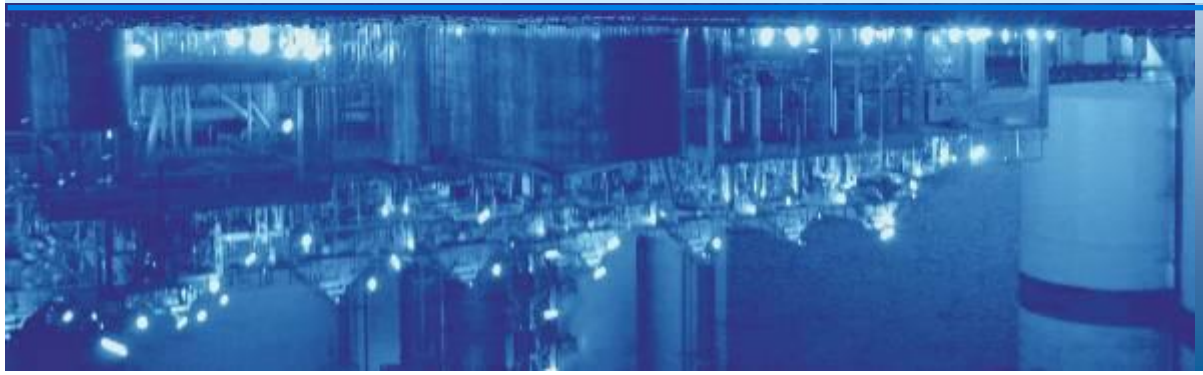
ADVANCES IN EUCALYPTUS PULP BLEACHING TECHNOLOGY



3rd ICEP

March 4-7, 2007

Belo Horizonte

Olavi Pikka, Andritz Oy

Advances in eucalyptus pulp bleaching technology

- **Advances in Eucalyptus pulp bleaching technology**

- **Introduction**

- **Bleaching process development**

- **Recent topics in pulp bleaching technology**
  - **Oxygen delignification**
  - **Pulp washing**
  - **Hexenuronic acid removal**

- **Modern bleaching sequences**

- **Pulp quality**

- **Power, steam, effluent**

- **Recent mill results**

- **Future topics and conclusion**

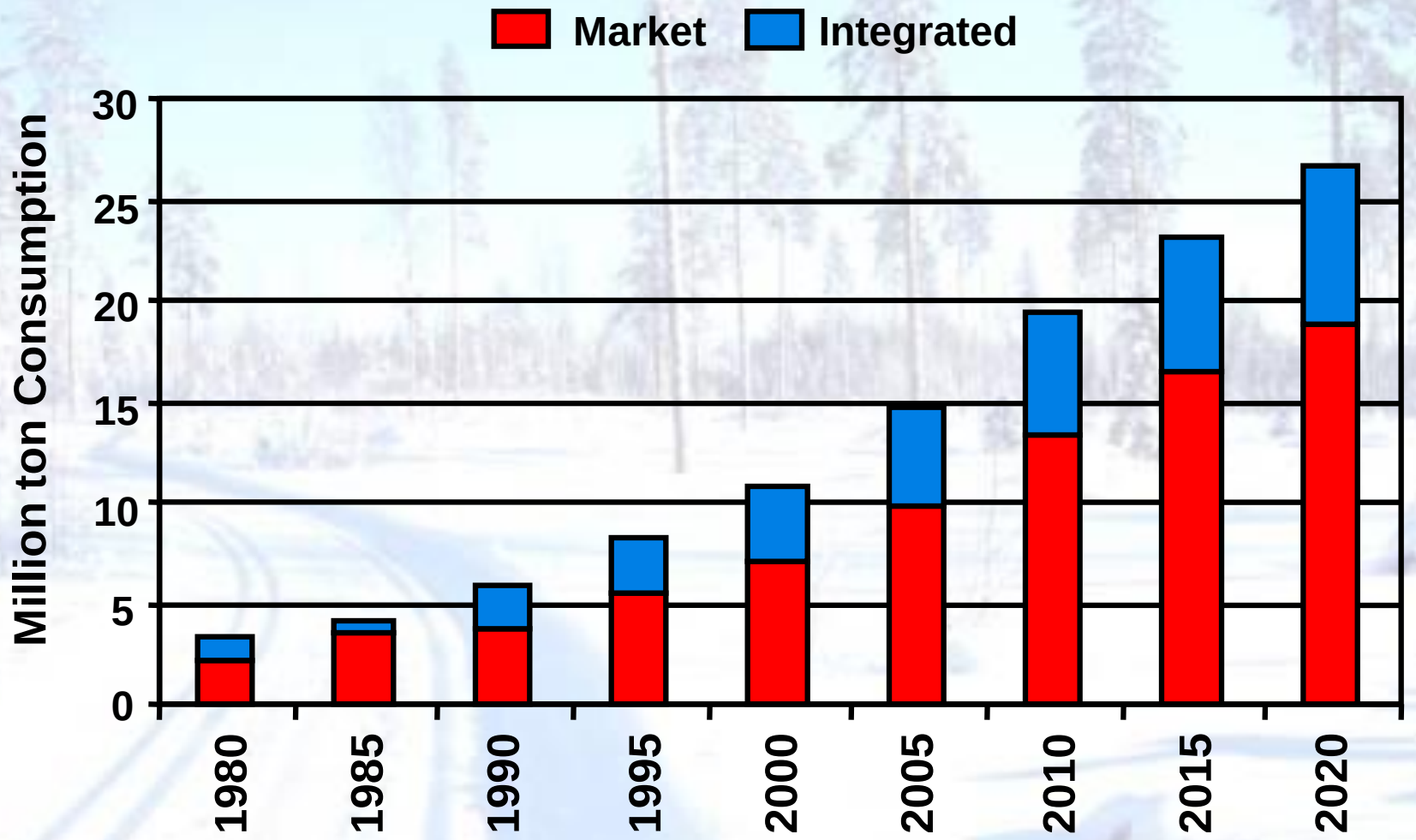
Advances in eucalyptus pulp bleaching technology

Introduction

- Use of eucalyptus pulp has increased rapidly
- Production capacity increase in the southern hemisphere
  - Fast-wood plantations
  - Uniform quality
- Mill capacities growing

Advances in eucalyptus pulp bleaching technology

WORLD Consumption of Bleached Eucalyptus Chemical Pulp



Source: JP World Fiber Outlook 2006 + cop

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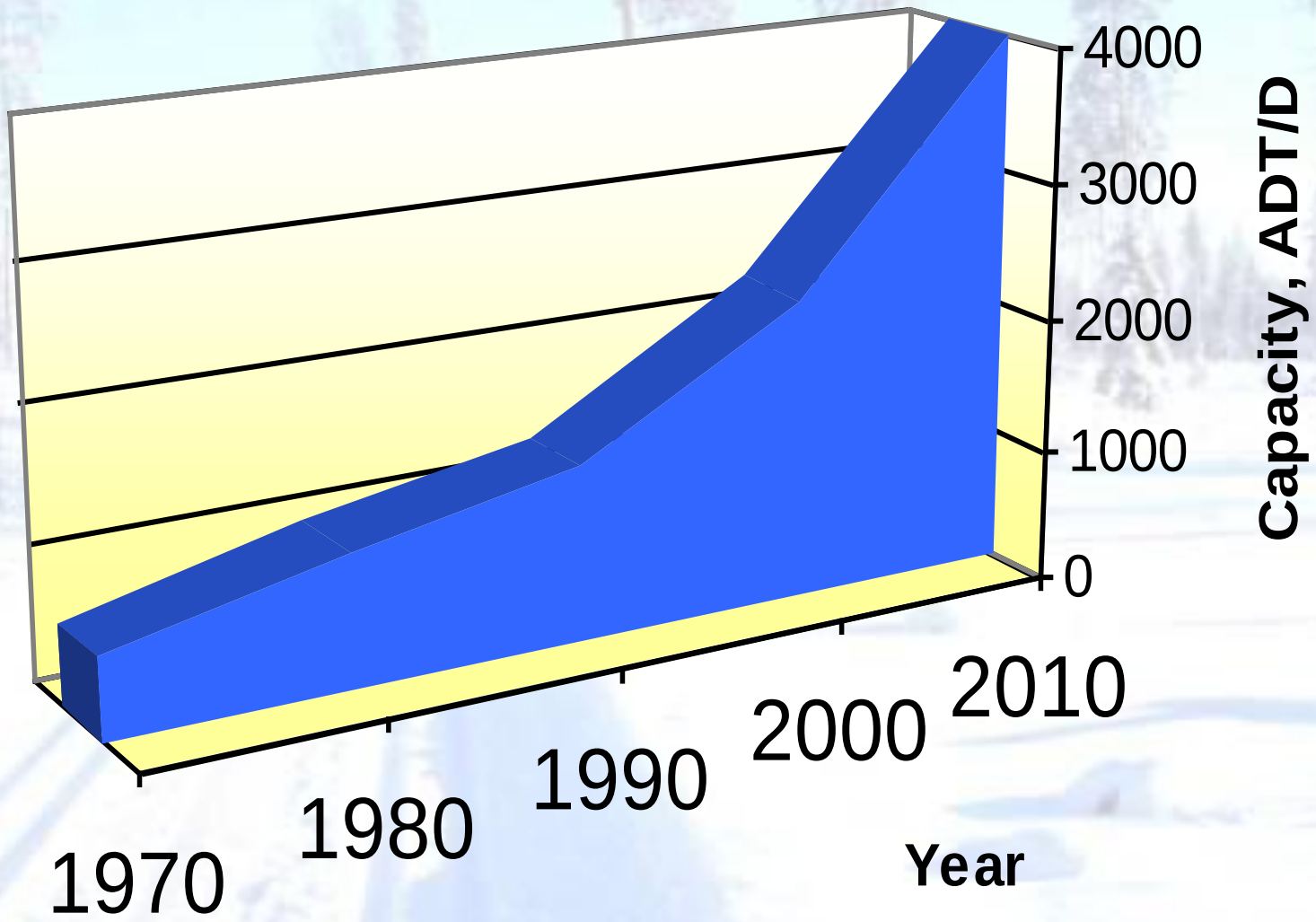
Development of pulp mill capacity



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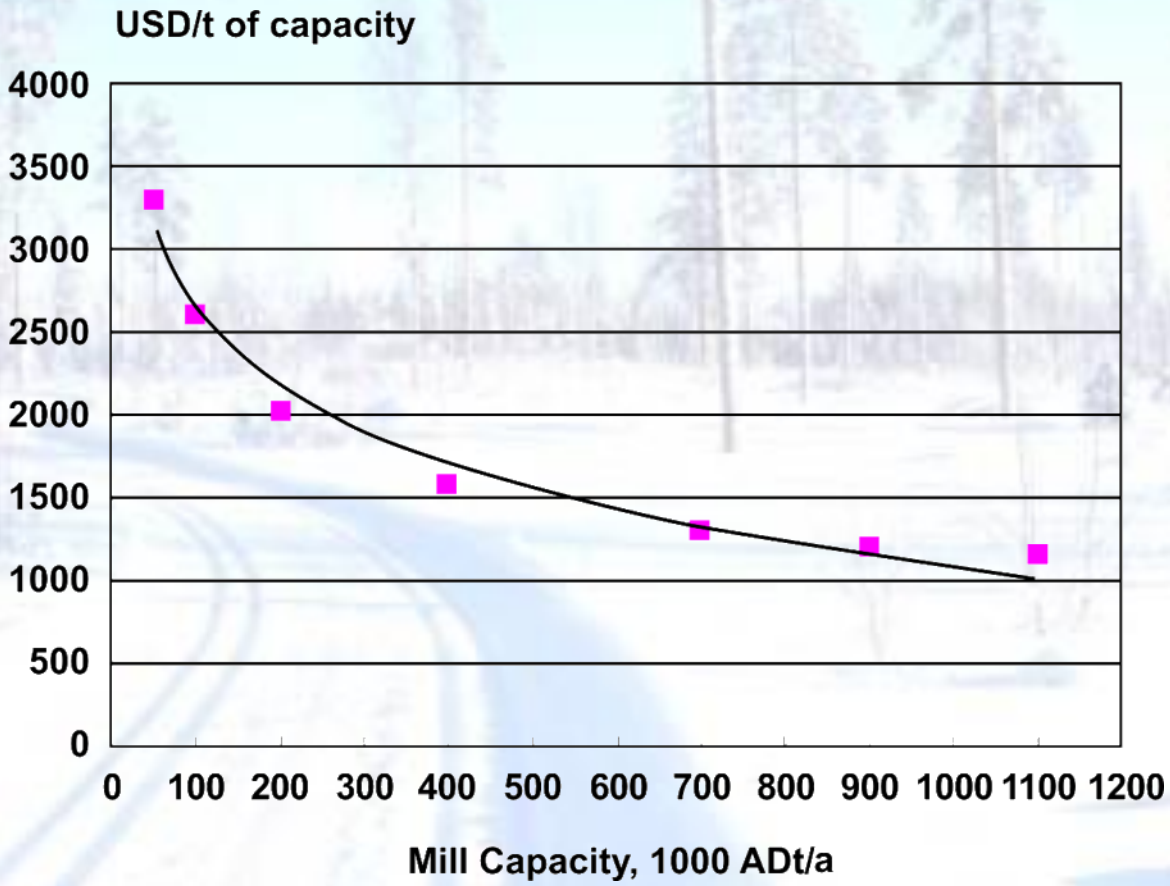
Specific Investment Requirements

Investment costs for new capacity continue to grow but so does the size. New hardwood pulp mill projects have a capacity as high as one million tons. Investment cost/ton continues to drop, but increasingly slowly.



Reduce fragmentation of industry and increase unit size. Adapt new technologies to reduce the operational costs (up-time, wood, chemicals, energy, maintenance, environment)

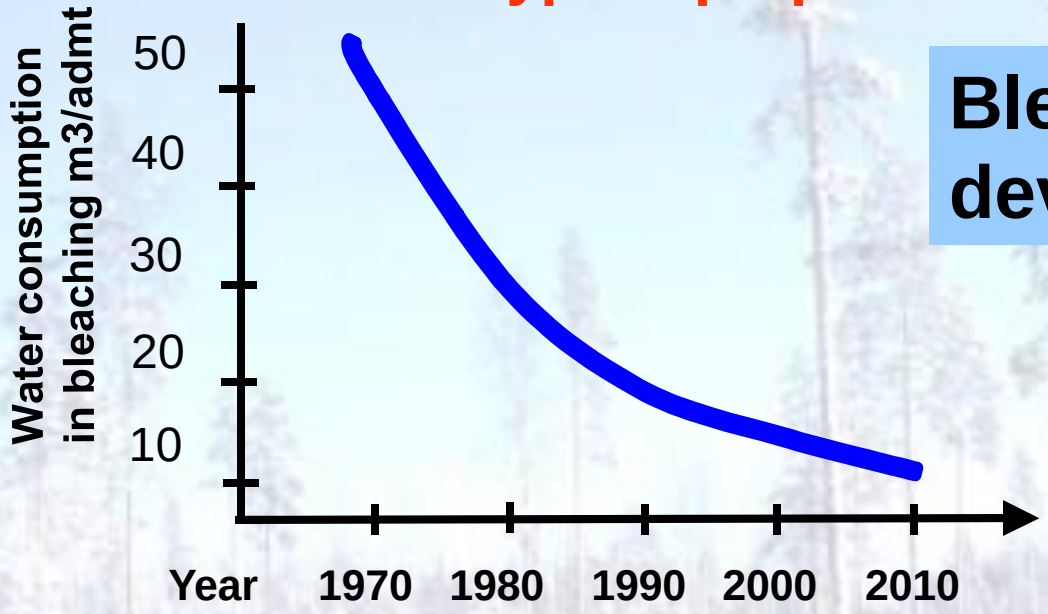
Source: JP World Fiber Outlook 2006

Advances in eucalyptus pulp bleaching technology

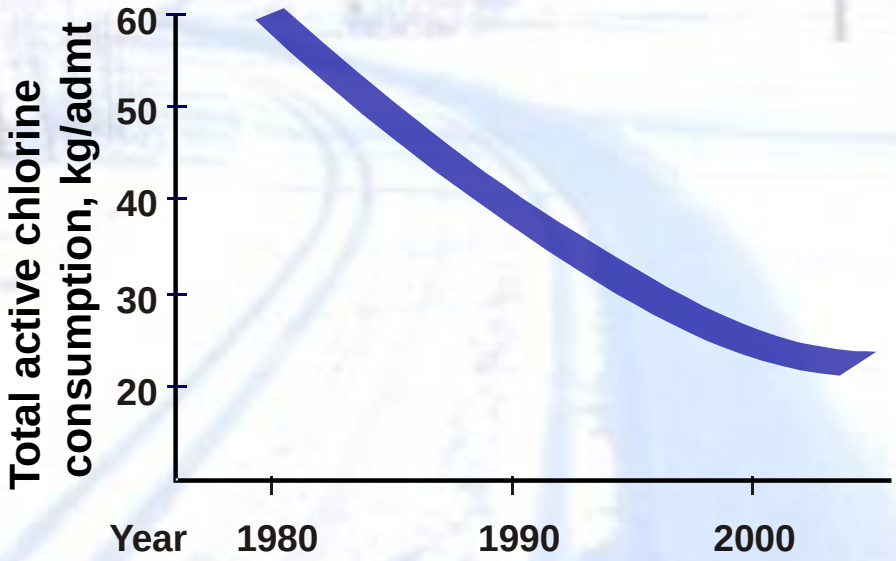
Bleaching process development

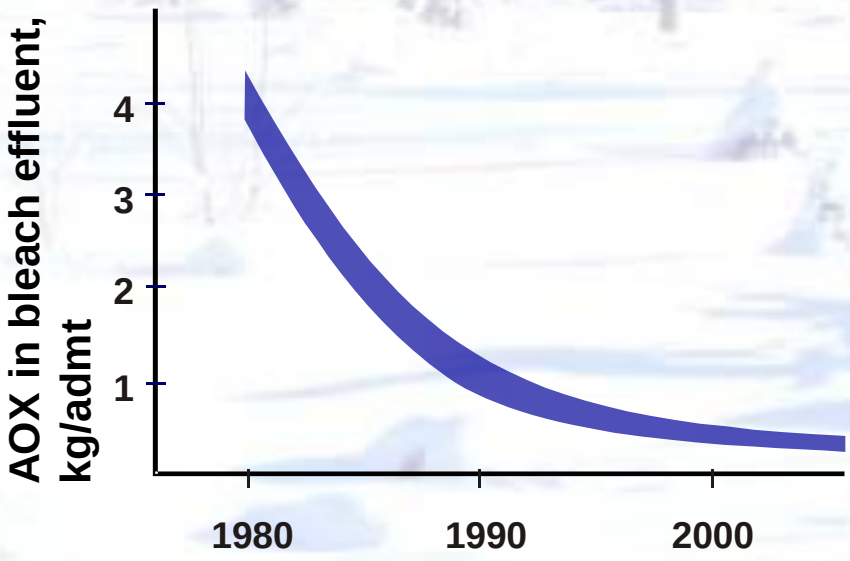
- ✓From elemental chlorine to chlorine dioxide
- ✓Less bleaching stages
- ✓Oxygen delignification
- ✓Oxygen and peroxide reinforced pulp bleaching
- ✓Medium consistency pumping
- ✓Equipment technique
  - High shear mixing
  - Pulp washers
- ✓ECF, Light-ECF, TCF bleaching
  - New bleaching chemicals
  - Ozone, Paa, PMo
- ✓Reduced effluent discharges

Advances in eucalyptus pulp bleaching technology



Bleaching process development





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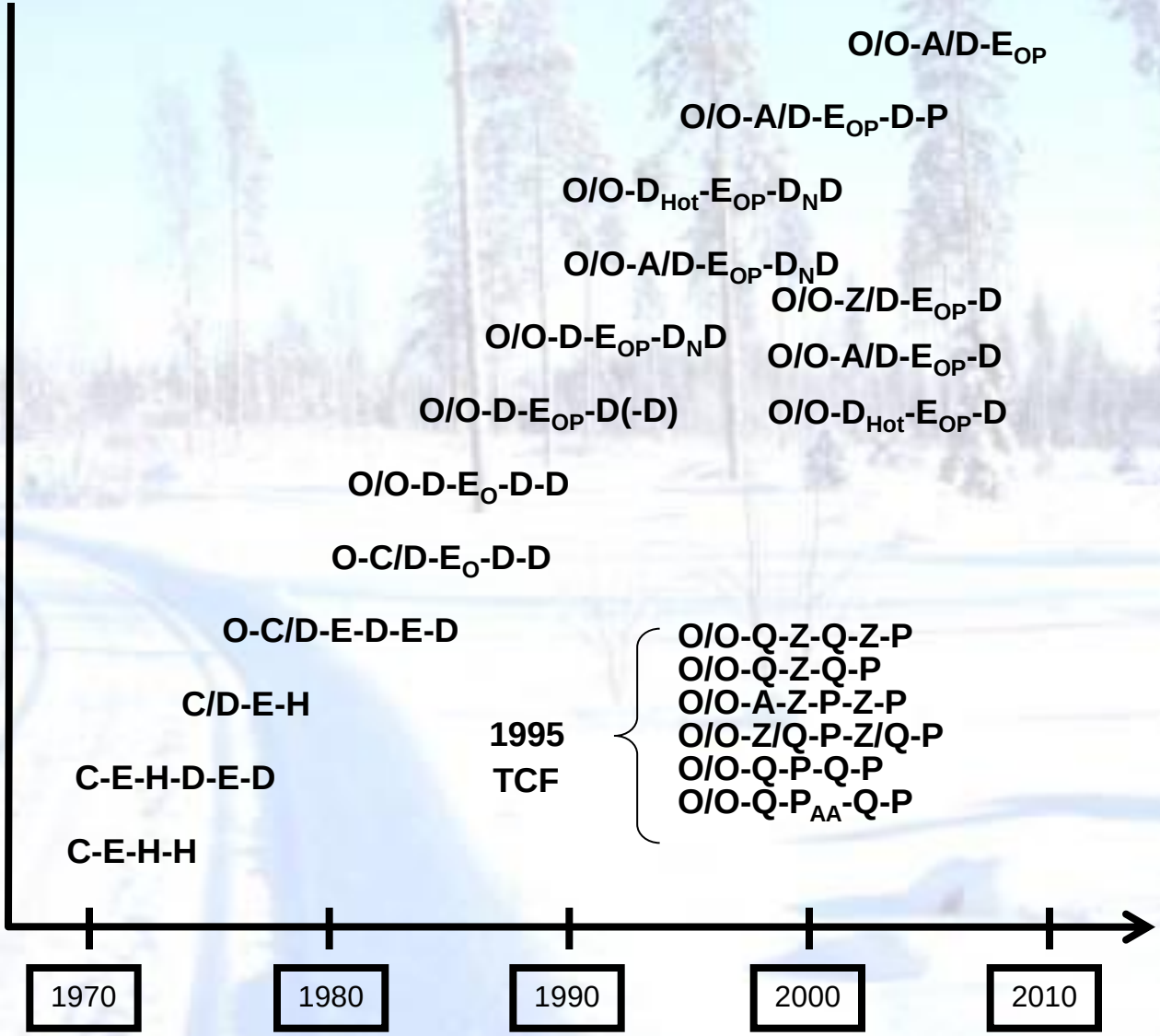
Bleaching process development



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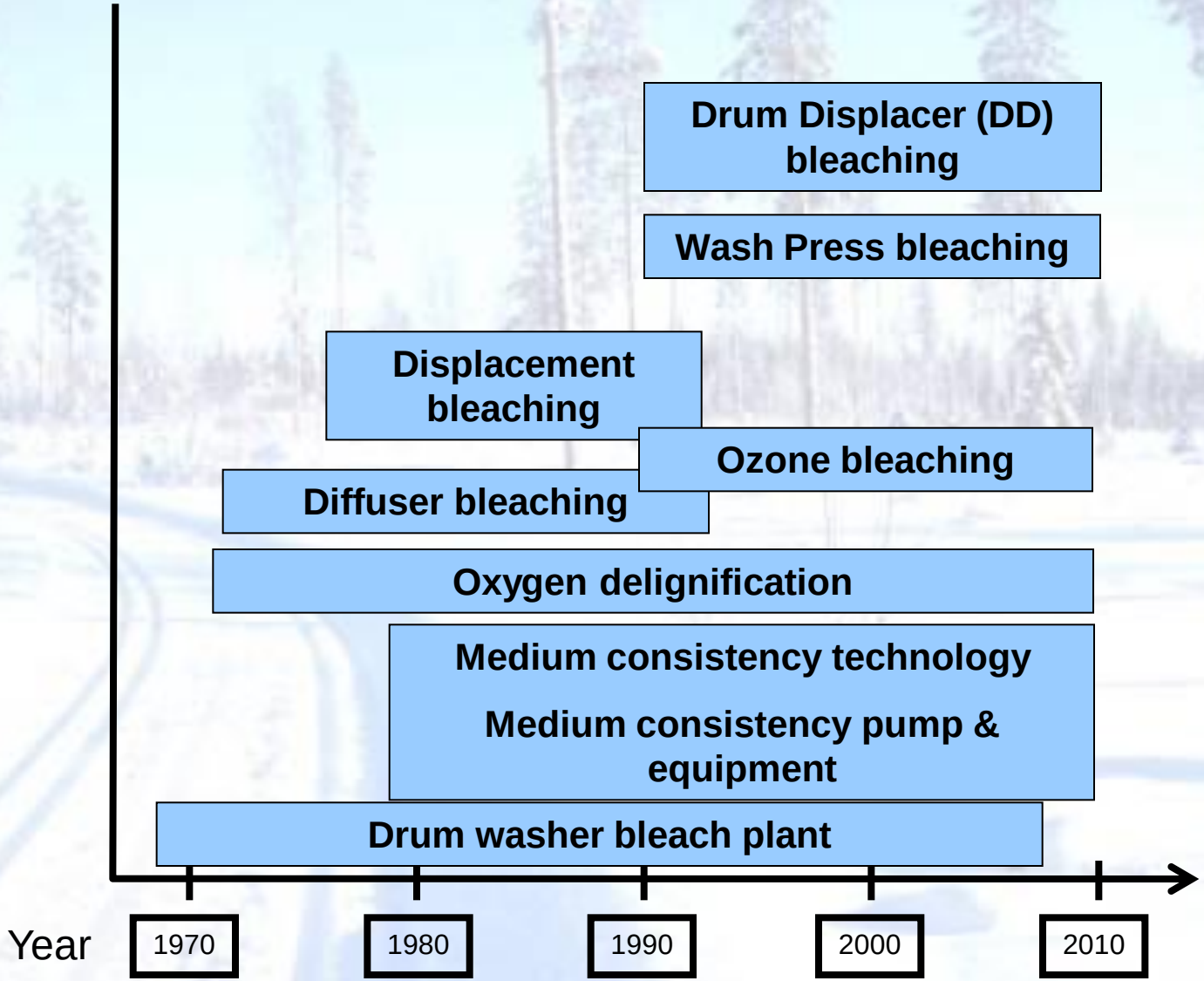
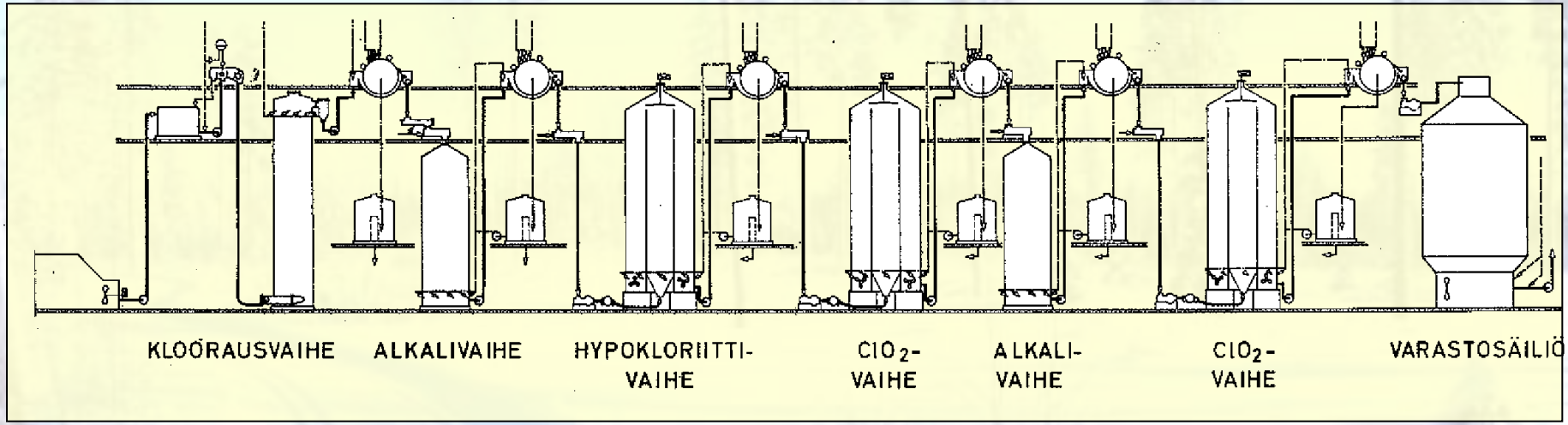
Bleaching process development



Advances in eucalyptus pulp bleaching technology

Bleaching process development

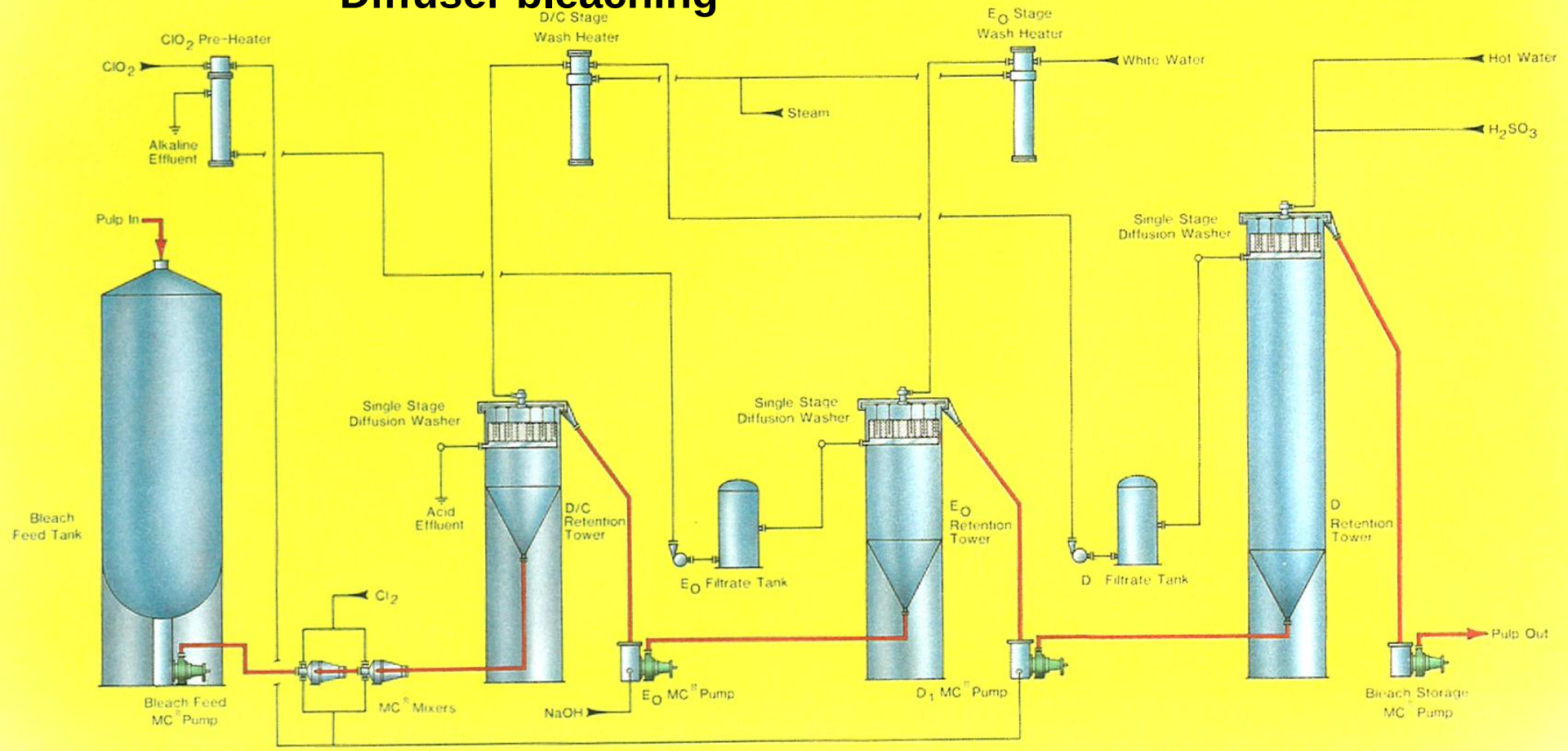
C E H D E D



Advances in eucalyptus pulp bleaching technology

Bleaching process development

Diffuser bleaching



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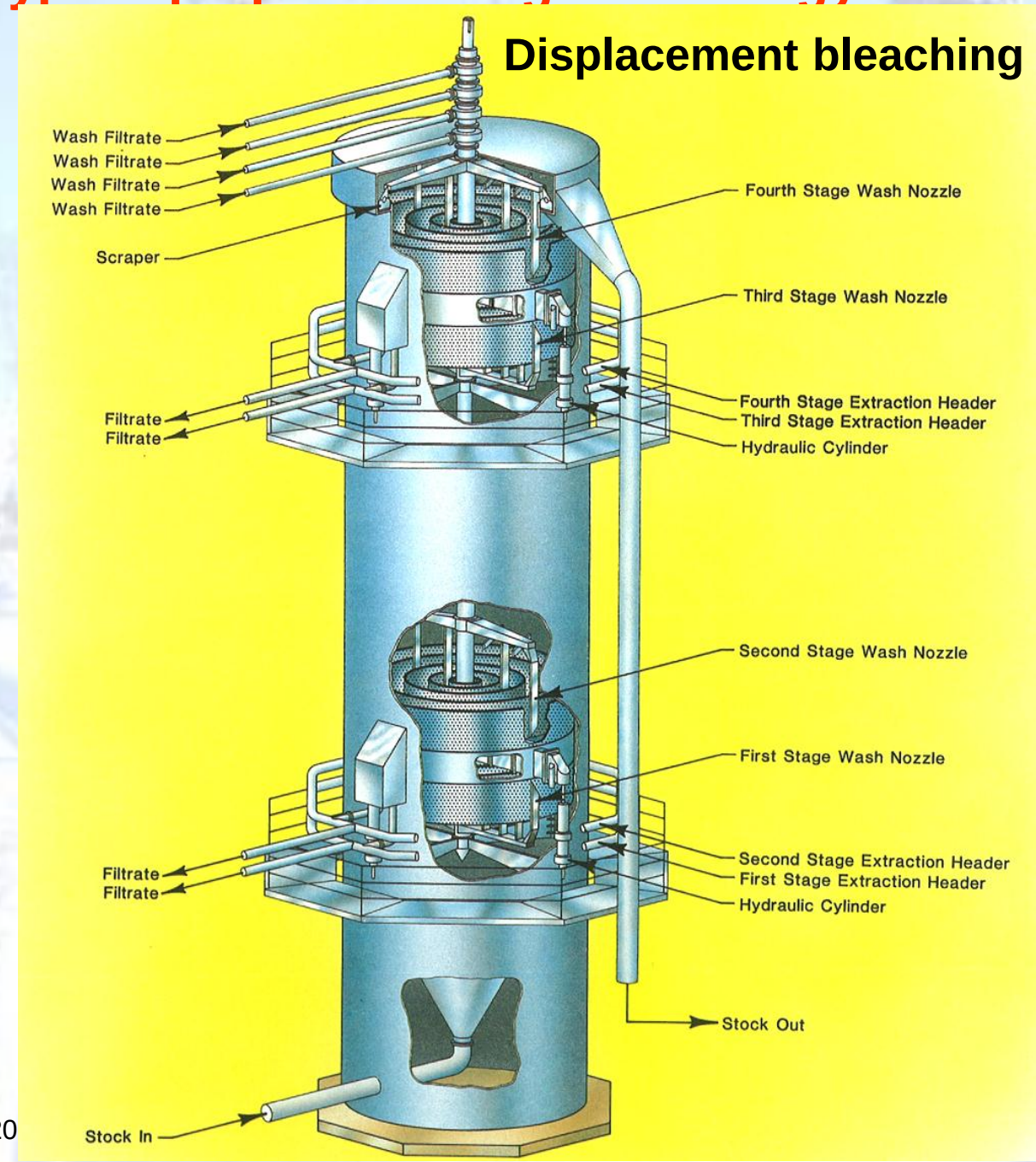
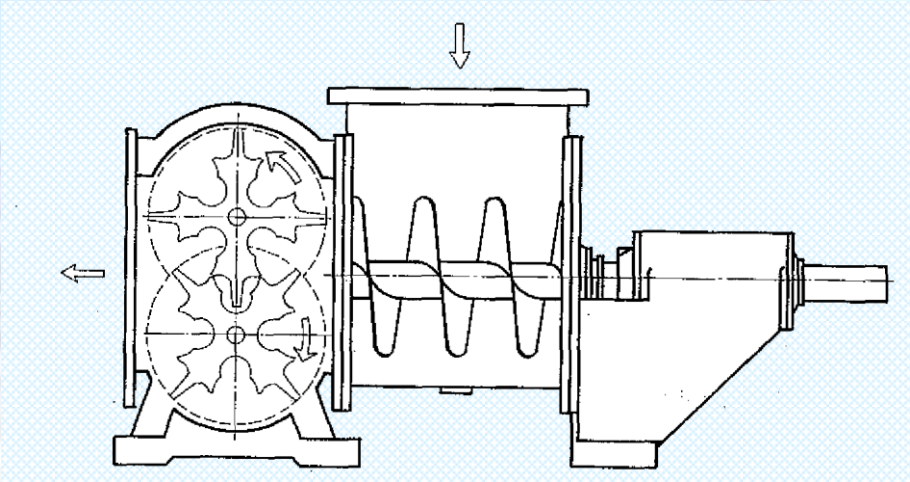
Bleaching process development

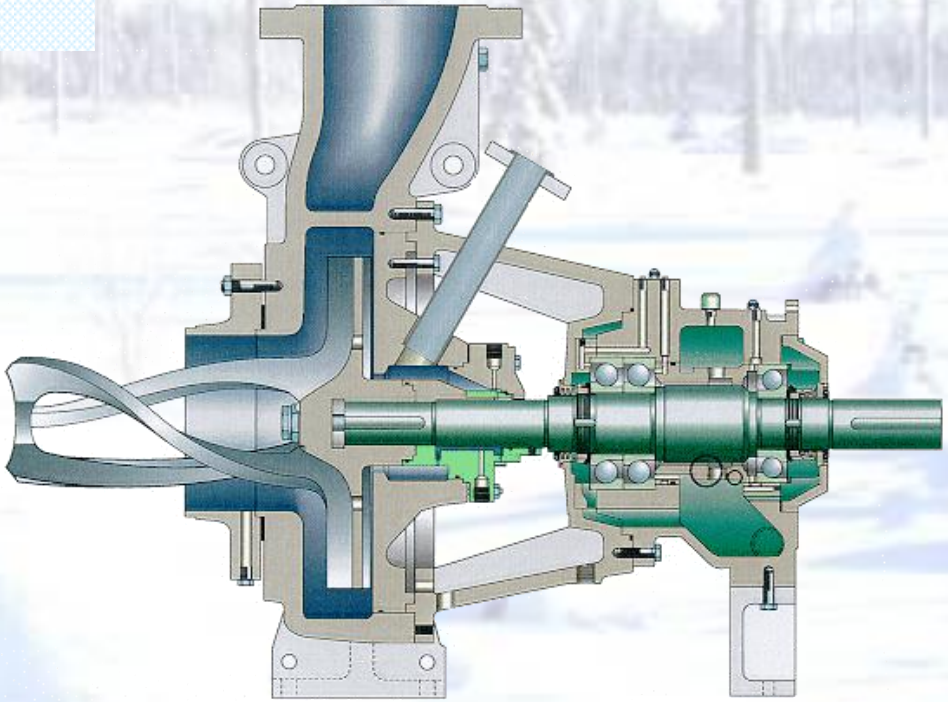


Bleaching process development



High density stock pump

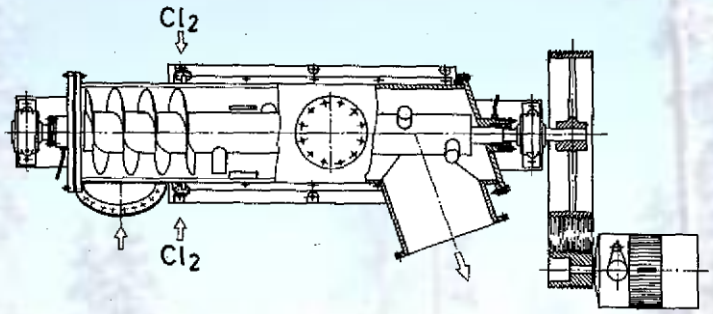
- **capacity <1500 admt/d**
- **head up to 100 m**
- **consistency 10…15%**



Medium consistency pump

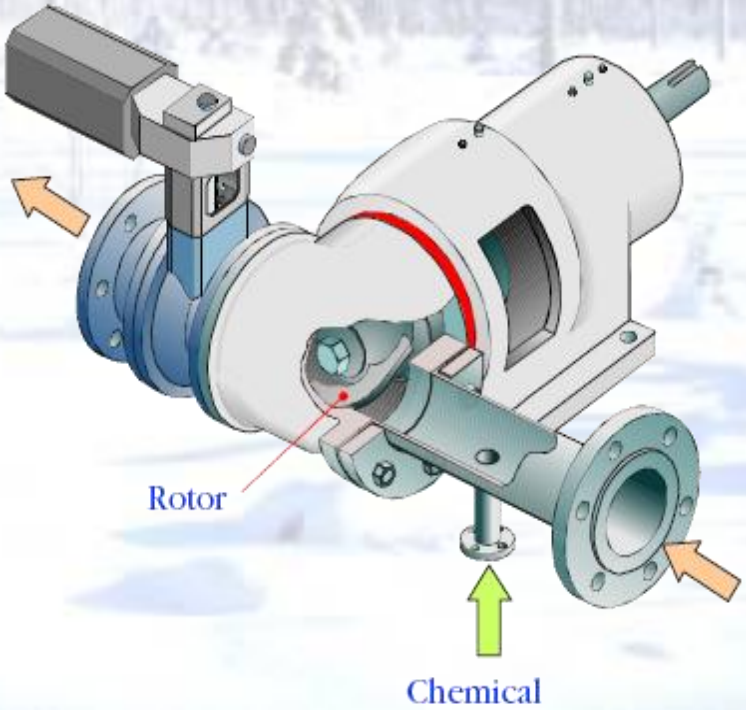
- **capacity >4000 admt/d**
- **head up to 200 m**
- **consistency 10…12%**

Bleaching process development



Chemical mixer
- **capacity <1500 admt/d**
- **consistency 10…13%**

Medium consistency chemical mixer
- **capacity >4000 admt/d**
- **consistency 10…13%**



Topics in pulp bleaching technology

- Oxygen delignification
- Removal of Hexenuronic acid
- Bleaching sequences
- Pulp washing
- Pulp quality

Advances in eucalyptus pulp bleaching technology

Oxygen delignification

Single-stage system

Two-stage system

Process parameters

- **Temperature profile**
- **Chemical profile**
- **Pressure profile**

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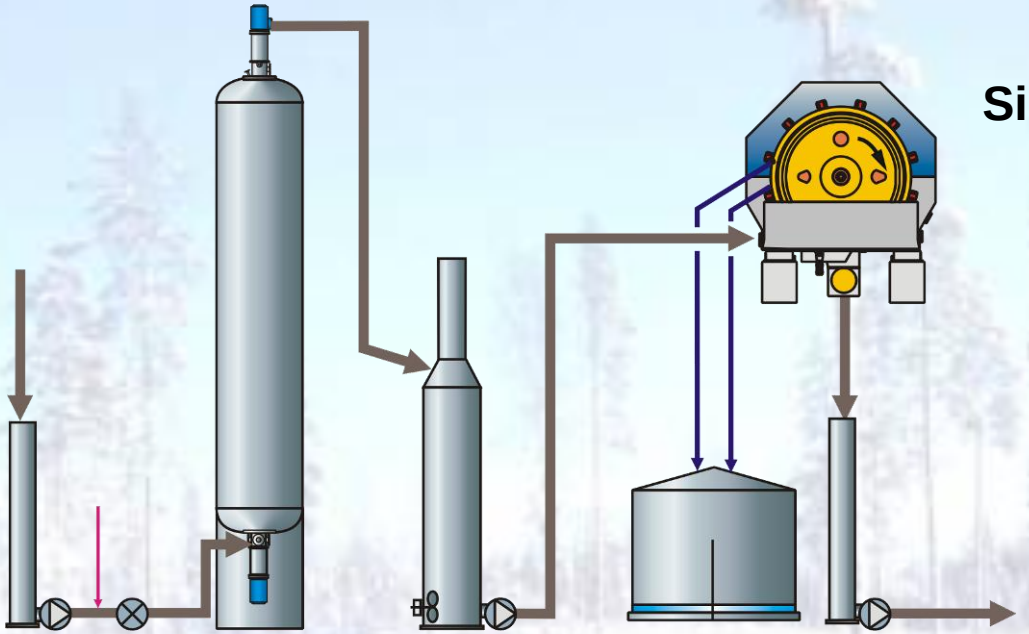
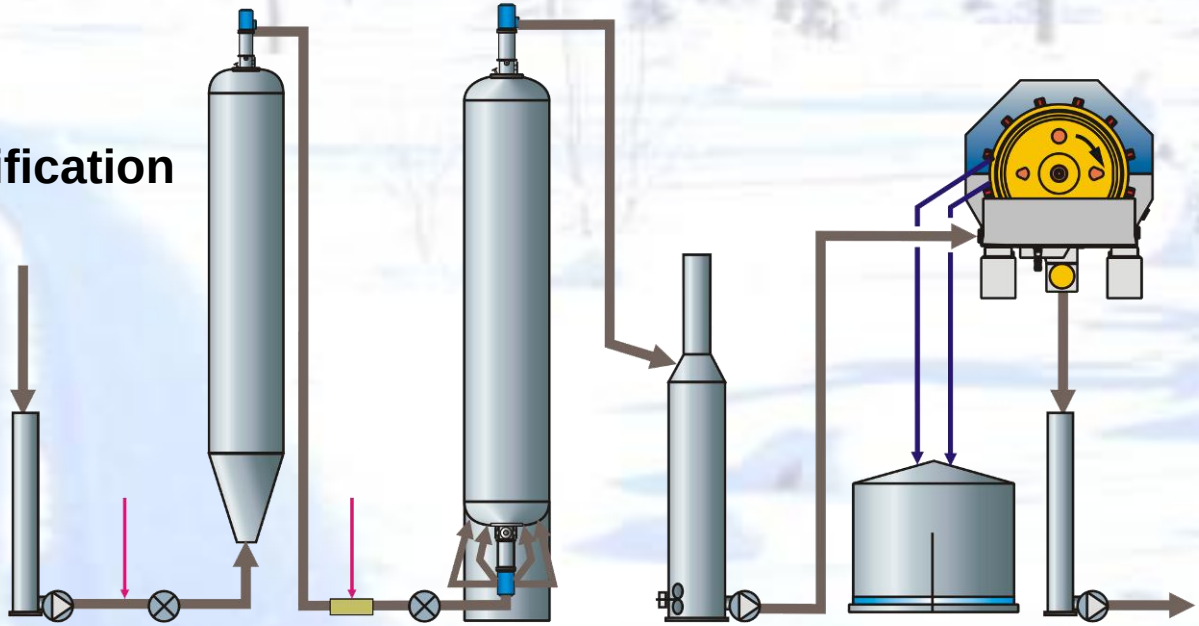


Single-stage oxygen delignification

Two-stage oxygen delignification



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Two-stage versus single-stage oxygen delignification

- ✓Enables better process parameter controls
  - ✓retention time, pressure, chemical, temperature
- ✓Enables better potential for kappa reduction, selectivity, brightness
  - ✓1-2 units higher kappa reduction
  - ✓5 - 10 units higher brightness
- ✓Pulp washing before oxygen delignification in a key role
  - ✓there is peroxide formation in oxygen reactions and black liquor catalyzes the degradation of peroxide
  - ✓COD carryover less than 90 kg/adt

Removal of hexenuronic acid

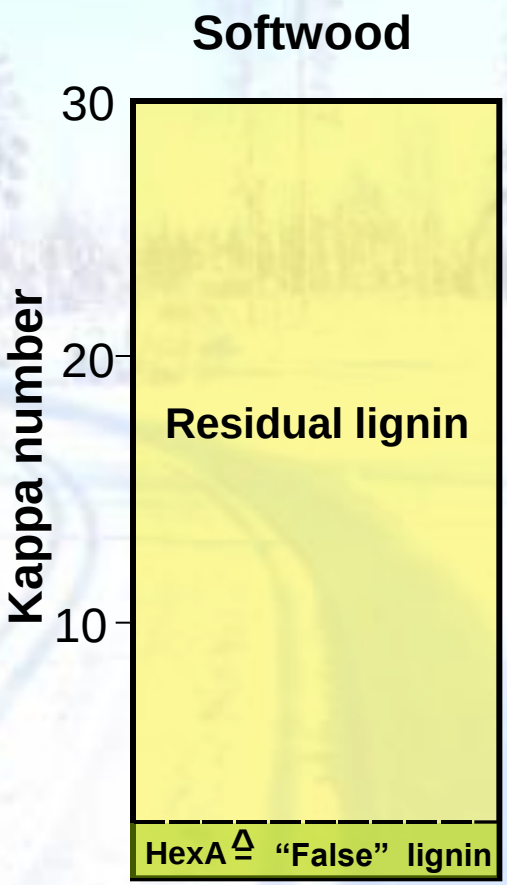
HexA contents in different pulps

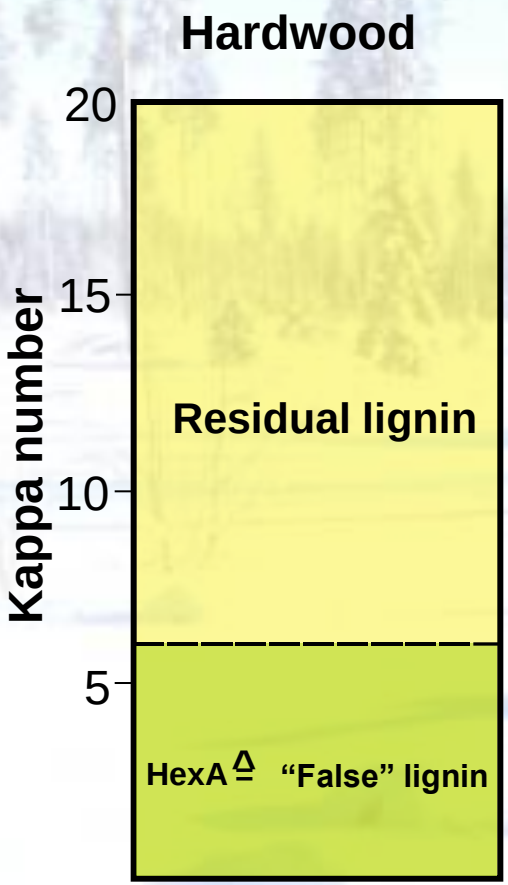
- ✓ Scandinavian softwood pulps 20 – 30 mmol/kg
- ✓ Scandinavian birch pulp 40 – 60 mmol/kg
- ✓ Eucalyptus pulp 45 – 85 mmol/kg
- ✓ Acacia and mixed hardwood pulps 35 – 50 mmol/kg

10 – 12 mmol HexA /kg corresponds to 1 kappa unit

Advances in eucalyptus pulp bleaching technology

Relation between HexA and residual lignin of the hardwood and softwood pulp kappa number





In eucalyptus pulp 30…50% of kappa can originate from HexA

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- **HexA consumes bleaching chemicals (O_3, ClO_2, and P_{AA})**
- **HexA does not react with O_2 and H_2O_2**

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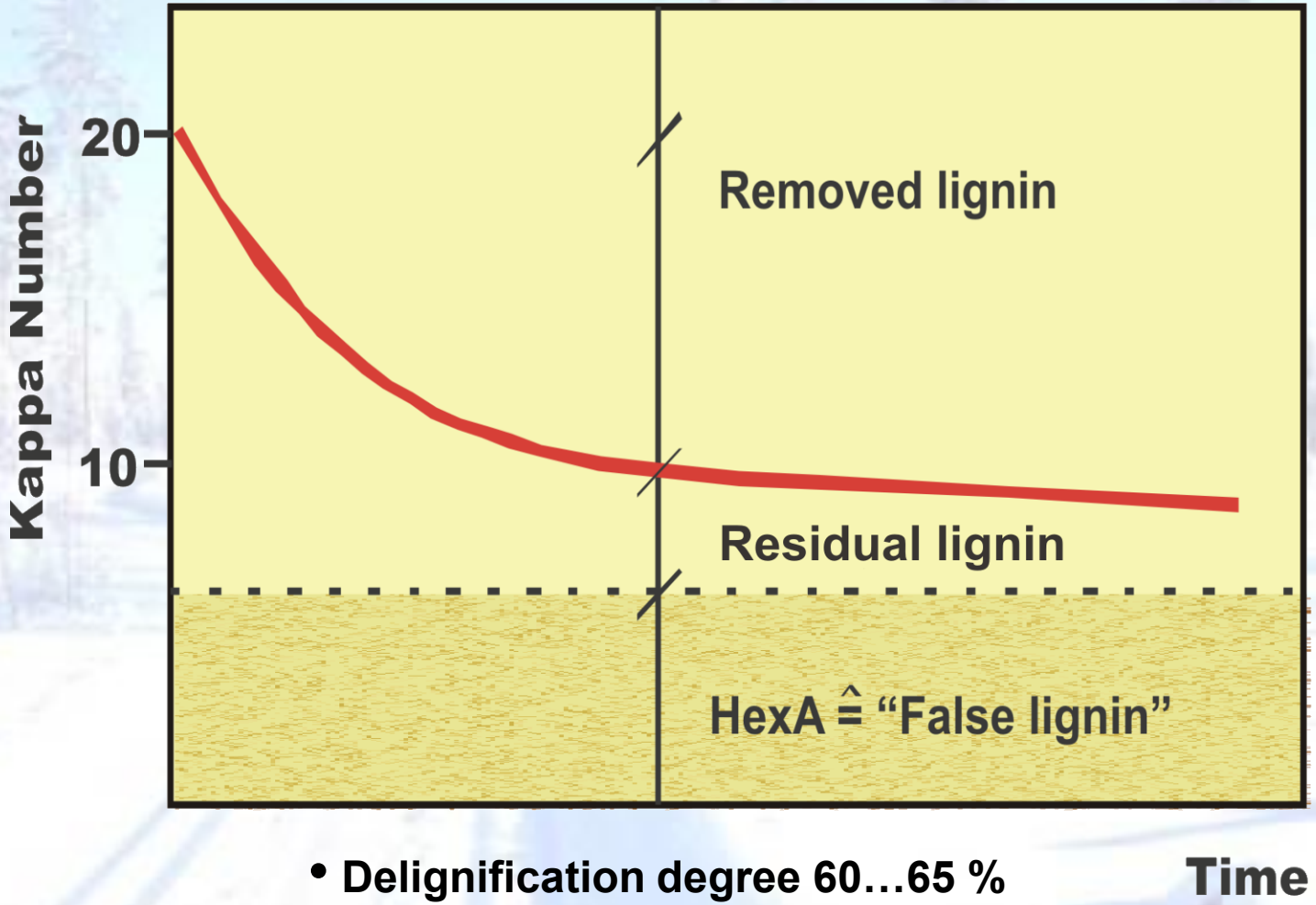
Oxygen Delignification, Hardwood



- Delignification degree 60…65 %
- Kappa reduction 40…50 %

A-Stage - typical process conditions

HexA content	40-80 mmol/kg	HW
	20-30 mmol/kg	SW
pH	3 – 3,5	
pulp consistency	medium; 10-12%	
COD carryover	∗10-15 kg/adt	
temperature	90 - 100°C	
time	2 - 4 h	
⇒	60-80% HexA decrease	
	3 - 5 kappa units, hardwood	
	1 - 3 kappa units, softwood	

Decrease in pulp metal content

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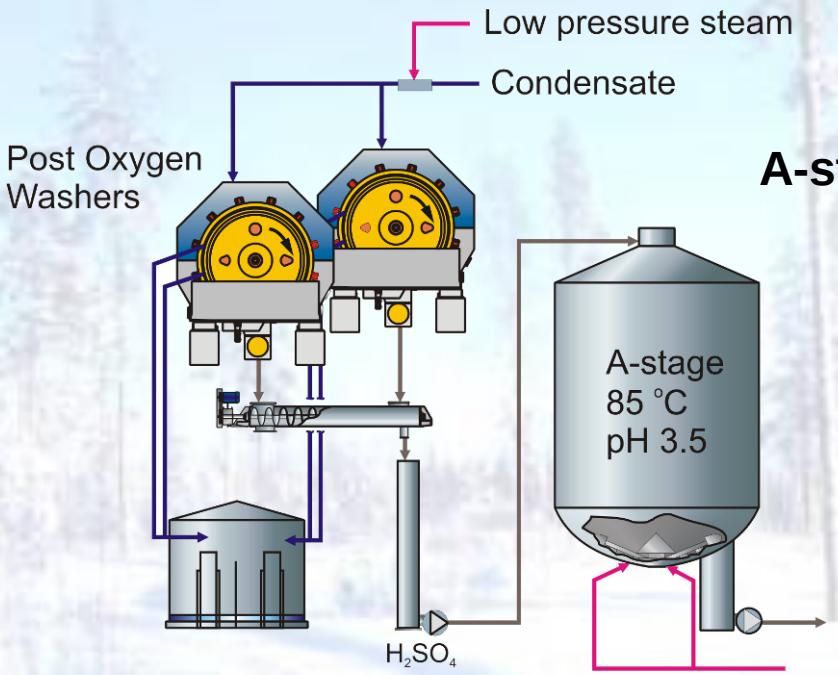
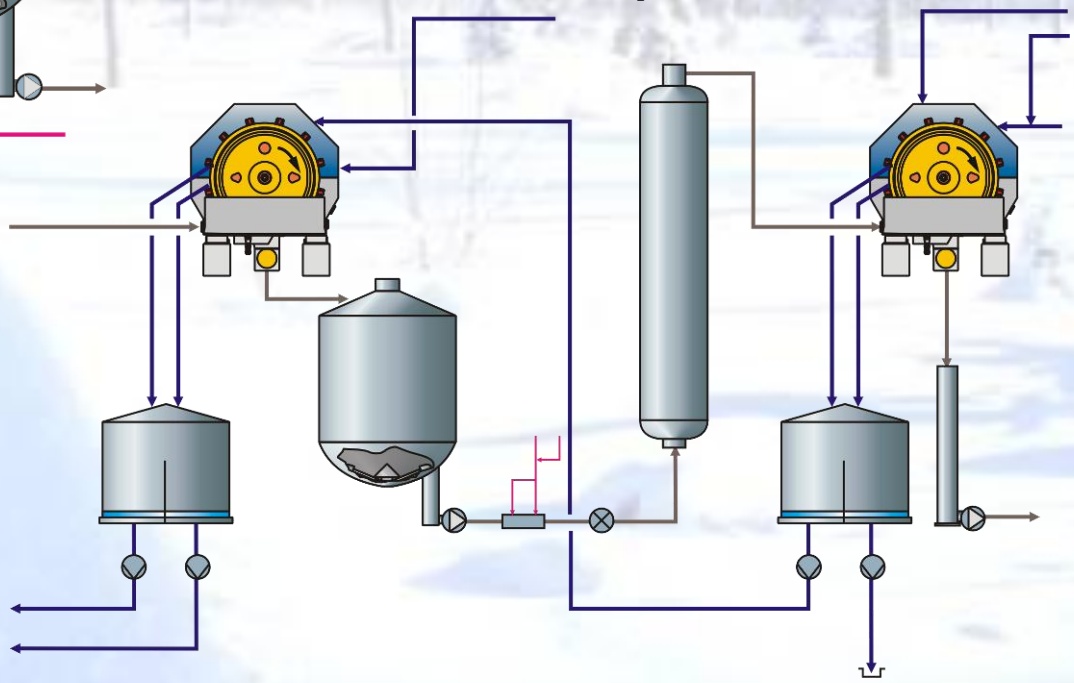
A-stage alternatives



A-stage in storage tower

A-stage in separate up-flow tower



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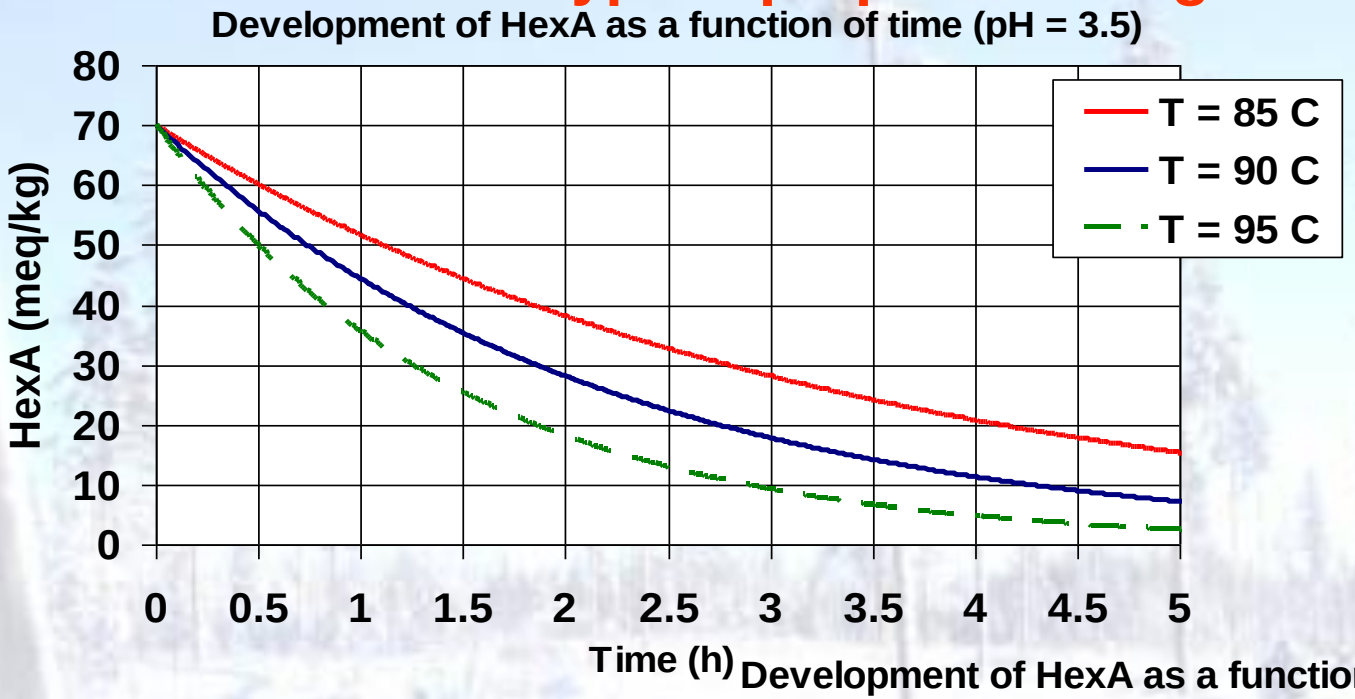

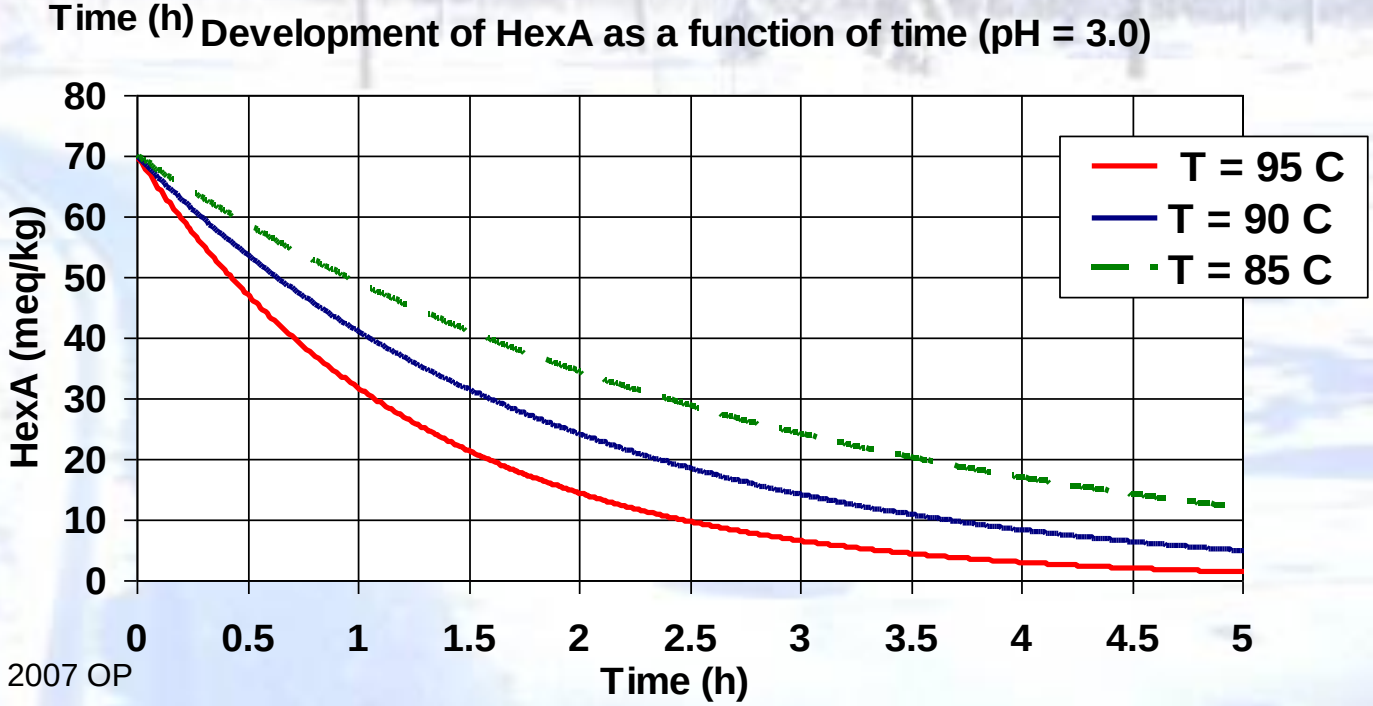

/1/, /2/ Vuorinen, T., Buchert, J., Teleman, A., Tenkanen, M. & Fagerström, P

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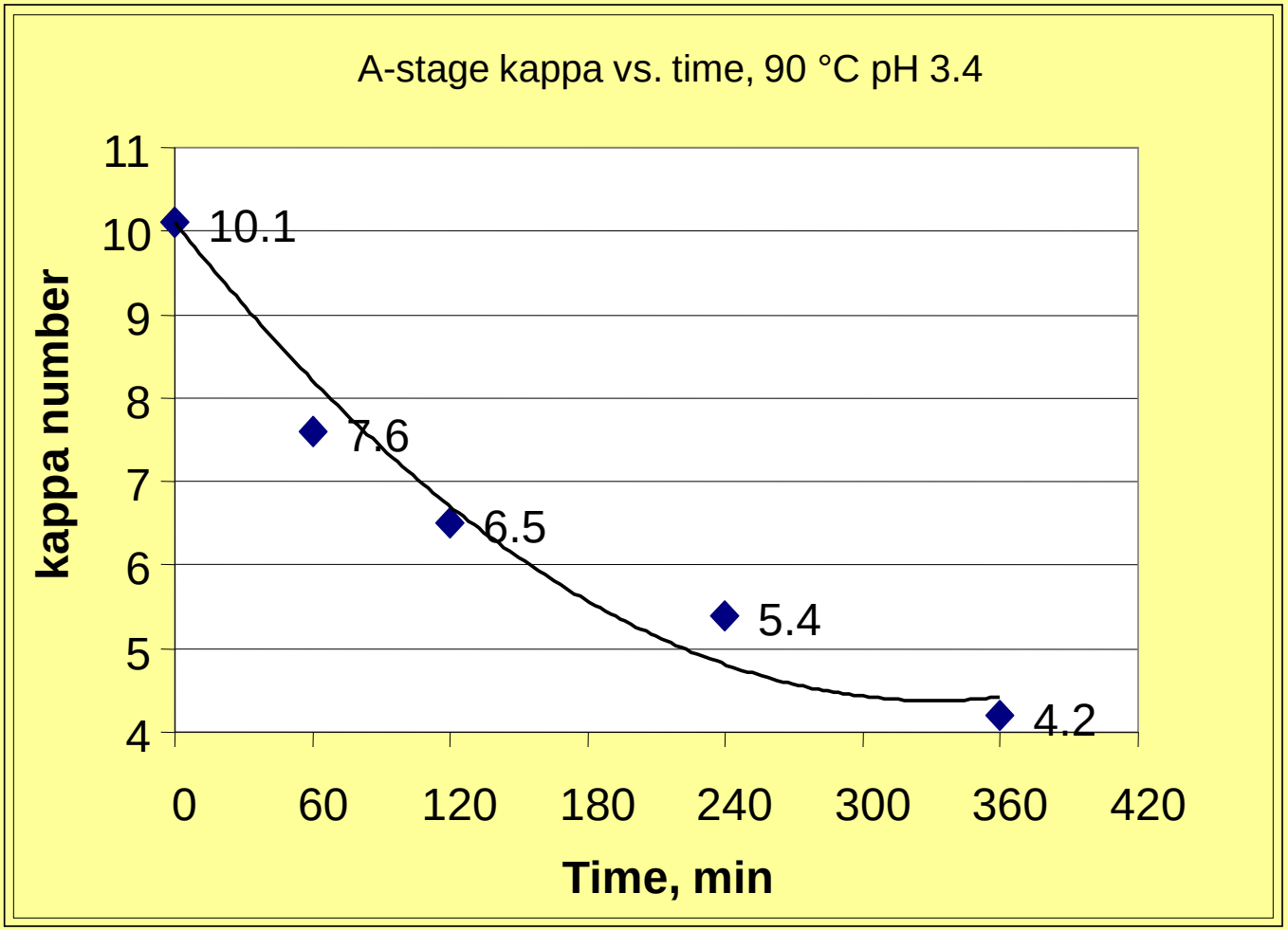
South-American euca, HexA content 54 mmol/kg



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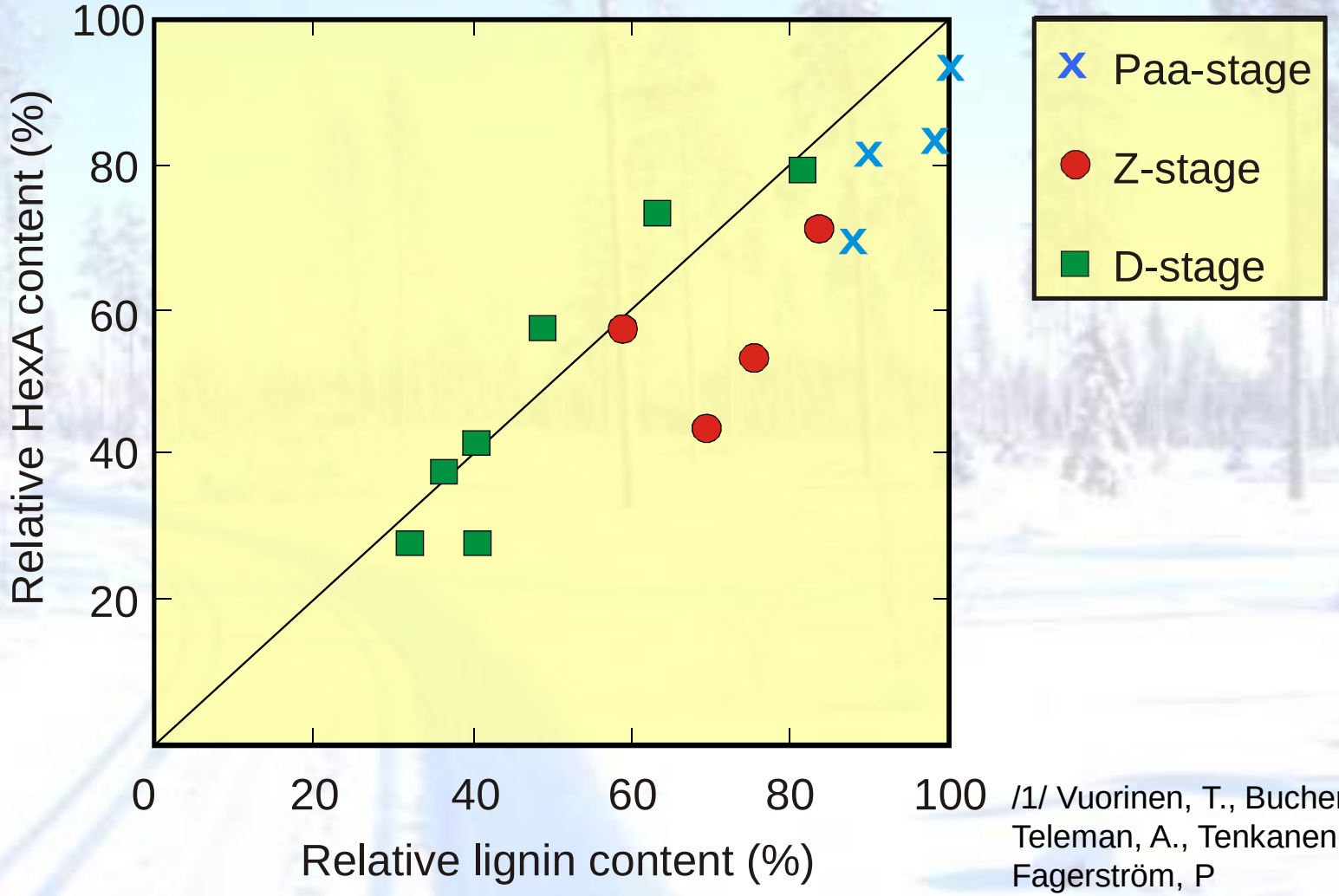
Competing removal of HexA and lignin



/1/ Vuorinen, T., Buchert, J., Teleman, A., Tenkanen, M. & Fagerström, P

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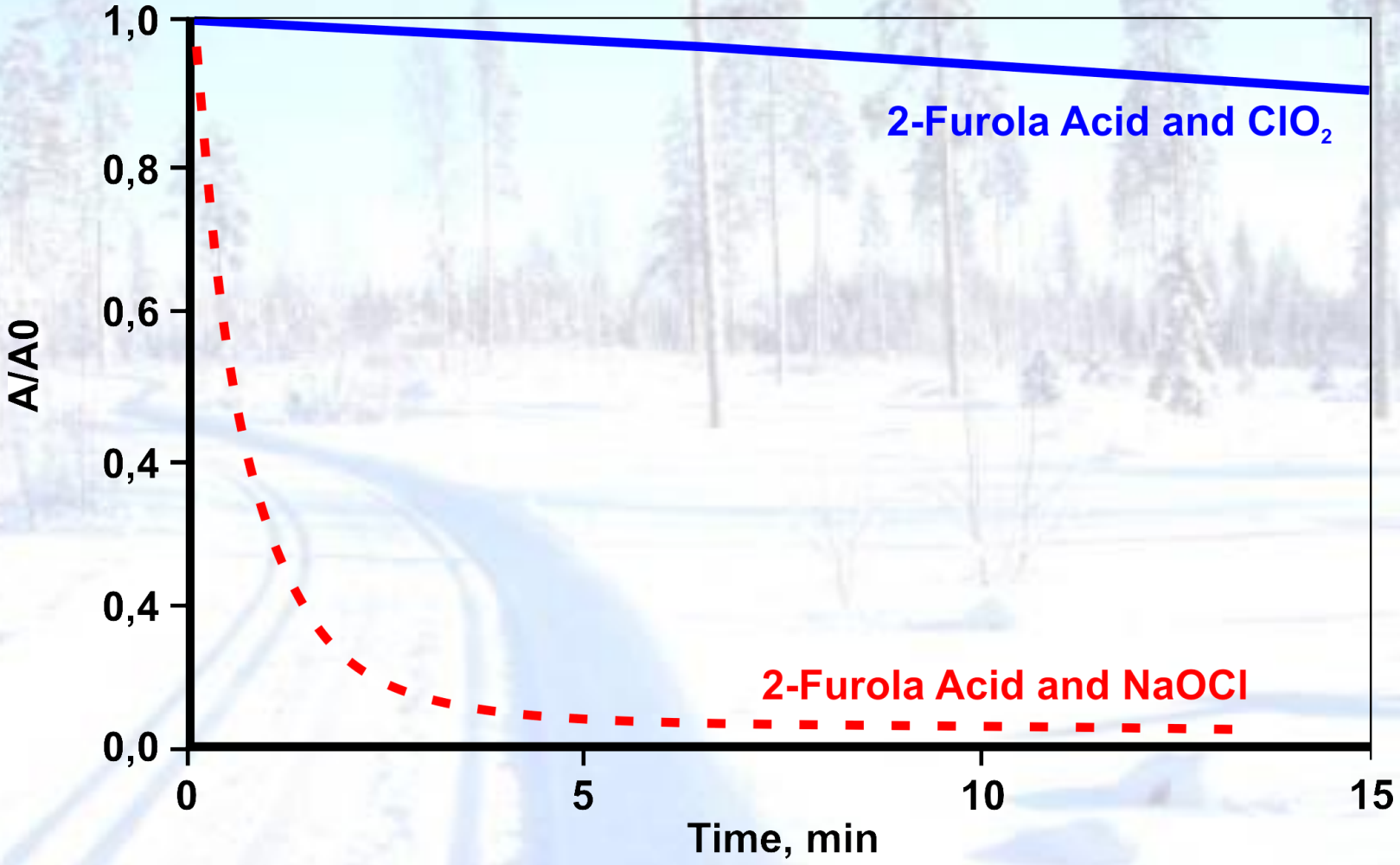
Reaction of 2-furoic acid with ClO_2 and $HOCl/Cl_2$ (T=90ºC, pH=2)



/3/ Toikka, K et al

Combining Hexa removal to bleaching
Modern bleaching sequences

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A / D_o^W

D_{Hot}^W

~~A / Z^W~~

$A^W - Z^W$

Z / D^W

$A^W - Z / D^W$

Advances in eucalyptus pulp bleaching technology

Effect of interstage washing on the performance of the selective hydrolysis of HexA in chlorine dioxide bleaching of birch kraft pulp

	A-D-E-D		A/D-E-D	
	Kappa A-D-E	Bright. ISO%	Kappa A/D-E	Bright. ISO%
Pulp 1	2.4	86.1	2.0	86.8
Pulp 2	2.7	84.5	2.8	84.2
Pulp 3	2.0	88.6	2.3	88.0

/1/ Vuorinen, T., Buchert, J., Teleman, A., Tenkanen, M. & Fagerström, P

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Effect of interstage washing on the performance of the selective hydrolysis of HexA in ozone bleaching of birch kraft pulp

	Kappa number	Brightness ISO%
O-A	4.1	53.6
O-A-Z	1.8	72.1
O-A/Z	3.7	56.2

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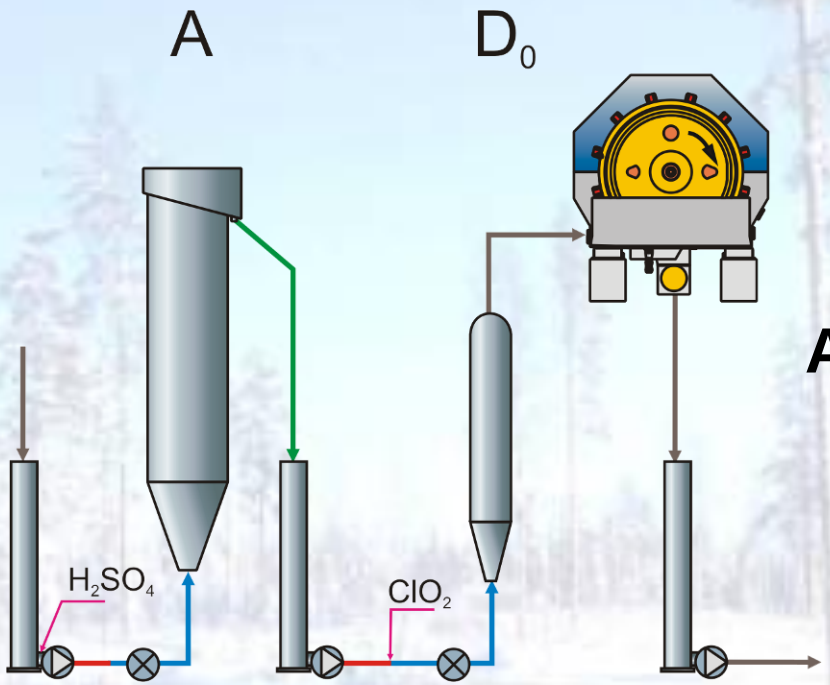
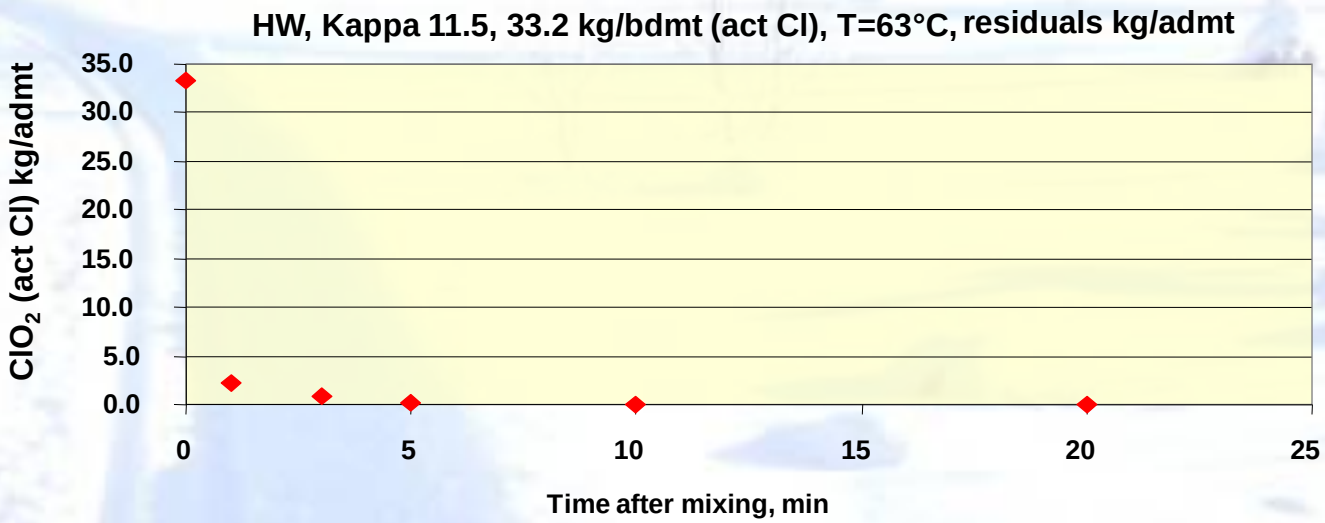


A stage combined with D_0 stage



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Relative benefits (+/-) of different bleaching sequences with respect to each other

Sequence	Capital cost	Chemical cost	Brightness flexibility	Brightness reversion	Effluent
Z/D-Eop-D-P	- - -	+ +	+ + +	+ + +	+ + +
A-Z/D-Eop-D	- - -	+ + +	+ + +	+ +	+ + +
A/D-Eop-D-P	-	+ + +	+ + +	+ + +	+ +
A/D-Eop-Dn-D	- -	+ +	+ +	+ +	+ +
A/D-Eop-DnD	0	0	0	0	0
A/D-Eop-D	+	-	0	-	-
Z/D-Eop-DnD	0	-	+	+	+
A/D-Eop-D/P	+	0	0	+	+
Z/D-Eop-D/P	+	0	0	+	+ +

Effect of pulp washing

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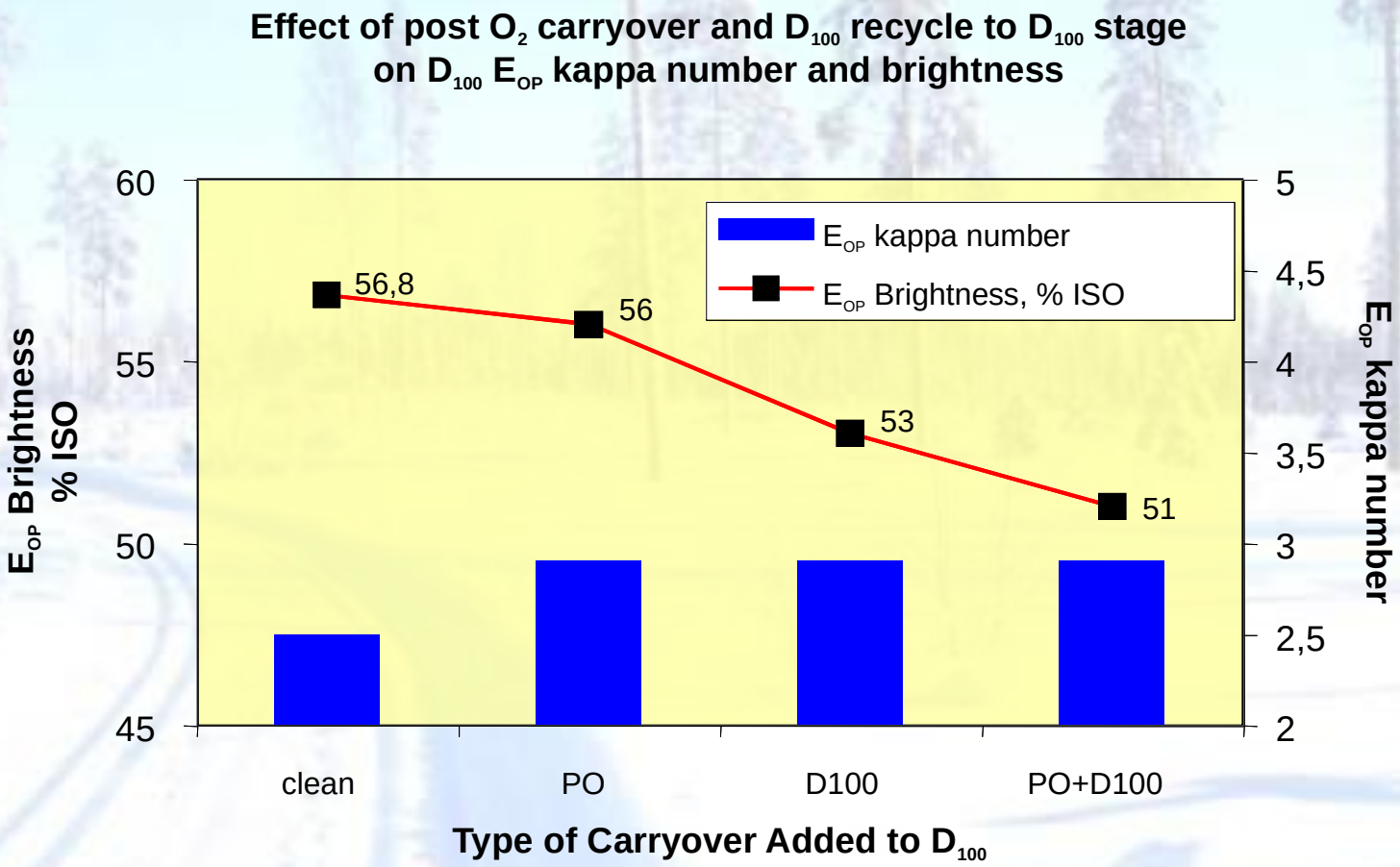
Effect of post O_2 carryover and D100 recycle to D100 stage on D100-Eop kappa number and brightness. The letters PO stand for post oxygen



Pulp: Southern Pine, PO kappa 18

D_{100} recycle 8.5 kg/t COD, PO carryover 10 kg/t COD, 18.5 kg/t COD total

/4/ Miller, W. J. & Lennon, V. E

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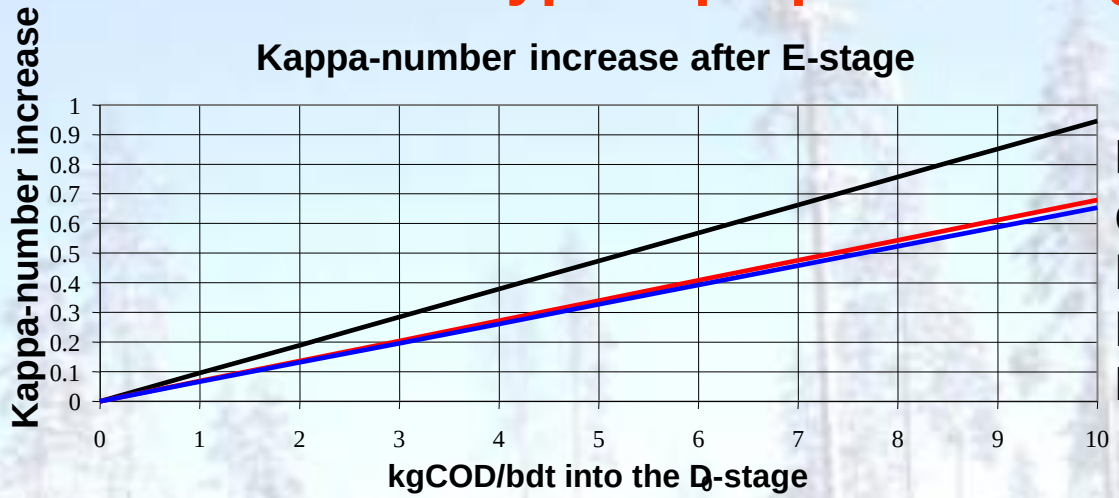
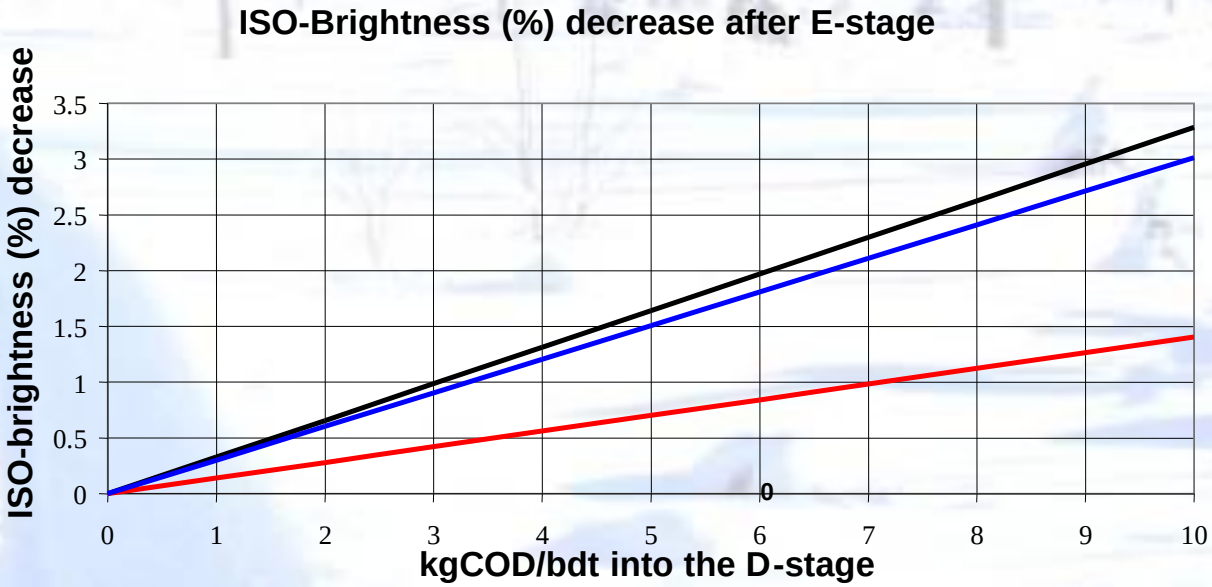


Effect of COD originating from different sources on brightness decrease and kappa increase after the E-stage

- **COD caused by lignin from cooking**
- **COD caused by lignin from oxygen delignification**
- **COD caused by lignin from D0-stage**



/5/ Viirimaa, M., Dahl, O., Niinimäki, J., Ala-Kaila, K. and Perämäki, P

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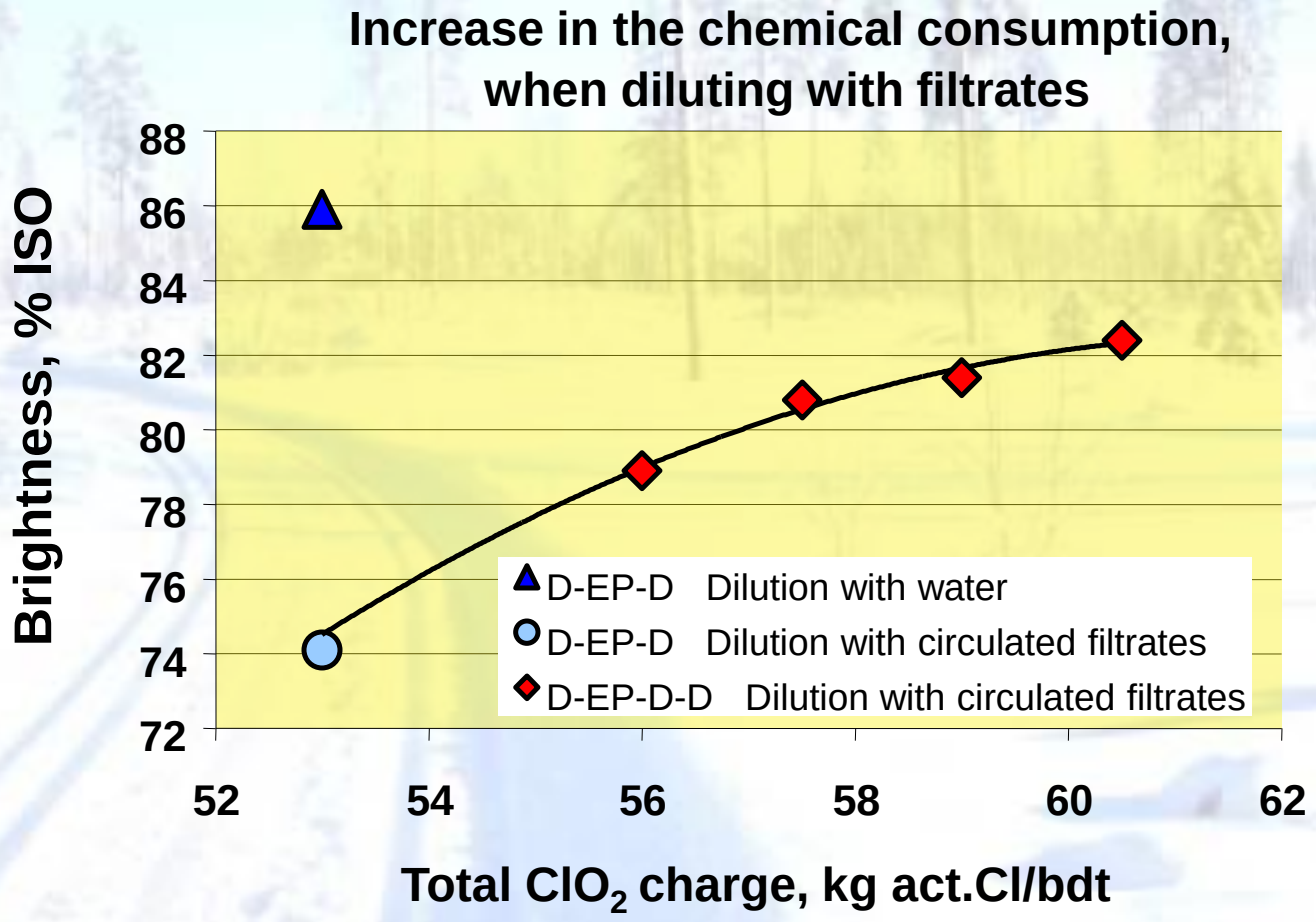
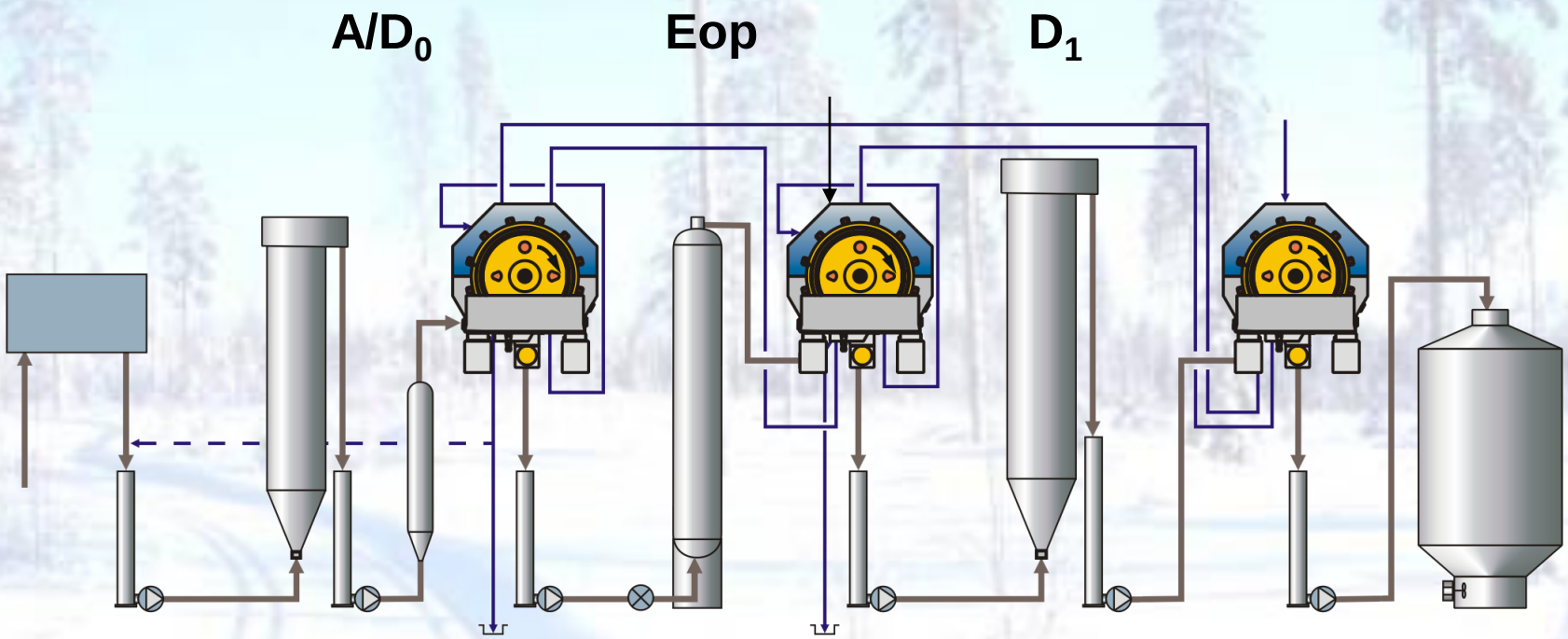
Laboratory bleaching trial dilution with clean water and circulating filtrate in D_o-stage. Bleaching sequence D_0-EP-D_1-D_2. SWSA, kappa 13.1. ClO_2 charge in D_0 3.8% and in D_1 1.5%.



/6/ Alastalo, J., Vehmaa, J., Pikka, O

Advances in eucalyptus pulp bleaching technology

3-stage bleach plant with fractional and non-fractional washing at normal and reduced effluent discharge



Total COD in pulp kg/adt

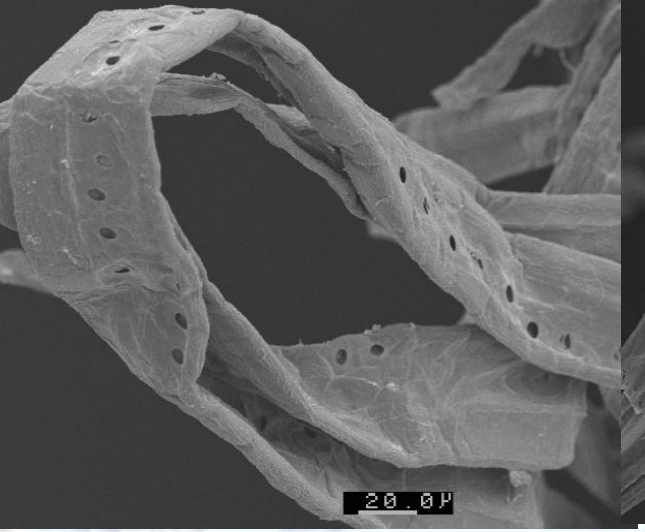
	A/D$_o$	Eop	D$_1$	DM
Bleach Plant Effluent 15 m^3/adt	5	8.9	5	1.9
Bleach Plant Effluent 10.8 m^3/adt				
Segregated washing	5	22.8	14.5	3.6
Non-segregated washing	17.9	16.6	11.5	5.4

Pulp quality

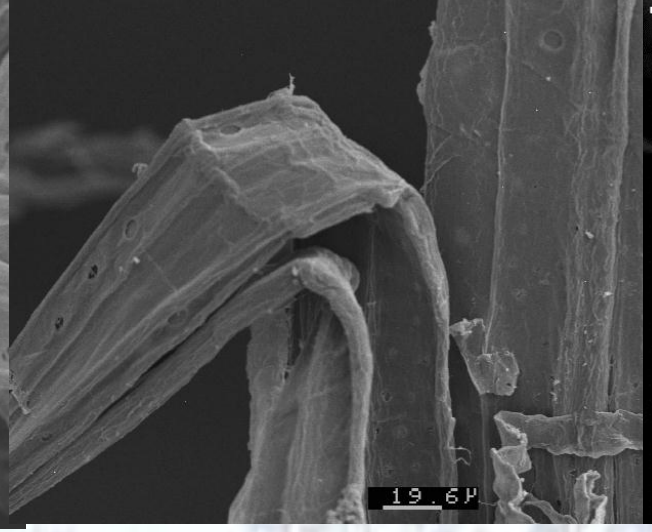
Fiber deformation/Fiber damage

Caused by chemical and mechanical treatment

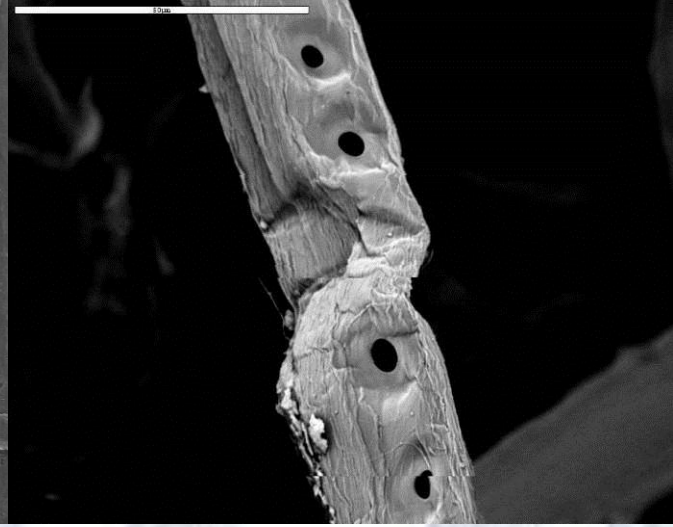
- **at high alkali concentration**
- **at high temperature**
- **brown stock/oxygen delignification areas most critical**



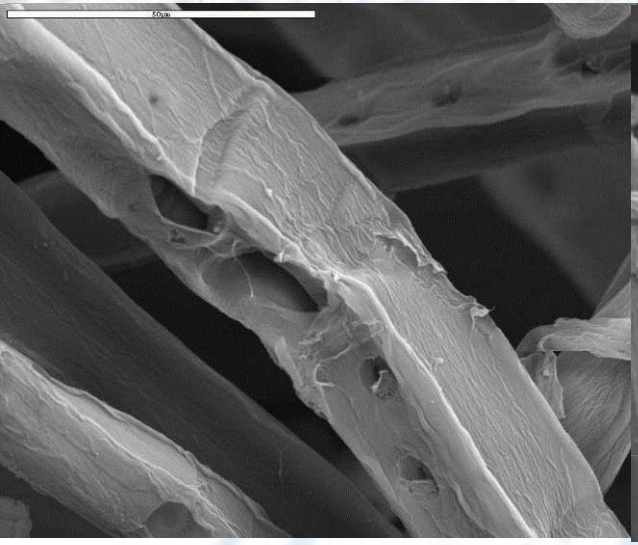
Fiber curl



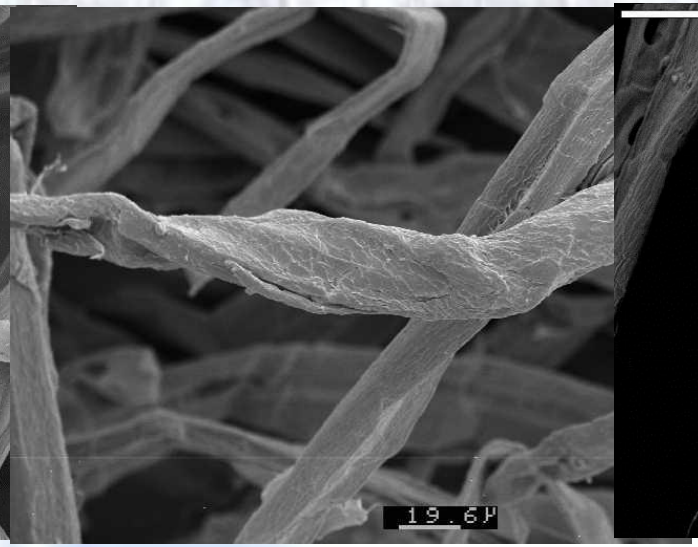
Fiber kink



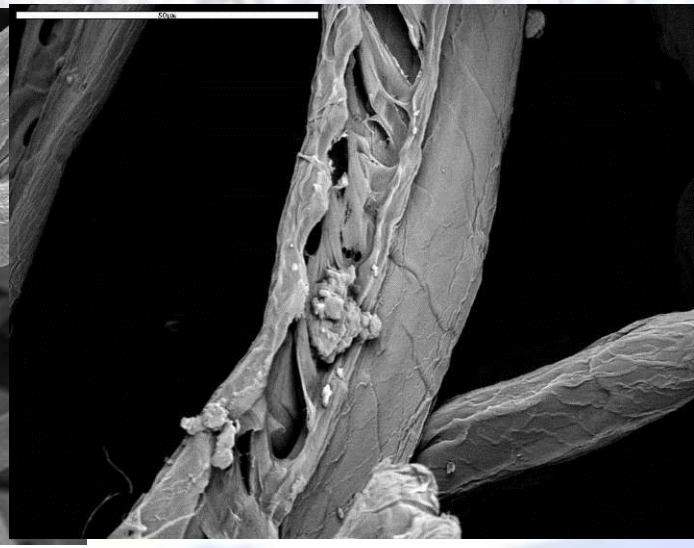
Microcompression



Dislocation



Fiber Twist

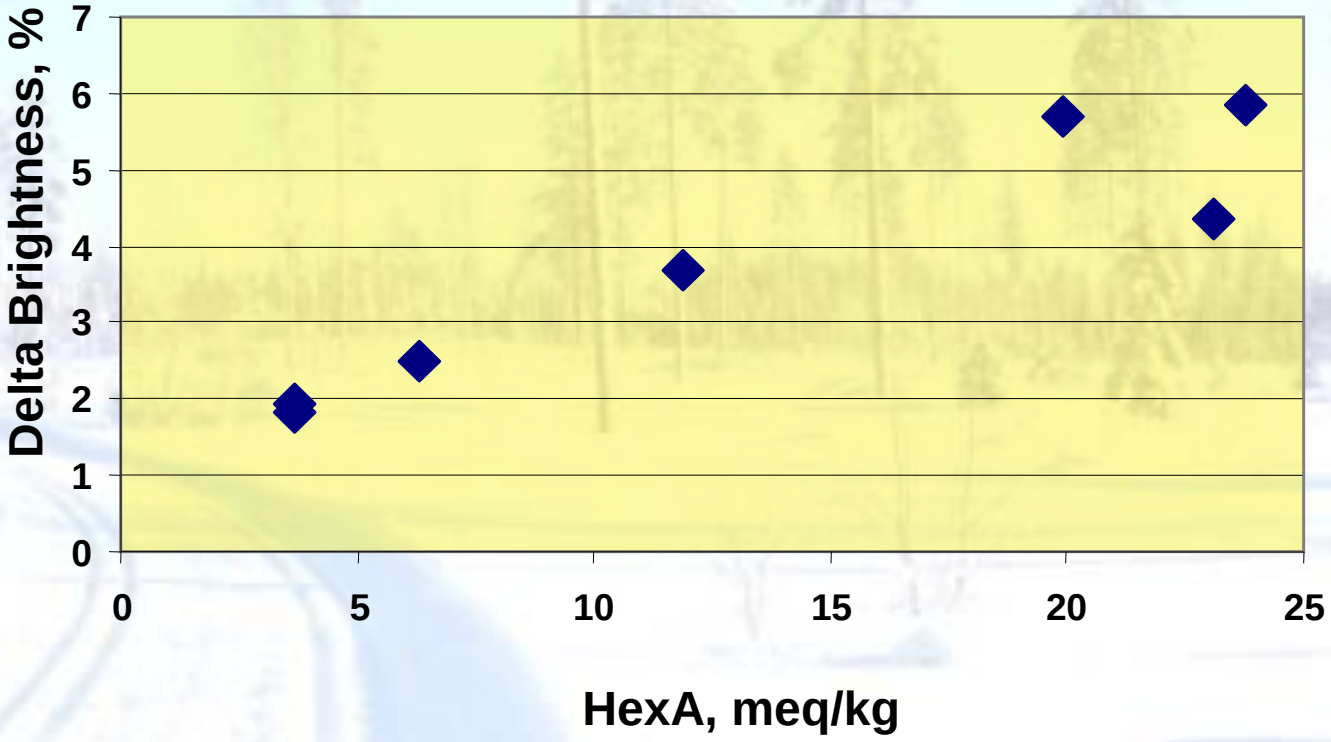


Fiber wall collapse

/11/ Rauvanto, I., Henricson, K.,

Advances in eucalyptus pulp bleaching technology

The effect of HexA in brightness reversion in laboratory-bleached eucalyptus pulps



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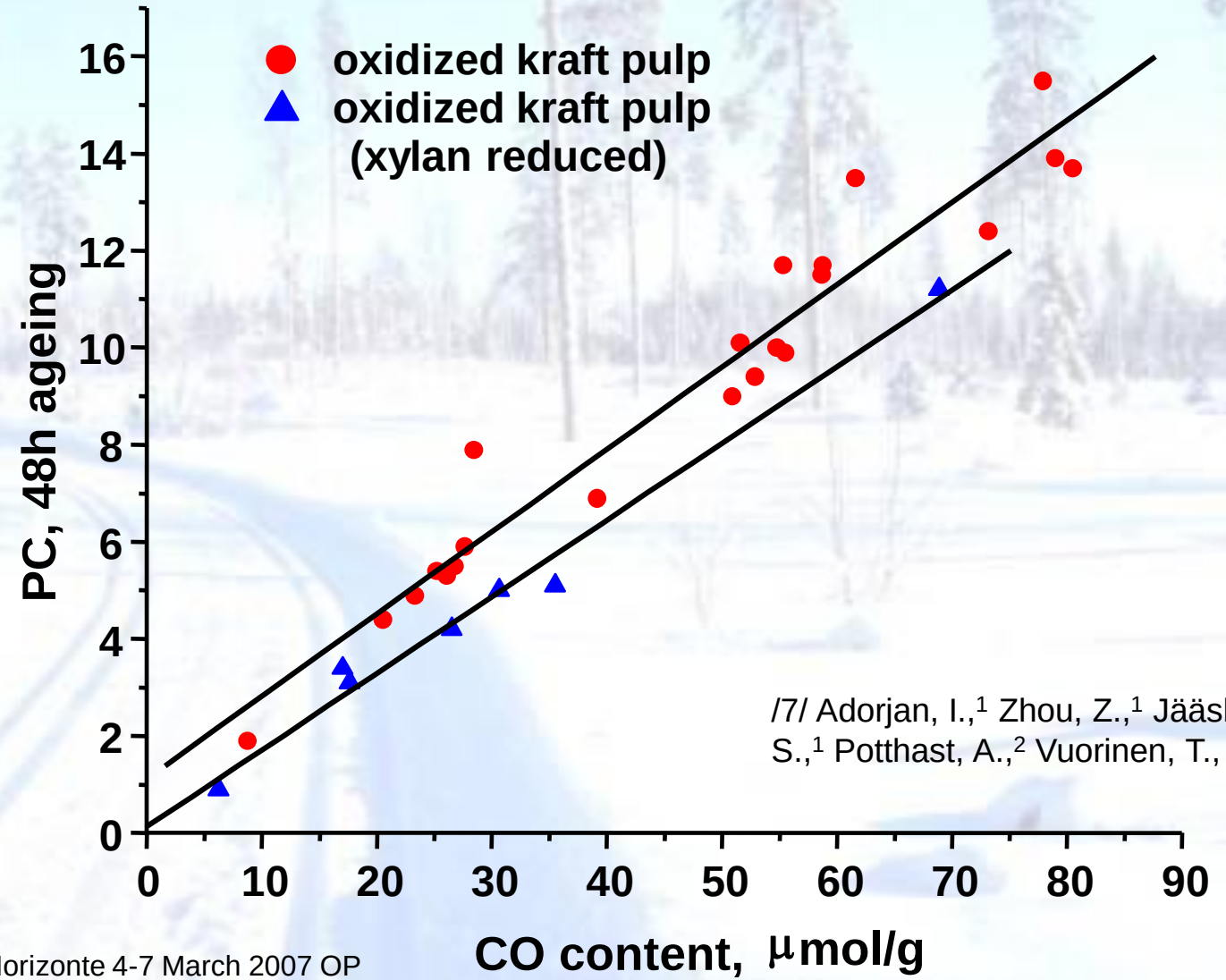
Correlation between PC and carbonyl content after 48 h of ageing at 80°C and 65% relative humidity



/7/ Adorjan, I.,[1] Zhou, Z.,[1] Jääskeläinen, A-S.,[1] Potthast, A.,[2] Vuorinen, T., [1]

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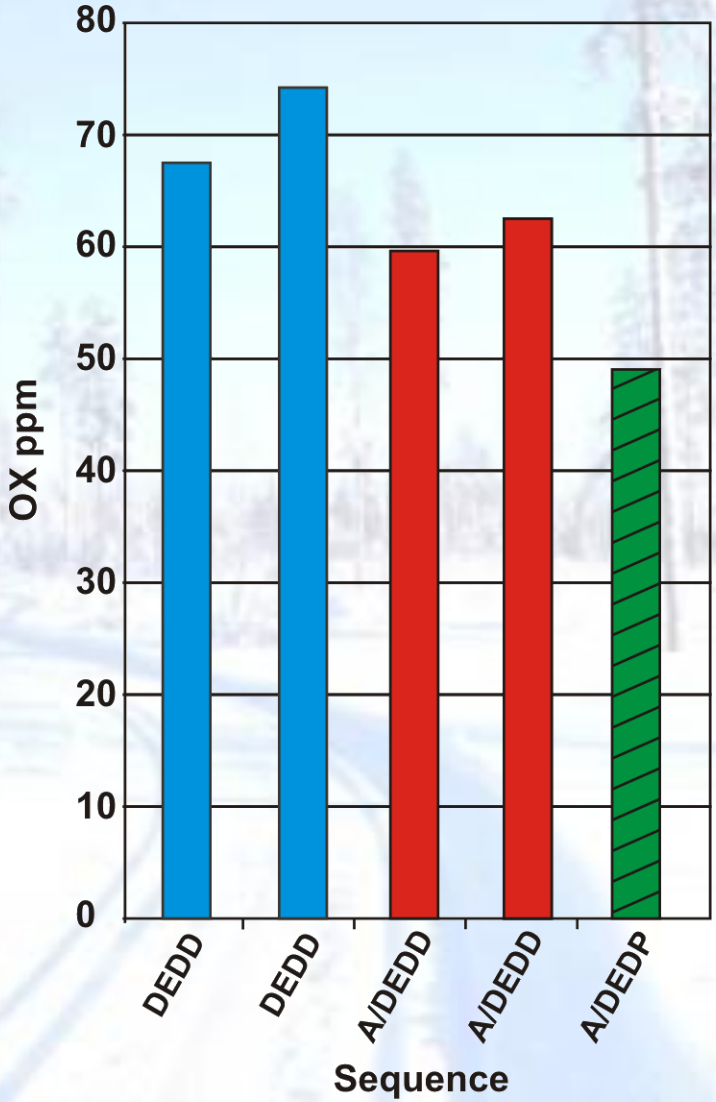

OX in pulp in different bleaching sequences

/8/ Martikka, M

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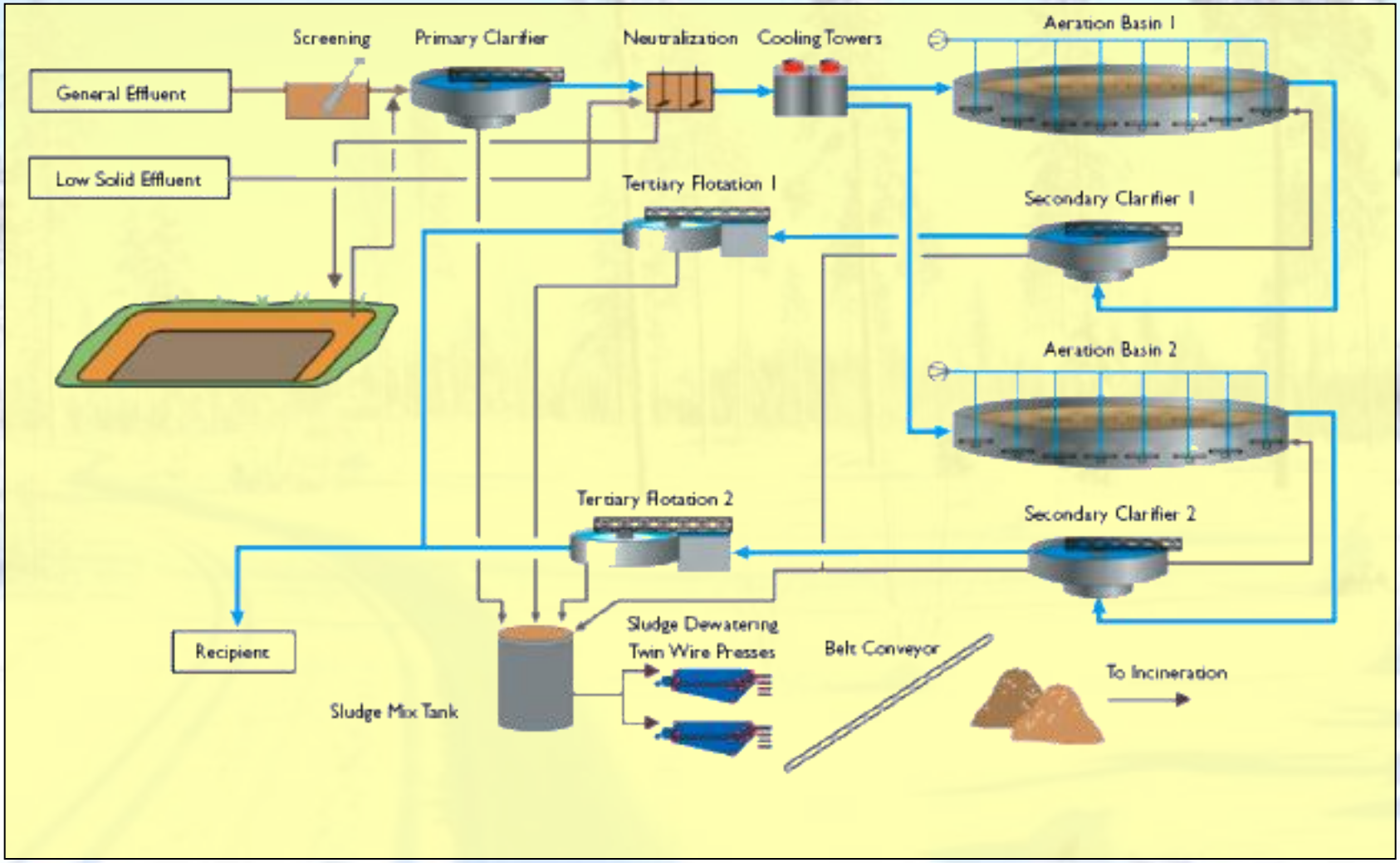
A modern effluent treatment system



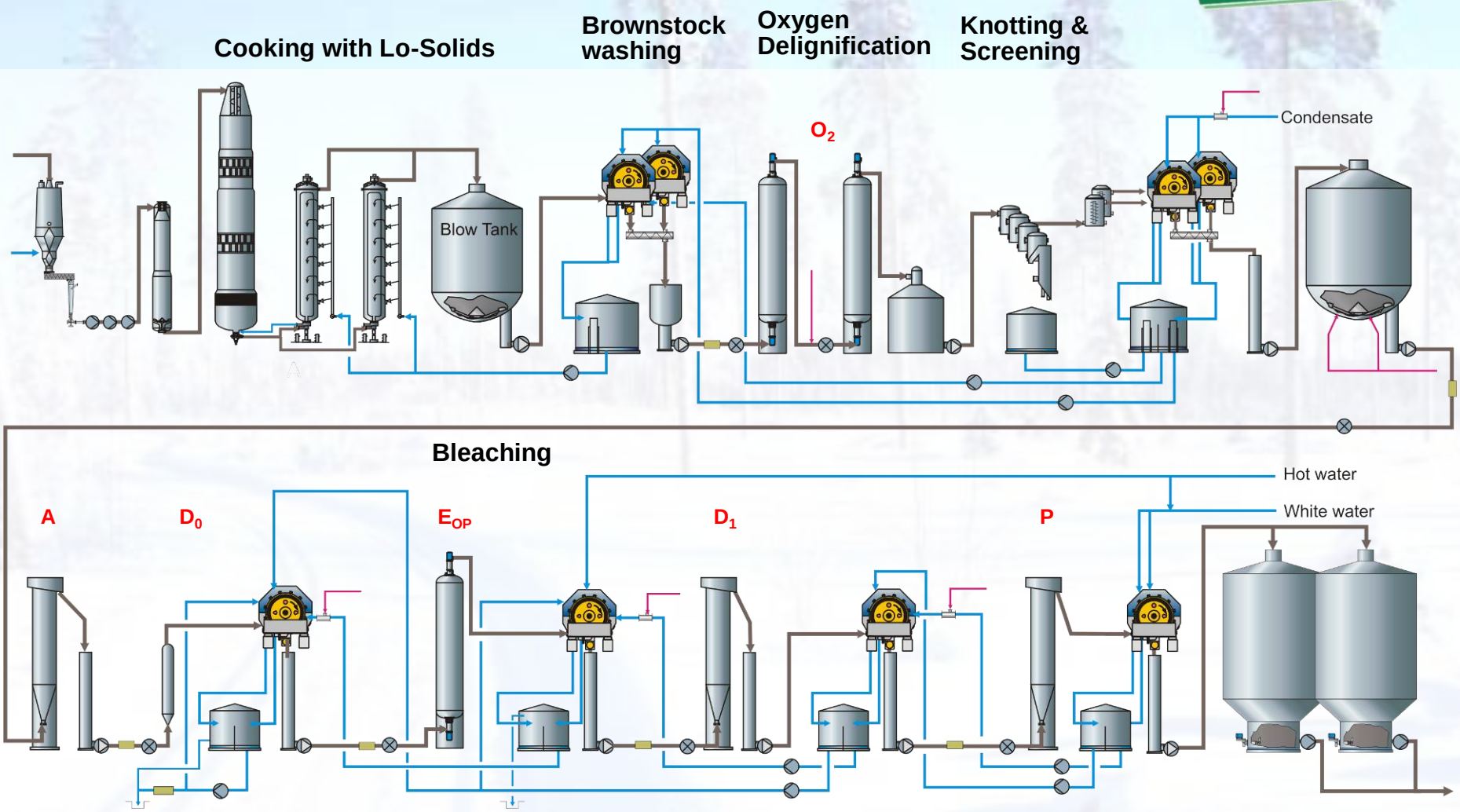
Reductions:				
	COD	70-75%	AOX	50-60%
	BOD5	95%	Color	60-70%

Recent mill results


VERACEL

Advances in eucalyptus pulp bleaching technology

Veracel Fiberline 3000 ADMT/D



Pulp brightness 92% ISO

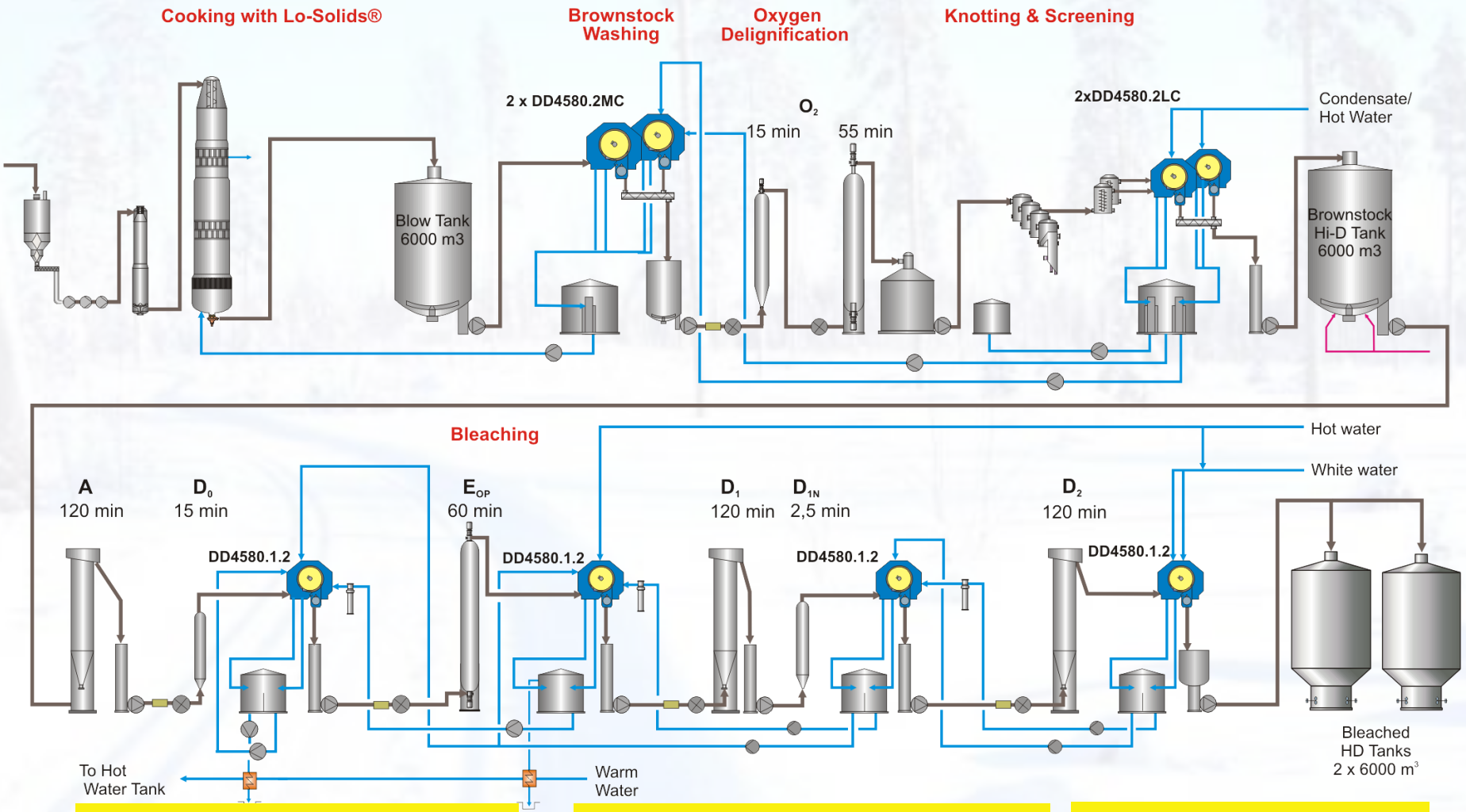
Active chlorine 23 kg/ADT

Peroxide 5 kg/ADT


cmpc
Celulosa
2405 ADMT/D
Eucalyptus
92 ISO
27.5 kg act Cl/adt
3.7 kg H_2O_2/adt
Viscosity >1000SCAN

Advances in eucalyptus pulp bleaching technology

Eucalyptus Fiberline, 800.000 ADMT/a



Pulp brightness 92% ISO

Active chlorine 27,5 kg/ADT

Peroxide 3,7 kg/ADT

Advances in eucalyptus pulp bleaching technology

Development of Chemical Pulp Mill during 10-15 years

Driving forces: Efficiency -Quality- Environmental safety/Energy- Raw materials

Single line capacity doubled, MC-technology in wider use

Improved control of chip raw material and pulp quality

1990

Improved cooking:
-LoSolids, EAPC,
-ITC, Supebatch

Modern mill:
1000-1300 tpd
C/DEDED
Effluent 50-70 m3/t
AOX 1,5-3,0 kg/t

1995

Oxygen based chemicals: O2,O3,P,PAA

Improved washing efficiency:
DD-washers,
New presses
Removal of hex.u

Modern mill:
1600-2000 tpd
DEoDD or ZPZP
Effluent 10-20 m3/t
AOX < 0.5 kg/t
Surplus electricity+

2000

High dry solids,
Control of non-process elements,
Improved combustion systems

Modern mill:
2500-3000 tpd
A/DEopD(PO) or
(ZD)EopDPO
Effluent 10-15 m3/t
AOX 0.1-0.2 kg/t
Surplus electricity ++
Advanced controls

+2007

Modern mill:
3000-4000 tpd
A/DEopD(PO) or
(ZD)EopDPO or
Shorter sequence
Bleach filtrate treatment
Chemical balance control
Effluent <10-15 m3/t or less
AOX < 0.1 kg/t
Surplus electricity +++
Advanced controls
Simulation

Conclusion

Double-stage oxygen delignification creates the basis for low chemical bleaching

Low carryover to bleaching and a low carryover amount in each bleach stage is very important

ECF bleaching is a dominant bleach concept. Several variations of bleach sequences are possible

HexA removal is an established stage in the bleaching sequence. A four-stage sequence A/D-Eop-D-P is recommended for 92+ISO brightness

Brightness reversion is improved through the removal of HexA. Reduction of act. chlorine usage and a final P-stage improve brightness stability

Advances in eucalyptus pulp bleaching technology

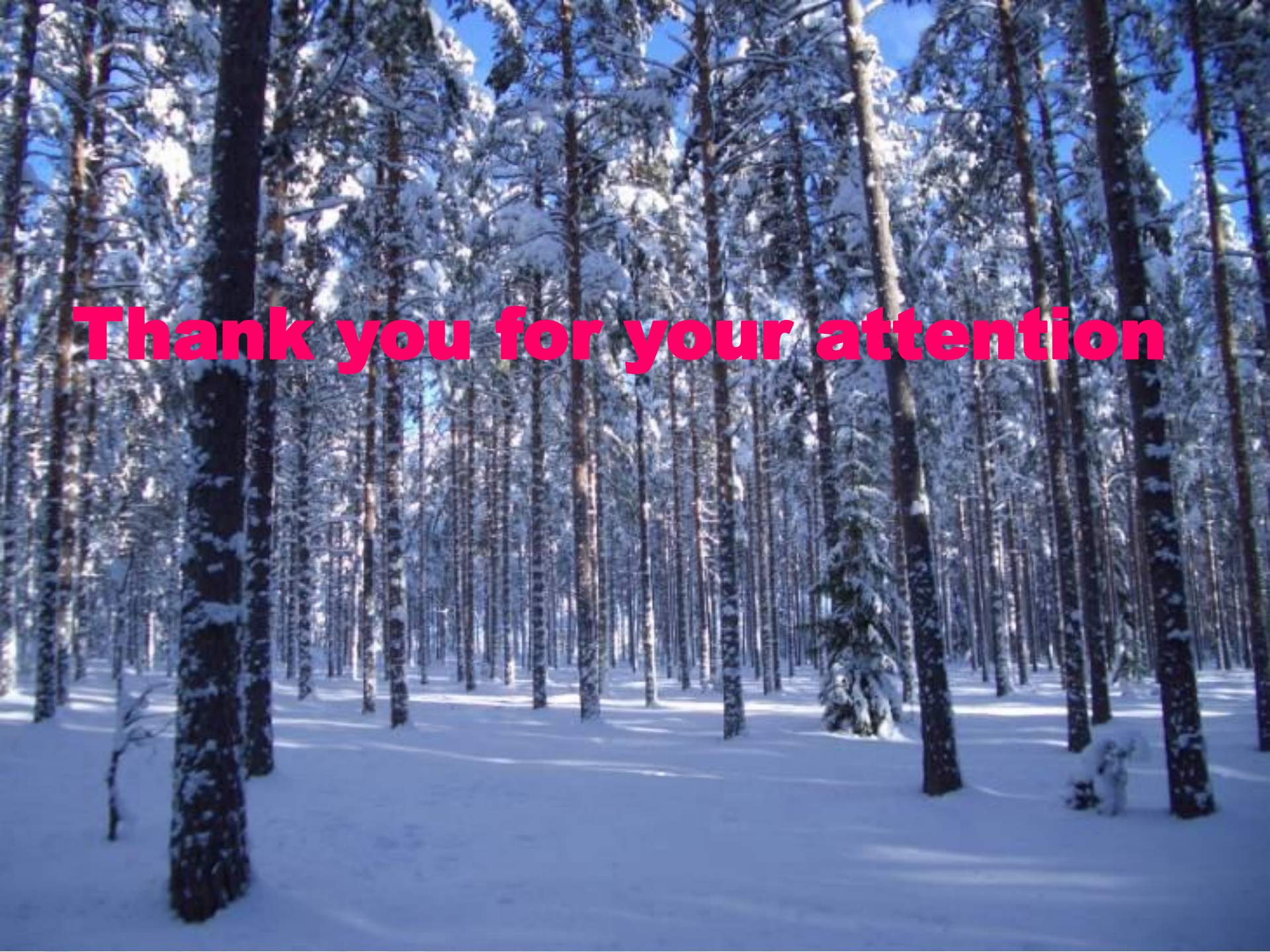
Conclusion …

OX in pulp is reduced by lower act. chlorine usage and a final P-stage

Electricity and steam consumption in a modern bleach plant is 70-80 kWh/adt and 359-450 kg/adt respectively

Effluent flow from ECF bleaching is 10-15 m^3/adt. AOX, COD and BOD5 discharges are very low after a modern effluent treatment system

Chemical consumption of 23 kg act. Cl/adt and 5 kg/adt peroxide in four-stage bleaching to 92.5 ISO in mill conditions has been achieved


Thank you for your attention