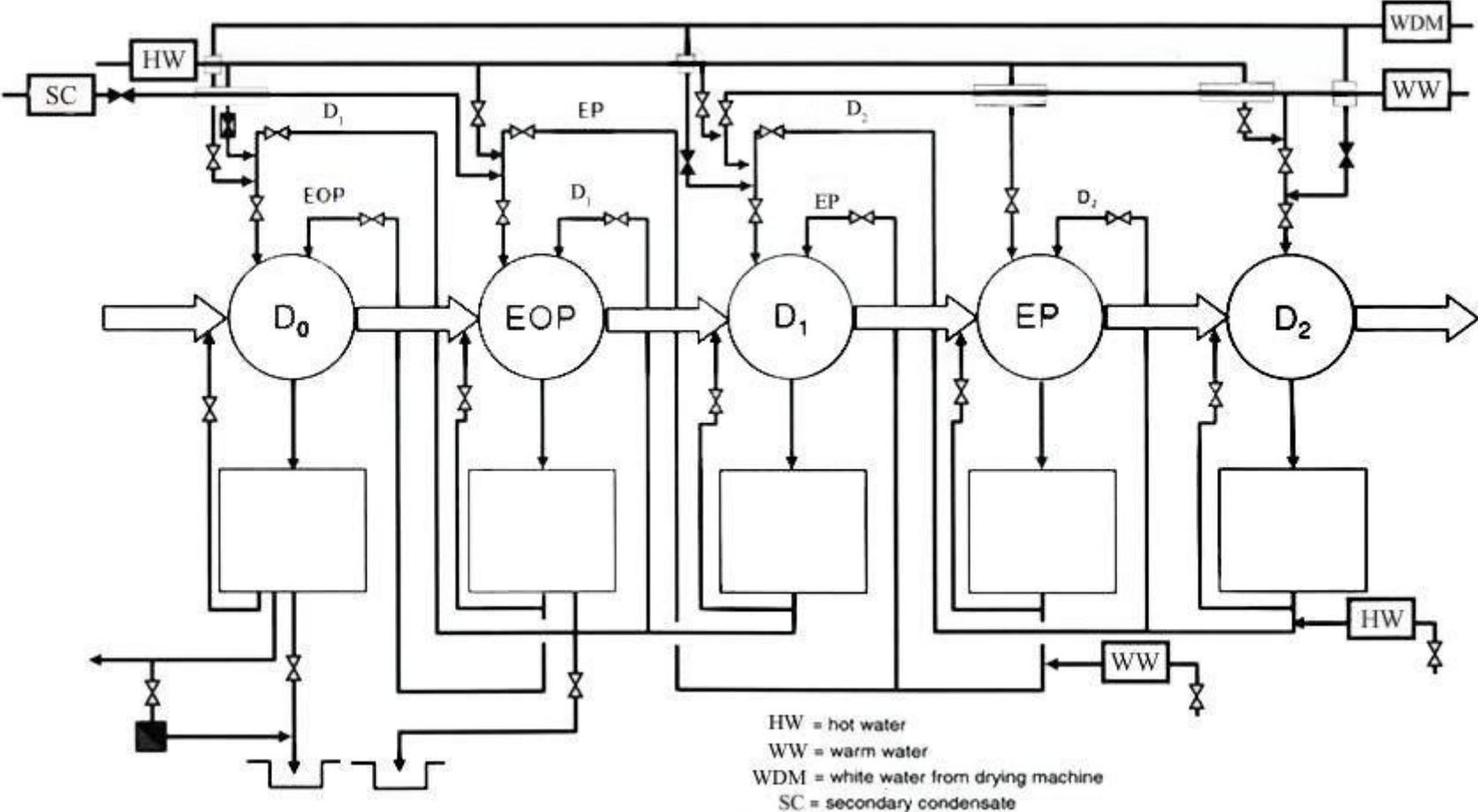


Figure 1. Scheme of washing on the bleaching plant, hardwood line.

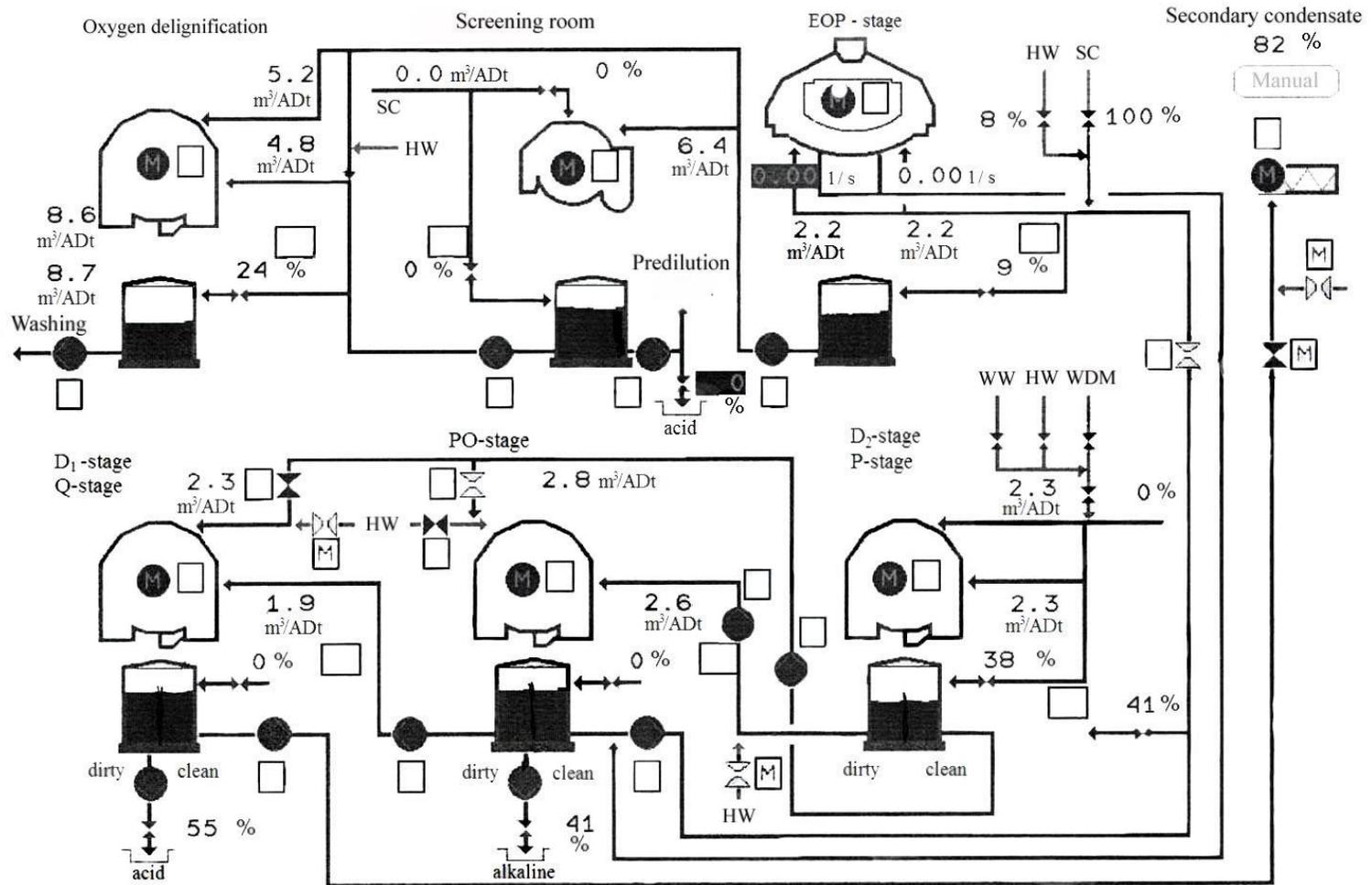
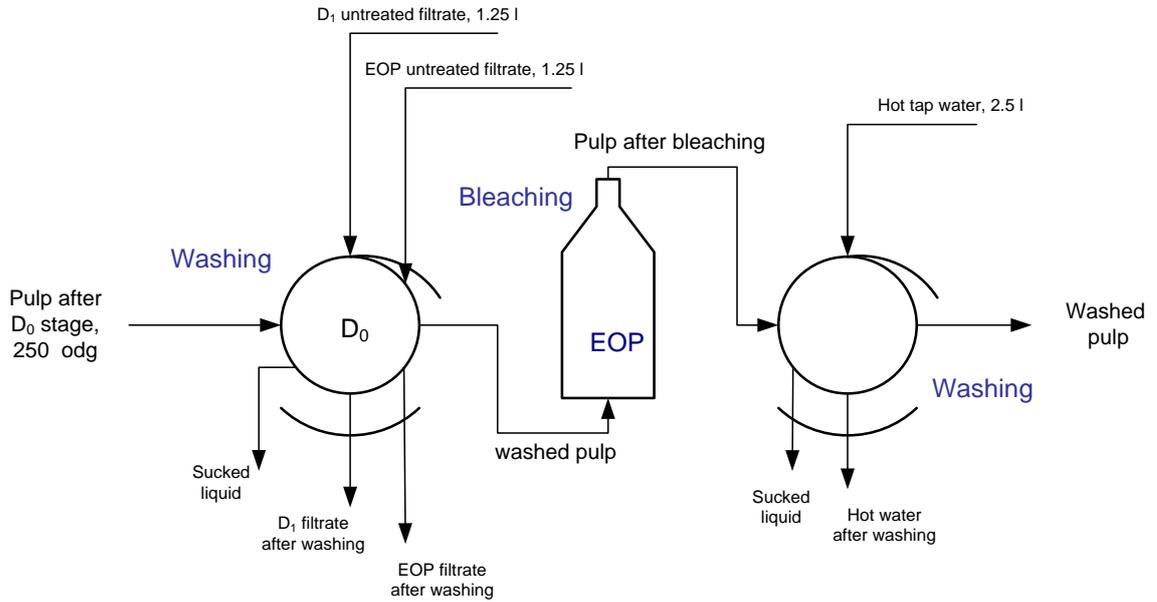
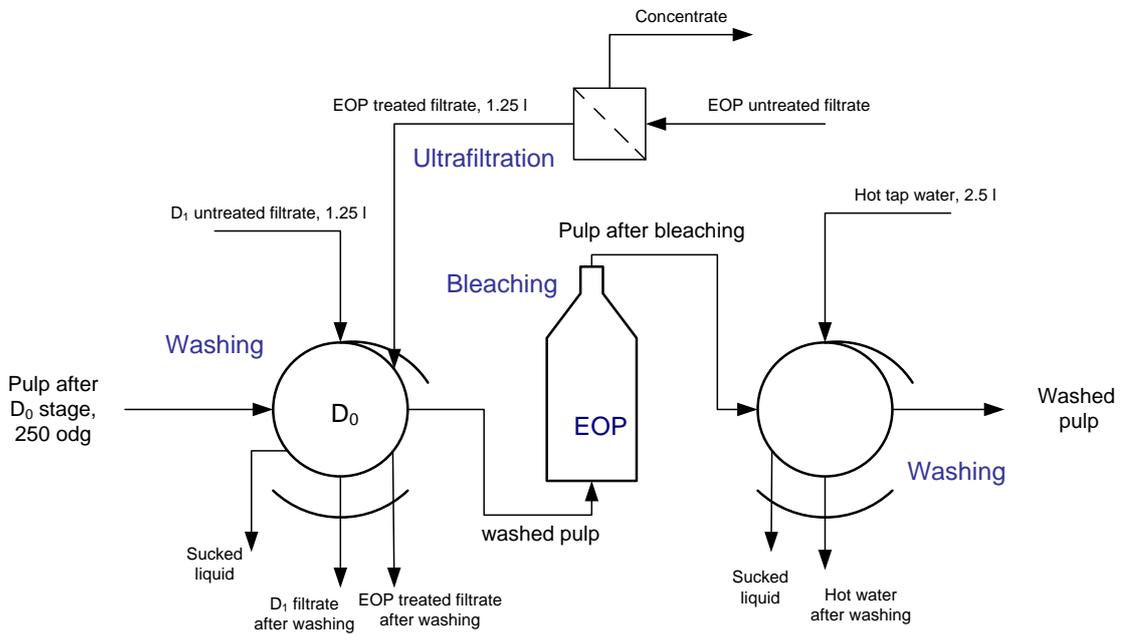


Figure 2. Scheme of washing on the bleaching plant on softwood line.



**Figure 1.** The flowsheet of experiment 1.



**Figure 2.** The flowsheet of experiment 2.

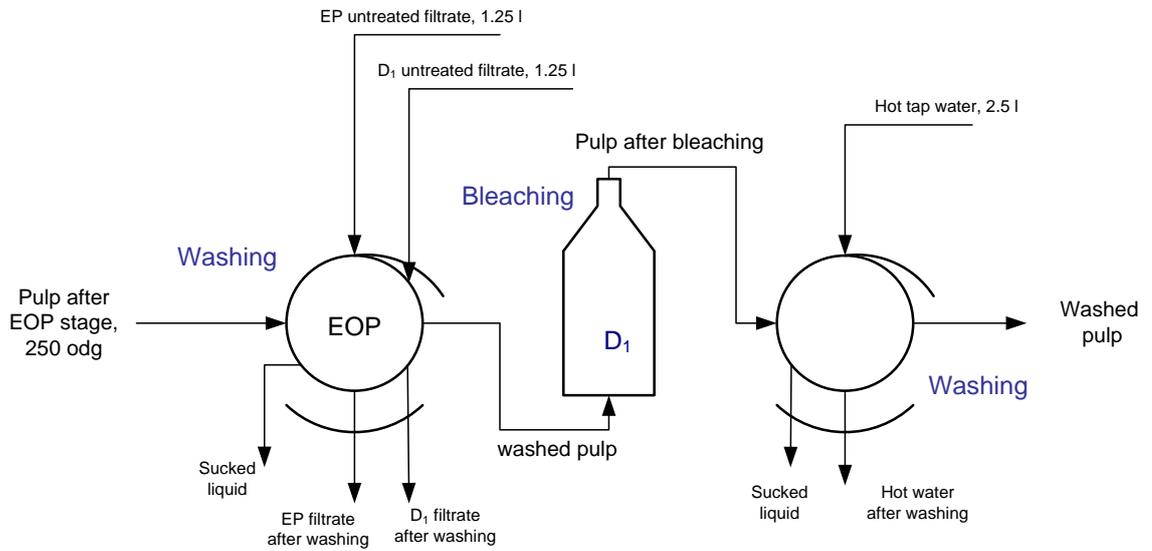


Figure 3. Flowsheet of experiment 3.

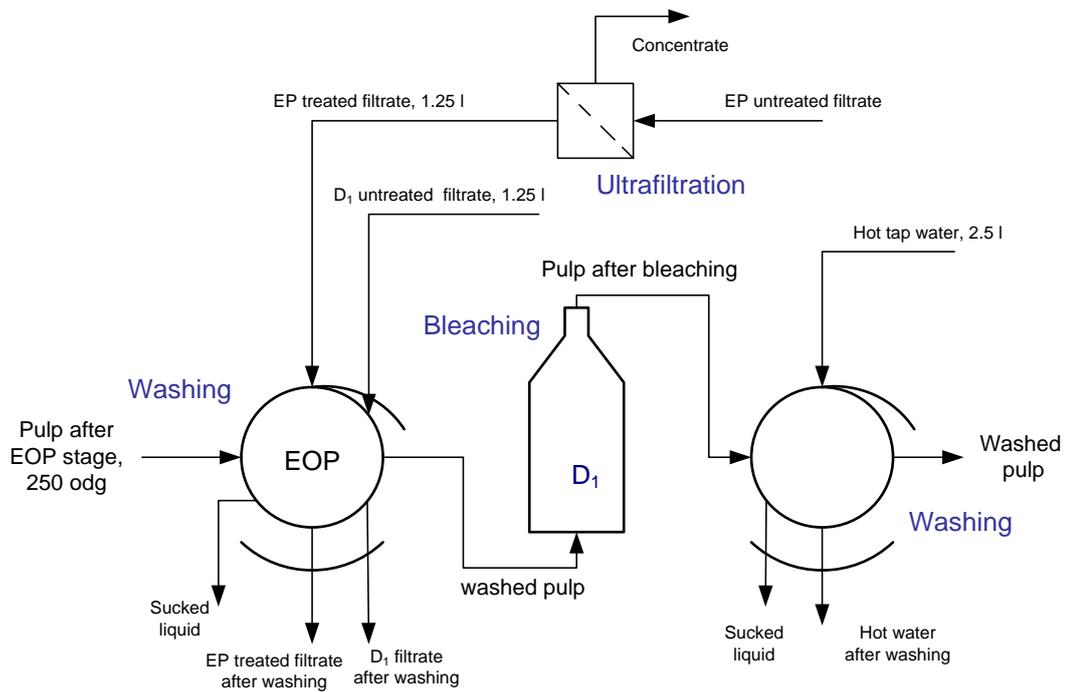


Figure 4. Flowsheet of experiment 4.

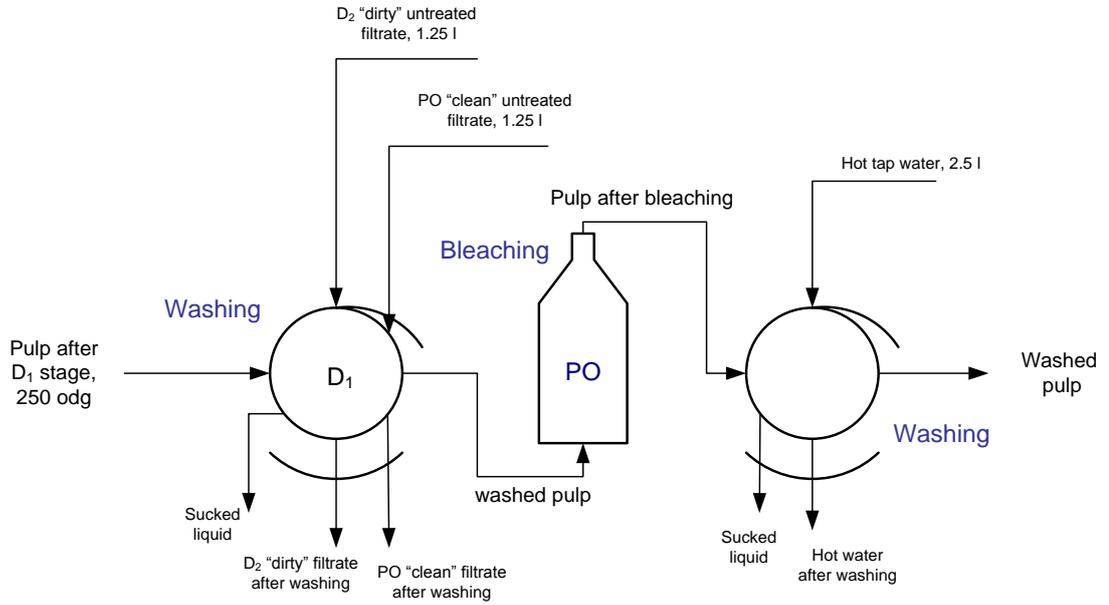


Figure 5. Flowsheet of experiment 5.

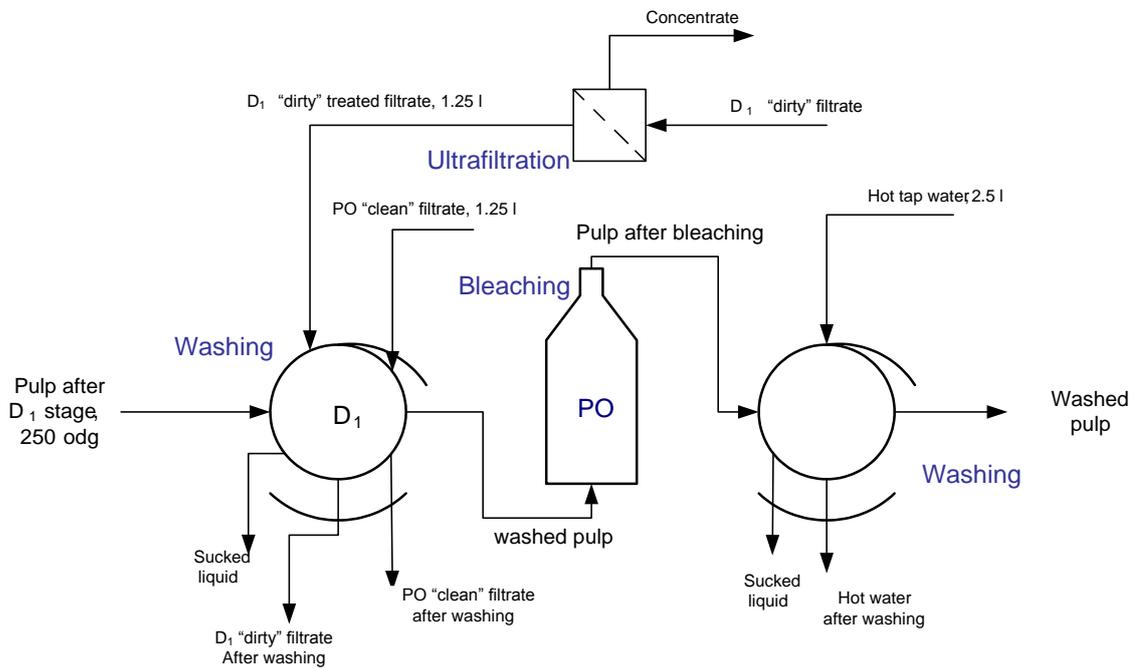


Figure 6. Flowsheet of experiment 6.

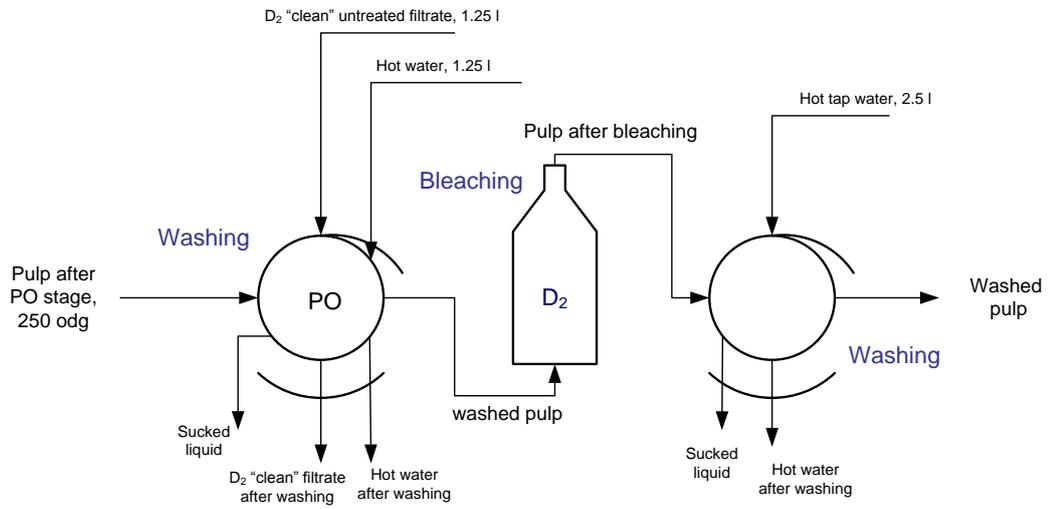


Figure 7. Flowsheet of experiment 7.

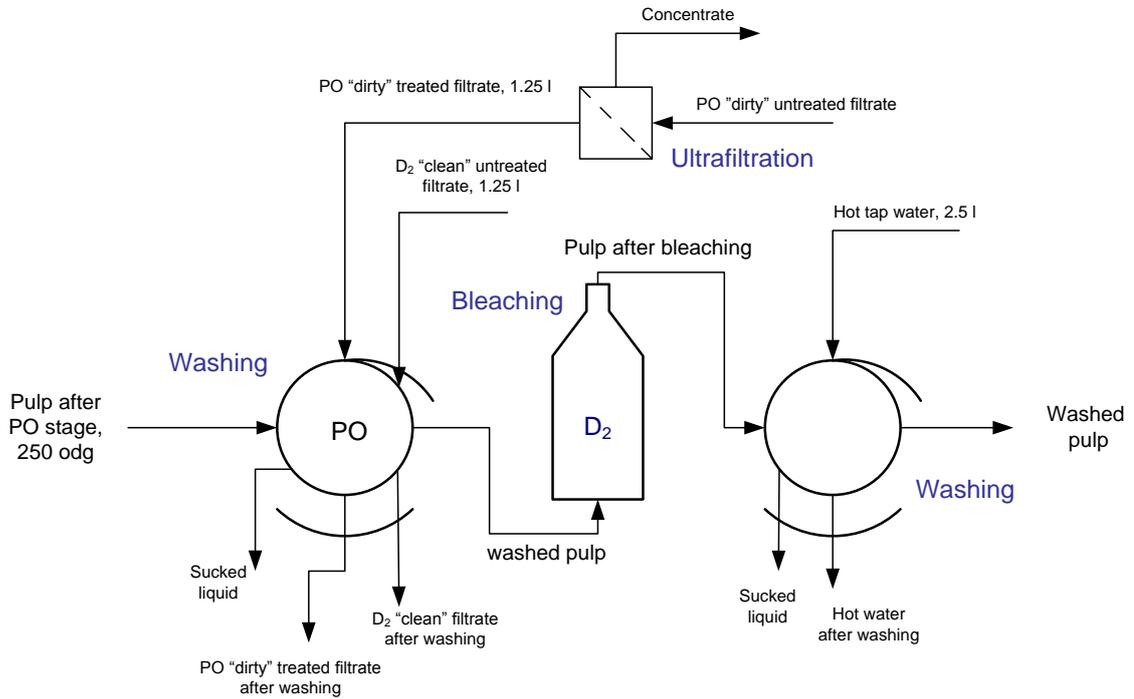


Figure 8. Flowsheet of experiment 8.

**Table 1.** Steam economy and specific heat consumption in multistage evaporation plant including an integrated stripper column [37]

Number of stages	Steam economy, kg steam/kg water	Specific heat consumption, kJ/kg water
4	3.7-3.6	630-650
5	4.3-4.1	550-570
6	5.1-4.9	460-480
7	6.2-5.9	390-400