



Juha Tamper

WATER CIRCULATIONS FOR EFFECTIVE BLEACHING OF HIGH-BRIGHTNESS MECHANICAL PULPS

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ABSTRACT

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The amount of water available is usually restricted, which leads to a situation where a complete understanding of the process, including water circulations and the influence of water components, is essential. The main aim of this thesis was to clarify the possibilities for the efficient use of residual peroxide by means of water circulation rearrangements. Rearranging water circulations and the reduction of water usage may cause new problems, such as metal induced peroxide decomposition that needs to be addressed. This thesis introduces theoretical methods of water circulations to combine two variables; *effective utilization of residual peroxide* and *avoiding manganese in the alkaline peroxide bleaching stage*. Results are mainly based on laboratory and mill site experiments concerning the utilization of residual peroxide. A simulation model (BALAS) was used to evaluate the manganese contents and residual peroxide doses.

It was shown that with optimum recirculation of residual peroxide the brightness can be improved or chemical costs can be decreased. From the scientific perspective, it was also very important to discover that recycled peroxide was more effective pre-bleaching agent compared to fresh peroxide. This can be due to the organic acids i.e. per acetic acid in wash press filtrate that have been formed in alkaline bleaching stage. Even short retention time was adequate and the activation of residual peroxide using sodium hydroxide was not necessary.

There are several possibilities for using residual peroxide in practice regarding bleaching. A typical modern mechanical pulping process line consist of defibering, screening, a disc filter, a bleach press, high consistency (HC) peroxide bleaching and a wash press. Furthermore there usually is not a particular medium consistency (MC) pre-bleaching stage that includes additional thickening equipment. The most advisable way to utilize residual peroxide in this kind of process is to recycle the wash press filtrate to the dilution of disc filter pulp (low MC pre-bleaching stage). An arrangement such as this would be beneficial in terms of the reduced convection of manganese to the alkaline bleaching stage. Manganese originates from wood material and will be removed to the water phase already in the early stages of the process. Recycling residual peroxide prior to the disc filter is not recommended because of low consistencies. Regarding water circulations, the novel point of view is that, it would be beneficial to divide water circulations into two sections and the critical location for the division is the disc filter. Both of these two sections have their own priority. *Section one before the disc filter: manganese removal. Section two after the disc filter: brightening of pulp.*

This division can be carried out if the disc filter pulp is diluted only by wash press filtrate before the MC storage tower. The situation is even better if there is an additional press after the disc filter, which will improve the consistency of the pulp. This has a significant effect on the peroxide concentration in the MC pre-bleaching stage. In terms of manganese content, it is essential to avoid the use of disc filter filtrate in the bleach press and wash press showers. An additional cut-off press would also be beneficial for manganese removal.

As a combination of higher initial brightness and lower manganese content, the typical brightness increase varies between approximately 0.5 and 1% ISO units after the alkaline peroxide bleaching stage. This improvement does not seem to be remarkable, but as it is generally known, the final brightness unit is the most expensive and difficult to achieve. The estimation of cost savings is not unambiguous. For example in GW/TMP mill case 0.6% ISO units higher final brightness gave 10% savings in the costs of bleaching chemicals. With an hypothetical 200 000 ton annual production, this means that the mill could save in the costs of bleaching chemicals more than 400 000 euros per year.

In general, it can be said that there were no differences between the behavior of different types of processes (GW, PGW, TMP and BCTMP). The enhancement of recycling gave a similar response in all cases. However, we have to remember that the utilization of residual peroxide in older mills depends a great deal on the process equipment, the amount of water available and existing pipeline connections. In summary, it can be said that processes are individual and the same solutions cannot be applied to all cases.

Keywords: mechanical pulp, bleaching, brightness, residual peroxide, peracetic acid, manganese, water circulations

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PREFACE

This study was carried out at Lappeenranta University of Technology in the Laboratory of Paper Technology with the support of the International PhD Programme in Pulp and Paper Science and Technology (PaPSaT).

I wish to thank my supervisors, Professor emeritus Hannu Manner and Professor Jari Käyhkö for their guidance, advice and encouragement during my research. I am also thankful to my colleagues, research assistants and to all of the students who have been working with me during these years. Furthermore, I wish to thank all of my industrial partners in cooperation (Kemira, Metso Paper, M-real, Myllykoski Paper, Stora Enso and UPM Kymmene) and TEKES (Finnish Funding Agency for Technology and Innovation) who made this thesis possible by funding and guiding my research work.

I wish to thank my wife Anne and my children Markus, Miika, Ida-Emilia and Eemil for giving me a wider perspective into life than just work and a career. I am also thankful to my father, who passed away few years ago, and my mother for their endless support during my studies.

All in all, the status quo in the paper industry is such that any savings in making pulp and paper are welcome. There are several great challenges that the paper industry is facing today. I hope that this thesis will shed at least some light on the future of the industry.

Taipalsaari, November 2009

Juha Tamper

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ABBREVIATIONS

b.d.	bone dry
BCTMP	bleached chemithermomechanical pulp
DM	drying machine
DTPA	diethylene triamine pentaacetic acid
EDTA	ethylene diamine tetraacetic acid
GW	groundwood
HC	high consistency
MC	medium consistency
PAA	peracetic acid
PGW	pressurized groundwood
PM	paper machine
TMP	thermomechanical pulp
TOC	total organic carbon

1 INTRODUCTION

1.1 Background

Development in the paper industry has focused on brighter paper grades, and this trend seems to continue. This has an effect on the mechanical pulp bleaching process, especially in magazine papers which contain a great amount of mechanical pulp. To achieve high brightness mechanical pulp (80% ISO units or higher), high consistency peroxide (HC) bleaching is always needed. A modern high consistency peroxide bleaching stage is typically placed between effective washing stages. In addition to the new process equipment, it is essential to understand the process chemistry and the functions of harmful substances to maximize the bleaching performance. In other words, it is not obvious that the production of cost effective high brightness mechanical pulp could be achieved only by using new process equipments.

To reach high pulp brightness, the hydrogen peroxide dose used in bleaching has to be relatively high, from 3 to 4 per cent on b. d. pulp. The typical amount of residual peroxide added varies from 20 to 50% of the total charge /1-4/. From the economical point of view, it seems most interesting to use residual peroxide as a pre-bleaching agent. Residual peroxide has been exploited in 2-stage processes, but at 1-stage process only to some extent, and the real potential of residual peroxide to affect the pulp brightness prior to the alkaline peroxide bleaching stage seems not to have been recognized. Each process is unique, and especially in older mills the reconstruction of water circulations may seem to be an insuperable obstacle. Nevertheless, the optimal utilization of residual peroxide can significantly reduce the bleaching chemical expenses also at 1-stage processes /2/. However, rearranging water circulations and reducing water usage may cause new problems that need to be addressed /5,6/.

A very critical issue regarding the bleaching performance is the metal content of pulp entering into the alkaline peroxide bleaching stage. A typical problem in the peroxide bleaching of mechanical pulps is the decomposition of peroxide caused by transition metals, such as manganese, iron and copper /7-17/. Usually the effect of copper on bleaching performance is negligible because the copper content of pulp is minor in Scandinavian wood species. The iron content is typically higher compared to the copper. Iron and copper tend to bound on the

fibers tightly /18/, which makes the complexation of these metals very difficult /8/. After chelation iron content usually remains the level of 10 to 30 mg/kg. The effect of iron on brightness in alkaline peroxide bleaching is not, however, as critical as that of manganese, which is known to be the most harmful metal /8,10,13,15/. This is due to the different mechanism to decompose hydrogen peroxide /18,19/. Manganese acts as a catalyst in ionic decomposition reactions, while iron decompose peroxide via the well known Fenton's reaction.

The typical manganese content in wood is much higher compared to the copper and iron contents /8,20,21,22/. Fortunately, manganese is the easiest one of these metals to complexate and remove to the water phase /8,22/. It is very important to remove manganese-chelate complexes from pulp prior to the alkaline bleaching stage. This can be done in an effective washing stage /23/. In addition to the chelating, sodium silicate is a frequently used chemical in the alkaline bleaching stage to stabilize peroxide /24/. The relatively easy removal of manganese will lead to the possibility of avoiding the transfer of manganese into the bleaching by the process engineering of water circulations.

It can be summarized that carefully considered water usage and water circulations assist operating the process in a healthy way. Usually the amount of water available is restricted, which leads to a situation where a complete understanding of the process, including water circulations and the influence of dissolved water components, is essential.

1.2 The aim of the study

The aim of this thesis is to examine the possibilities of

- 1) an efficient use of the residual peroxide and
- 2) the prevention of the convection of manganese into the alkaline peroxide bleaching stage by means of water circulation rearrangements.

Exploitation of this knowledge can provide a chance to create a bleaching process that is more economical and effective. As a combination of these two variables, the effective utilization of residual peroxide and avoiding manganese in the alkaline peroxide bleaching stage, some theoretical methods of water circulations are introduced in the thesis.

1.3 Outline

This thesis is divided into a theoretical part, an experimental part and a simulation part. The theory part presents related results found from the literature concerning the recycling of residual peroxide, and an overview of the bleaching chemistry in mild pre-bleaching conditions.

The experimental part consists of two sections: 1. laboratory experiments and 2. mill experiments. The laboratory experiments were mainly carried out in the Laboratory of Paper Technology at Lappeenranta University of Technology. In practice, all of the laboratory experiments were conducted and supervised by the author. Most of the experiments were done by author himself and the rest by research assistants or M.Sc. students under the supervision of the author. The experiments simulating the mill conditions were carried out on a laboratory scale using pulp and filtrate samples taken straight from the running processes. The idea of the mill simulating experiments was to describe better the real conditions compared to the traditional laboratory experiments. The mill experiments were carried out by the author together with the help of his research assistants.

In the third part of this thesis, the simulation model (BALAS) was used for the evaluation of the manganese contents and residual peroxide doses. Basic process, including the water circulations for the simulation model and all modifications for the model, were designed by the author. The simulation work itself was done by a researcher specialized in simulation.

THEORY

2 BASIC PRINCIPLES OF WATER CIRCULATIONS IN DIFFERENT MECHANICAL PULPING PROCESSES

Different mechanical pulping processes, including high consistency peroxide bleaching, are typically quite similar to each other. Differences can mainly be found in the fiberising methods at the beginning of the process. The raw material used in Scandinavia has typically been Norway spruce. At present, aspen is used more frequently especially in BCTMP lines. The lack of spruce has led to a situation where the use of pine has also been considered. In this thesis, the most important focus area is typical water circulation solutions and principles. In the following simplified process concepts, the basic differences in water circulations between different process concepts are presented.

2.1 Stone groundwood pulp

Stone groundwood pulping (GW) is one of the oldest process concepts which still is widely in use [25]. The GW process is an atmospheric grinding process. Figure 2.1 shows a simplified flow sheet of a GW process.

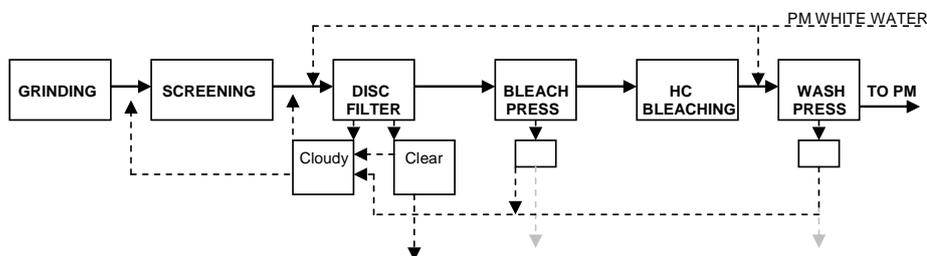


Figure 2.1 A typical GW process including bleaching and water circulations.

In respect of water usage, the essential aspects are how the water circulations are arranged and from which position the waste water can be taken out. Paper mill (PM) white water is typically introduced to the groundwood process for the washing of the bleached pulp. Some water may also be introduced to the process near the disc filter, but that is not always necessary. Depending on the type of the presses around the high-consistency (HC) stage, it is also possible that PM white water is used in showers in the case of twin wire presses.

In the GW process, waste water is typically taken out from the clear filtrate tank of the disc filter. The reason for this is that the disc filter is the first thickening unit in the process line and the metal contents of filtrates are high especially in the first part of the process. In addition, the fiber content of the disc filter clear filtrate is minor. This will minimize the fiber loss. If a full scale backward flow is not desired, some part of the waste water can be taken out from the wash press or bleach press filtrate tanks.

2.2 Pressurized ground wood pulp

The differences between the pressurized groundwood pulp (PGW) process and the traditional ground wood (GW) process pulp are minor. In the PGW process, grinding takes place under pressurized conditions and often elevated temperatures /25/. Considering water circulations, the hot loop is the main difference between these two processes; see Figure 2.2. The purpose of the hot loop is to circulate the hot filtrate from the pressure thickener to the pressurized grinding in the beginning of the process.

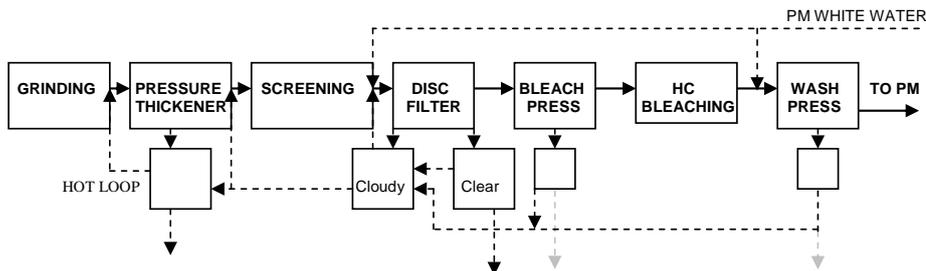


Figure 2.2 A typical PGW process including bleaching and water circulations.

Because of the hot loop, there is one possibility more to take waste water out compared to the conventional GW process. Taking waste water out from the hot loop is beneficial regarding the metal removal.

2.3 Thermomechanical pulp

Thermomechanical pulping (TMP) is the leading refiner-based mechanical pulping process. Compared to groundwood pulp properties, its fibers are longer and the formation of fines during defibering is minor /26/. Basically water circulations of the TMP process resemble GW process a lot. The TMP process does not include a thickening stage before the disc filter; see Figure 2.3.

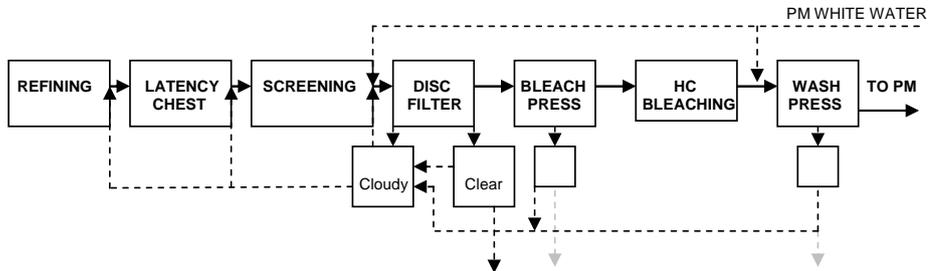


Figure 2.3 A typical TMP process including bleaching and water circulations.

2.4 Bleached chemithermomechanical pulp

The bleached chemithermomechanical pulping (BCTMP) process combines chemical pre-treatment and mechanical defibering; see Figure 2.4.

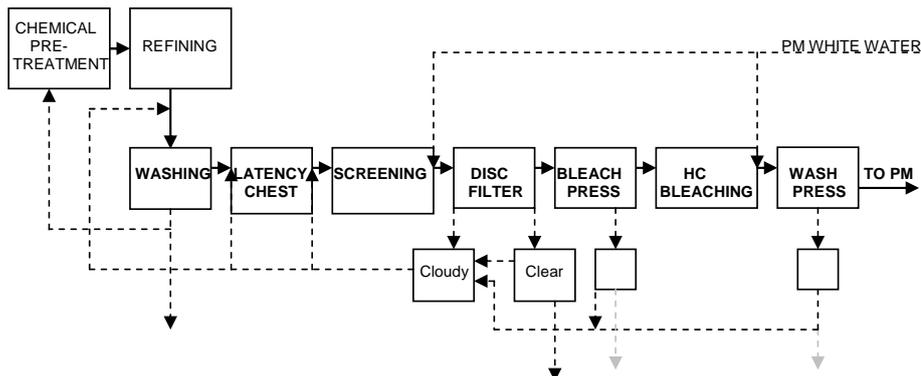


Figure 2.4 A typical BCTMP process including bleaching and water circulations.

Chemical pre-treatment does not have a remarkable effect on the water circulations compared to the conventional TMP process. An additional washing stage is included because of pre-treatment chemical circulation. This allows taking out waste water also at the beginning of the process. In practice, the chemical pre-treatment means sulphonation. It is carried out with sodium sulphite (Na_2SO_3) or with sodium bisulphite (NaHSO_3) together with sodium hydroxide (NaOH) /27/.

3 RECYCLING OF RESIDUAL PEROXIDE

3.1 Fundamentals of recycling

Currently, high consistency (HC) peroxide bleaching is performed in a consistency range of 25 to 35%. The peroxide bleached pulp is washed by diluting the pulp either with paper mill white water or with a combination of wash press filtrate and PM white water. Pulp is pressed back into a high consistency after the dilution, and hence residual peroxide is removed to the filtrate in the wash press. The washing of pulp is very important because of anionic trash that has been formed in the alkaline bleaching stage. The amount of anionic trash is related to the chemical doses used in bleaching [28]. Figure 3.1 shows a typical HC bleaching and washing stage with the possibility to recycle residual peroxide to pre-bleaching prior to the alkaline peroxide bleaching stage.

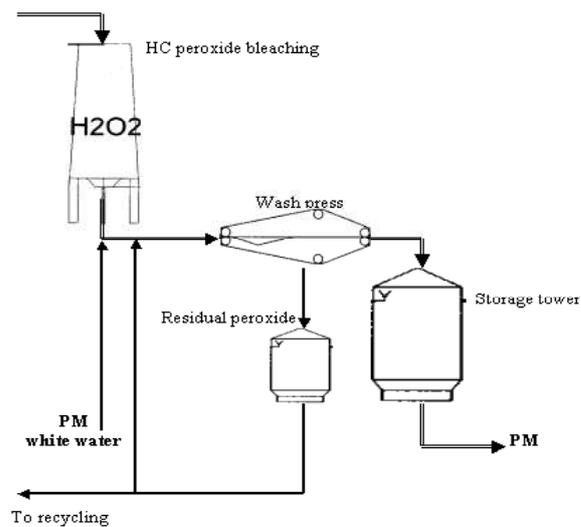


Figure 3.1 A typical HC bleaching and washing stage with the possibility to recycle residual peroxide.

The amount of wash press filtrate that can be recycled depends on the amount of PM white water used in the dilution of the bleached pulp. The situation is optimal if all of the wash press filtrate available can be used in pulp dilution in the pre-bleaching stage. In such cases, one can maximize the use of residual peroxide and achieve the highest peroxide dosage in pre-bleaching.

The common range for peroxide concentration in the wash press filtrate is between 0.5 and 2.0 g/l. It depends on the peroxide dose, peroxide consumption and the amount of PM white water used in dilution after the HC bleaching tower. The pulp consistency in the wash press feed is adjusted by the wash press filtrate and PM white water. The ratio of the wash press filtrate and the PM white water affects the peroxide concentration in the wash press feed and also in the wash press filtrate tank. Furthermore, this affects the amount and peroxide concentration of the filtrate available for recycling in the process prior to alkaline peroxide bleaching.

The most common and reasonable way to recycle residual peroxide is to recycle the wash press filtrate to dilute the disc filter pulp /2,3/. In such cases, we are quite close to the MC-HC bleaching system. The consistency of disc filter pulp is, however, so low that it is almost impossible to achieve even a relatively high peroxide concentration in the pre-bleaching stage. The situation could be even more favourable if an additional press for the pre-bleaching stage would be available.

There are, of course, many possibilities to recycle residual peroxide prior to the disc filter. This is however not advisable because a high peroxide concentration is difficult to achieve due to the low pulp consistencies. Furthermore, the residual alkali might disturb complexation of metals if the wash press filtrate would be recycled prior to the disc filter /29/. In neutral conditions, the influence of transition metals is slightly negative in terms of brightness, but not as hazardous as in the alkaline peroxide bleaching stage. In acidic conditions, manganese is not able to decompose the peroxide /12/. The pH range 8-12 is favourable for catalytic decomposition caused by manganese. It has also been observed that hydrogen peroxide may reduce the oxidation state of manganese in acidic conditions /30/. This should improve bleaching performance at the alkaline peroxide bleaching stage.

Typical conditions of pre-bleaching are listed below:

- pH 6-8
- Consistency 5-15%
- Temperature 60-90 °C
- Retention time 0.5-2 hours
- Peroxide dosage 0.2-1.0% on dry pulp

Because of a relatively low peroxide dose, the activation of residual peroxide by adding alkali is questionable. Alkali might increase brightness slightly, but also the risk of alkali darkening would increase. Furthermore, the addition of chemicals would raise the costs of bleaching chemicals, which is not desirable. In addition to the increased costs of chemicals, the benefits of a further alkali addition to the final brightness of pulp are debatable. The possibilities to utilize residual peroxide in older mills depend a great deal on the process equipment, the amount of water available and the existing pipeline connections. In brief, it can be said that each process is unique, and thus the same solutions cannot be applied to all cases.

3.2 Utilization of residual peroxide – reference results

A number of studies have been conducted regarding the reuse of recyclable peroxide /31-35/. For the most part it seems that two-stage bleaching – utilizing residual peroxide – is an economical choice especially for high-brightness grade mechanical pulps. Nevertheless, also less encouraging results have been obtained.

It has been reported that the optimization and control of two-stage processes is not an easy task. Washing between the bleaching stages is advantageous, and the brightness obtained in the first stage for a known amount of bleaching chemicals can be used to predict the required chemical charges for a given brightness in stage two /31/.

Froass has concluded after TMP and CTMP studies that recycling of residual peroxide is economically reasonable. He also found that dissolved organic compounds have no significant effect on the peroxide decomposition in filtrates under neutral conditions. Also recycled silicate was competitive compared to the fresh silicate added /32/.

Berger *et al.* have stated that with the peroxide dose of 3% or lower, the bleaching efficiency is in one stage bleaching nearly equal to two-stage bleaching of TMP. Economical benefits of using two bleaching stages were achieved only with higher peroxide doses /33/.

Figure 3.2 illustrates the results of Haveri's Master's thesis on the effects of retention time and temperature on the pulp brightness at the pre-bleaching stage when the wash press filtrate is recycled to the dilution of the disc filter pulp /36/.

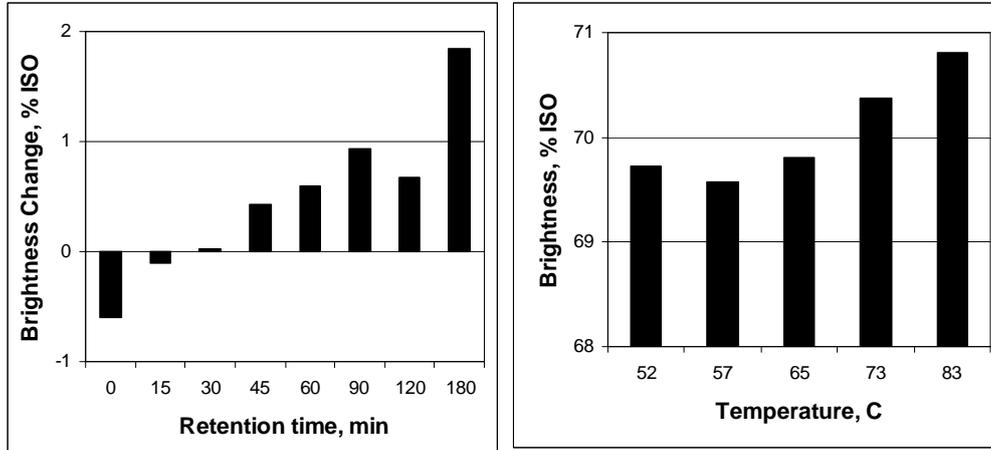


Figure 3.2 Effect of retention time and temperature on brightness of disc filter GW pulp in a pre-bleaching stage. Consistency 7%, peroxide dosage 0.62%, pH 6.55, temperature 60°C /36/.

If the retention time was short, the brightness of the pulp decreased slightly. After a drop at the beginning, the brightness increased again. After 2-3 hours, the brightness gain was about 1-2% ISO units compared to the initial brightness of the pulp. Also a rise in temperature increased the brightness. The final result of this study after a mill trial was that despite the increased initial brightness after the pre-bleaching stage, no improvement was found in the final brightness /36/. Observation of the the benefit was difficult due to the great divergence in the final brightness during the trial.

Lippert /2/ has studied similar recycling of wash press filtrate to the dilution of PGW disc filter pulp; see Figure 3.3. The consistency of disc filter pulp before the dilution was approximately 12%, and after the dilution about 8%. So, it can be calculated that in this case the need for wash press filtrate in dilution is about 4 m³ per b. d. ton of pulp. The retention time in pre-bleaching was only 10-15 minutes, which means that chemical reactions take place very rapidly at the pre-bleaching stage. The results concerning final brightness were more encouraging; see Figure 3.4.

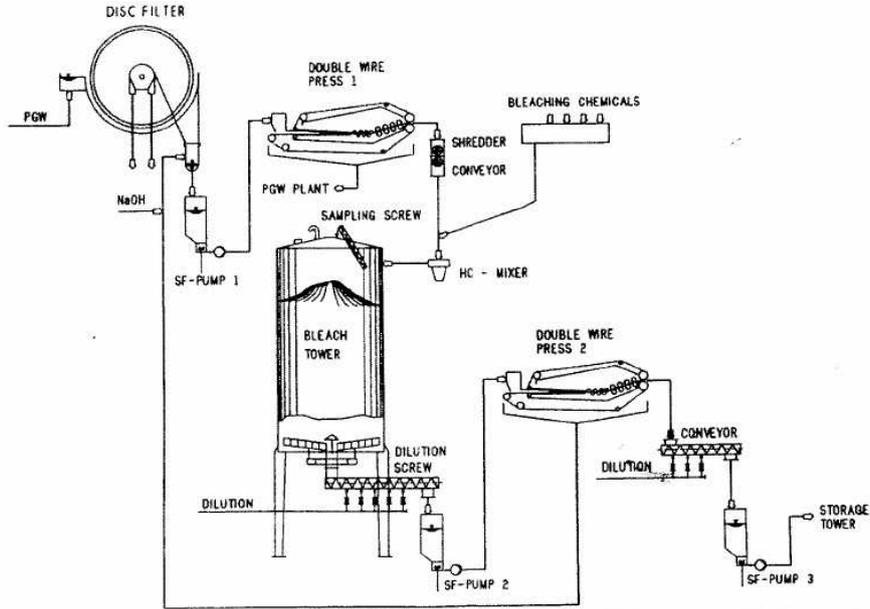


Figure 3.3 A process with recycling of residual peroxide to the dilution of disc filter pulp. /2/

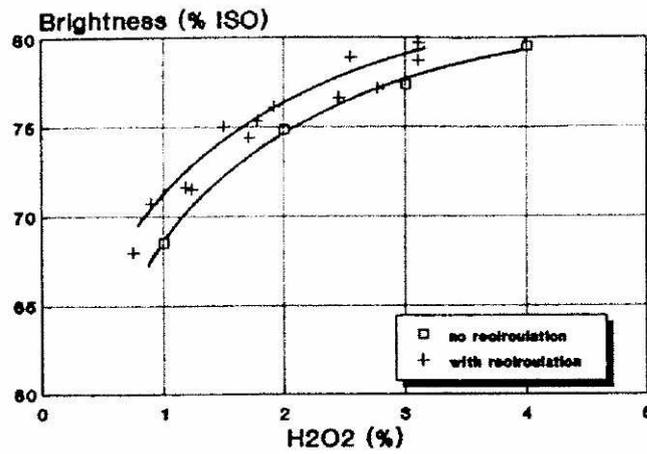


Figure 3.4 Bleachability of PGW with (+) and without (□) recirculation of residual peroxide /2/.

A 2% ISO units higher final brightness was reached in the mill scale trial, as can be seen in Figure 3.4. It was estimated that this could save 10-15% in costs of bleaching chemicals. Also manganese removal was excellent because of several washing stages /2/.

A similar pre-bleaching effect was identified also by Lachenal *et al.* /3/ The two-stage SGW process does not require as high charge of hydrogen peroxide for the same brightness level as a conventional single-stage bleaching. In another study, Lachenal *et al.* have stated that in two stage processes, high alkalinity especially in the second stage is beneficial /34/. It was observed that savings of up to 20% in peroxide could be achieved by recycling of residual peroxide. A similar reduction was observed also by Lougheed and Presley /35/. In their study, the total alkali charge remained the same despite the two stage bleaching.

One research group found out that by adding peroxide with silicate to the shower waters in grinding, the brightness of the pulp increased without sodium hydroxide even more than 6% ISO /37/. The pH of the shower water was 8.1 in the experiments. The results indicate that peroxide could also increase the brightness of the pulp even if the pH was not at the same level as in typical alkaline peroxide bleaching. Part of the brightness gain was lost in the alkaline peroxide bleaching stage. The difference in the final brightness between pre-bleached and non pre-bleached decreased if more peroxide was used at the alkaline peroxide bleaching stage. Lönnberg *et al.* have also estimated that the recycling of peroxide concentrates peroxide into the hot loop so that the peroxide dosage could be about 1-3% on dry pulp. In such cases, the recycling of residual peroxide should have a remarkable effect on pulp brightness. /37/

Residual peroxide can be utilized cost-efficiently in mills where two different pulp grades with different brightness targets are produced. In this kind of process, consisting two separate bleaching lines, part of the pulp passes by the primary alkaline peroxide bleaching and is bleached by residual peroxide at another line to meet a lower brightness target. This kind of solution is illustrated in Figure 3.5 /4/.

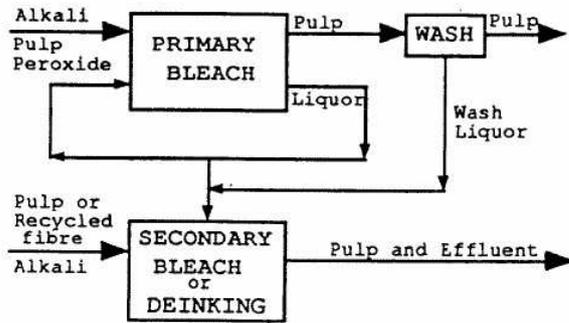


Figure 3.5 Utilization of residual peroxide in two parallel bleaching lines /4/.

The peroxide dosage in the secondary line is approximately 2% on b. d. pulp if the primary line is bleached with a 3% peroxide dosage. The amount of residual peroxide is 25% of the initial charge and the unbleached pulp is divided at a ratio of 1:3 between the secondary and the primary bleaching. The consistency of the pulp in the secondary bleaching depends on how much PM white water is led to the dilution after the HC tower (primary bleaching), but the range should be at a medium consistency level. My personal experience is that these kinds of solutions have not been in use. The reason for this might be that it would mix the water circulations of two paper machines to some extent.

4 BRIGHTENING OF PULP IN MILD PRE-BLEACHING CONDITIONS

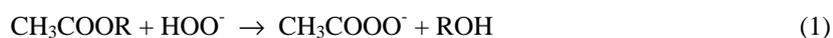
The reason why brightness increases in neutral pH conditions (typical conditions listed on page 11) has remained rather unclear. A small increase in pH would activate residual peroxide and add the amount of perhydroxyl (HOO^-) ions at the pre-bleaching stage, but at the same time, the risk of alkali darkening increases. Also the costs of bleaching chemicals would increase. Besides, as stated before, an increase in pH in pre-bleaching might cause some problems in the chelating and washing of metals /29/.

While recycling wash press filtrate, also a large amount of fines are recycled, which might cause a part of the brightness increase. It has also been shown that peracetic acid is formed during the alkaline peroxide bleaching. Organic peracids, especially peracetic acid, can cause chemical reactions which bleaches the pulp also at lower pH /38/. One possibility could also be reactions of radicals but the problem of those reactions is low selectivity. Reactions of radicals may either bleach /39/ or darken the pulp. In conclusion, it cannot be said for sure what the reaction mechanism is in neutral pre-bleaching conditions. The truth may be a combination of a conventional understanding of peroxide bleaching and special behavior of less-known components.

4.1 Organic acids

4.1.1 Formation of acetic and peracetic acid

Hemicelluloses in mechanical pulp contain a large amount of acetylic groups. Acetylic group content in softwood species, which is available to be cleaved in the alkaline peroxide bleaching releasing acetic acid, is about 1.5%. Formation of peracetic acid (PAA) from acetylic groups is very rapid reaction in alkaline peroxide bleaching . See Equation (1) /40/.



where R is hemicellulose.

The perhydroxyl ion reacts at alkaline conditions much faster with the acetylic group than the hydroxide ion, which means that reaction (1) will also consume peroxide. The formation and consumption of PAA in the peroxide bleaching of TMP and GW is shown in Table 4.1.

Table 4.1 Formation and consumption of PAA in peroxide bleaching of TMP and GW /40/. Conditions: H₂O₂ 4%, NaOH 3.2%, silicate 3.12%, MgSO₄ 0.05%, consistency 10%, temperature 70 °C

Reaction time (min)	TMP			GW		
	Residual H ₂ O ₂ (mmol)	Peracetic acid formed (mmol)	Brightness (% ISO)	Residual H ₂ O ₂ (mmol)	Peracetic acid formed (mmol)	Brightness (% ISO)
0	5.88	0	61.7	5.88	0	61.3
2	4.46	0.96	73.5	4.67	0.83	70
5	4.23	0.63	75.2	4.4	0.42	72.7
10	3.92	0.31	77.4	3.95	0.13	75.8
120	2.1	0	78.6	2.94	0	77.8

From Table 4.1 it can be seen that the PAA content is at its highest just after two minutes. The peracetic acid anion formed reacts or decomposes rapidly and is consumed during the alkaline bleaching stage /40, 41/. This means that the concentration of peracetic acid in the wash press filtrate is negligible in practice, and cannot therefore be the reason for the rapid brightness gain in the pre-bleaching stage. However, especially when the pH of the wash press filtrate is above neutral, it is also possible that a small peracetic acid content is formed in pre-bleaching conditions. That reaction would be slower compared to the alkaline peroxide bleaching stage because of the slow cleavage of acetylic groups and the low perhydroxyl ion content. A small increase in pH would also increase the amount of dissolved acetylic groups, but at the same time, the risk of alkali darkening increases. It has been recognized that a pH between 7 and 8 would be optimal in the pre-bleaching of mechanical pulps. An increase in pH in the pre-bleaching stage might also cause some problems with the chelating and washing of metals.

In neutral or slightly acidic pre-bleaching conditions there are no perhydroxyl ions present, so Equation (1) should not be possible. Also the consumption of peroxide is minor. There is an approximately equal amount of OH⁻ and H⁺ ions in the neutral water phase which react very slowly with acetylic groups of hemicellulose forming acetic acid.

There is always some peroxide in the wash press filtrate which can also react with acetic acid. Hydrogen peroxide is a strong oxidant, but with a stronger oxidant it may also be a reductive component /42/, Equation (2).



Reaction 2 is very slow, which means that a very long retention time might be beneficial in the pre-bleaching stage, as stated in Haveri's Master's thesis /36/.

Similarity in bleaching performance was observed in comparison to recycled peroxide when peracetic acid was used in the pre-bleaching stage /43/. Brightness gain in the pre-bleaching stage was approximately 2-2.5% ISO units with 1% PAA dosage at neutral conditions. Pan *et al.* /38/ have stated that peracetic acid should brighten mechanical pulps more efficiently than hydrogen peroxide due to the overall rate of reaction which is faster with peracetic acid than with hydrogen peroxide. Also the reaction products should contain less colorful chromophores.

If the acidification of bleached pulp is carried out with sulphuric acid, the formation of Caro's acid is also possible /44/. The chemical properties of Caro's acid in terms of bleaching ability are very similar to those of peracetic acid. However, by assuming that acidification is performed conventionally after the washing stage, it is not probable that Caro's acid is the reason for the brightness gain.

4.1.2 Reactions of peracetic acid

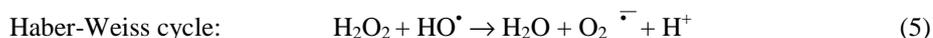
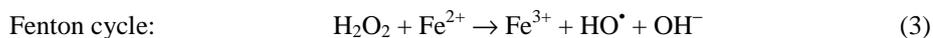
Under alkaline conditions, peracetic acid reacts in the same way as perhydroxyl ion in peroxide bleaching. Under acidic conditions, peracetic acid is known to act like a delignification agent /45/ but at neutral or slightly alkaline conditions dissolving is negligible. Reaction mechanism in pre-bleaching conditions is not obvious but one can assume that the bleaching mechanism is more like in alkaline conditions than in acidic.

4.2 Radicals

Reactions of radicals may play a role in the neutral or slightly alkaline pre-bleaching conditions, but the reliable measurement of radicals from the pulp sample is quite difficult. Radical species are formed in a low pH range /46/, but also alkaline conditions are able to enhance the generation of radicals. The reactions of radicals are very rapid. Radicals are able to break the conjugated double bonds of lignin and open ring structures. These kinds of reactions would increase brightness but also dissolve lignin into the water phase. Certain metal ions such as copper and iron have been found to activate radical formation /46, 47/. Several articles maintain that radicals react with lignin more often than with cellulose, but they are still able to degrade cellulose /48, 49/. Researchers have also speculated on the role of radicals in the alkaline peroxide bleaching stage. Hobbs and Abbot /50/ have stated that radicals may have an important role in alkaline conditions. It has also been suggested that the reactions of radicals break the lignin matrix so that bleaching chemicals can better penetrate the fiber wall /51, 46/. However, it is not clear whether the effect of radicals is negative or positive. Reactions of radicals may form also new colorful structures.

4.2.1 Formation of radicals

The formation of radicals has usually been studied in the bleaching of chemical pulps aiming delignification. The pH and presence of metal catalysts have a great influence on the formation of radicals. There are several reactions that can form radicals. Two common and quite well known mechanisms are shown below. One of the known radicals is the hydroxyl radical HO[•].



There is a great difference in the formation of radicals between the neutral pre-bleaching and alkaline peroxide bleaching conditions. The next figure shows how an increase in pH affects the formation of radicals.

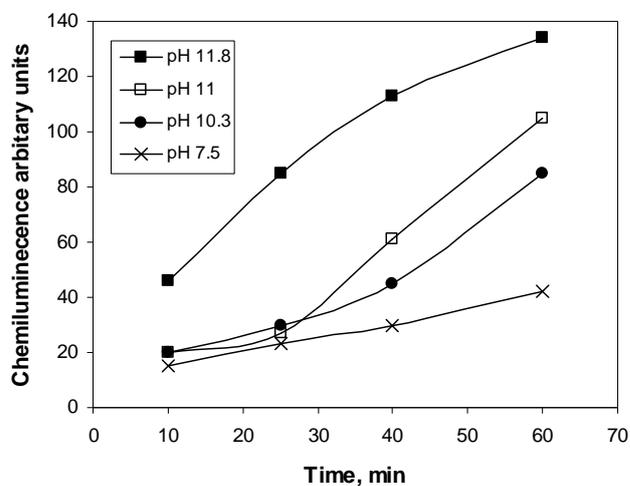


Figure 4.1 Effect of pH on formation of hydroxyl radicals. Conditions: Temperature 70 °C, H_2O_2 30 mmol/l /47/.

In typical neutral pre-bleaching conditions, the formation of radicals is lower than in alkaline conditions; see Figure 4.1. The amount of hydroxyl radicals was two to three times higher in highly alkaline conditions (pH 11.8). These experiments were performed in a water solution without fibers. The catalytic effect of iron and copper on the formation of radicals can be seen in Figures 4.2 and 4.3. The effects of manganese were the opposite; see Figure 4.4.

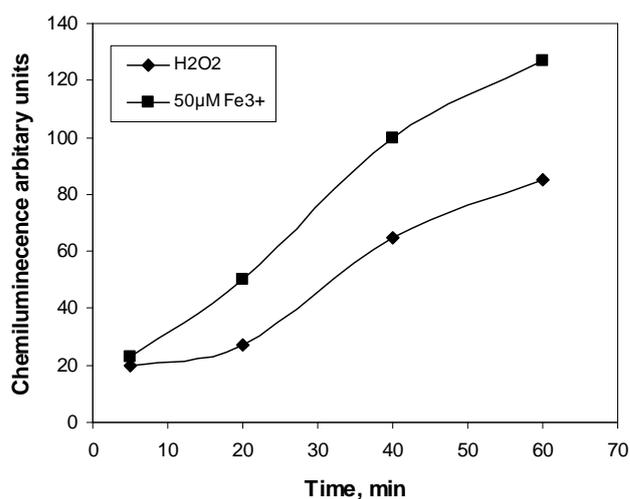


Figure 4.2 Effect of iron on formation of hydroxyl radicals in alkaline conditions. Conditions: pH 10.3, temperature 70 °C, H_2O_2 30 mmol/l /47/.

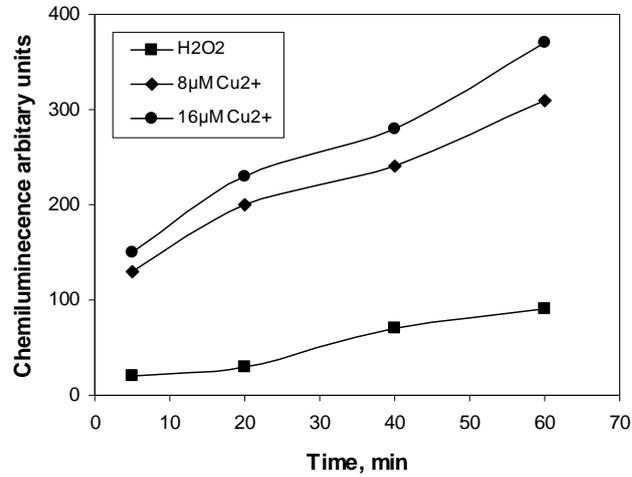


Figure 4.3 Effect of copper on formation of hydroxyl radicals in alkaline conditions. Conditions: pH 10.3, temperature 70 °C, H₂O₂ 30 mmol/l /47/.

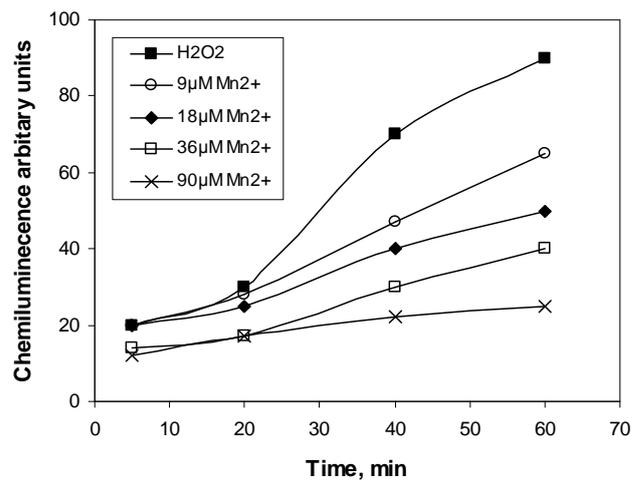


Figure 4.4 Effect of manganese on formation of hydroxyl radicals in alkaline conditions. Conditions: pH 10.3, temperature 70 °C, H₂O₂ 30 mmol/l /47/.

Figures 4.2 to 4.4 accurately describe the difference in the characteristics of these metals in forming radicals in water solution. Copper is the most reactive catalyst in the generation of radicals. However, the amount of copper in pulp is minor compared to iron and manganese. Iron catalyzes the formation of radicals, but not as effectively as copper. Manganese, which is

known to be very harmful in alkaline peroxide bleaching, does not decompose peroxide by the radical mechanism /47/.

4.2.2 Reactions of radicals

The selectivity of radical reactions is very low. The age of radicals is very short, and they react with the first compound which they can seize. In fact, that is the main problem in the bleaching of chemical pulps. Radicals decrease strength properties because of the degradation of carbohydrates /52/. For mechanical pulps, the situation is different: there is much more lignin left in the pulp. Fibers are usually covered by lignin, so it may be possible that radicals react more often with the lignin than the polysaccharides. This is the reason why the reactions of radicals could be beneficial in the bleaching of mechanical pulp. Of course, on a large scale, reactions of radicals might cause a reduction in strength properties similar to chemical pulps. Radicals may be formed continuously in pre-bleaching conditions, but it is almost impossible to say how much the reactions of these radicals affect the brightness of the pulp.

5 SUMMARY OF THE LITERATURE REVIEW

Based on the results from published literature, it seems to be possible to arrange a cost effective bleaching stage using residual peroxide as a pre-bleaching agent. The pre-bleaching stage does not necessarily need a long retention time, which makes the versatile utilization of residual peroxide possible. The reaction mechanism in mild pre-bleaching conditions does not seem to be self-evident. Peroxide, peracetic acid and perhaps also reactions with radicals may play an important role in such conditions. When changing water circulations, the most critical factor regarding the performance of alkaline peroxide bleaching is the manganese content. Residual peroxide should be used so that the amount of manganese is reduced rather than increased in the bleaching stages.

It was observed that by recycling, the gain of final brightness was at its best about 2% ISO units. Cost savings can, thereby, be as high as 10-15% for bleaching chemicals. Also less encouraging results have been obtained. The most restrictive issue regarding the utilization of residual peroxide seems to be the technical possibilities to arrange an effective pre-bleaching stage, especially in older mills.

EXPERIMENTAL

6 LABORATORY EXPERIMENTS – THE PRE-BLEACHING STAGE

6.1 The aim of the laboratory experiments

The aim of the laboratory experiments was to find out how the recycling of residual peroxide affects the brightness of unbleached pulp. The effect of basic variables such as the peroxide dosage, pulp consistency, pH and reaction time at the pre-bleaching stage was studied. Also the effects of fines, fresh and recycled peroxide, metals and stabilizers on the bleachability of pulp in mild pre-bleaching conditions were studied. Based on the effect of these variables, it would be more reliable to estimate the feasibility of the alternatives to circulate residual peroxide.

6.2 Materials and methods

Materials

The pulp used in most of these experiments was taken from a Finnish PGW mill using Norway spruce as raw material. Unbleached pulps were obtained from either the disc filter or the bleach press. The pulps were stored in a freezer. The consistency of the disc filter pulp after freezing varied between 11 and 14%, and the consistency of bleach press pulp between 37 and 42%. The pulp was mill chelated with DTPA (diethylenetriaminepentaacetic acid). Deionized water was used in the dilution of the pulp.

In the laboratory experiments, chemicals were used for a number of purposes. These chemicals and their use are listed in Table 6.1.

Table 6.1 Chemicals used in the experiments.

CHEMICAL	PURPOSE
Hydrogen peroxide, H ₂ O ₂	Bleaching
Sodium hydroxide, NaOH	Bleaching, pH adjustment
Sodium silicate, 2Na ₂ O·5SiO ₂	Bleaching
Sulphuric acid, H ₂ SO ₄	pH adjustment, determination of residual peroxide
Potassium iodide, KI	Determination of residual peroxide
Sodium thiosulphate, Na ₂ S ₂ O ₃	Determination of residual peroxide
Ammonium molybdate, (NH ₄) ₂ MoO ₄	Determination of residual peroxide
Starch	Determination of residual peroxide
Manganese sulphate, MnSO ₄	Determination of peracetic acid, pre-bleaching
Potassium permanganate, KMnO ₄	Determination of peracetic acid
Calcium chloride, CaCl ₂	Pre-bleaching
Iron sulphate, FeSO ₄	Pre-bleaching
Copper sulphate, CuSO ₄	Pre-bleaching
Aluminium chloride, AlCl ₃	Pre-bleaching
Chromium oxide, Cr ₂ O ₃	Pre-bleaching
Diethylene triamine pentaacetic acid (DTPA)	Chelate in pre-bleaching

Methods

In the laboratory experiments, the wash press filtrate had to be prepared first. The experimental set up for the wash press filtrate preparation is presented in Figure 6.1. The experimental set-up of the pre-bleaching stage is shown in Figure 6.2.

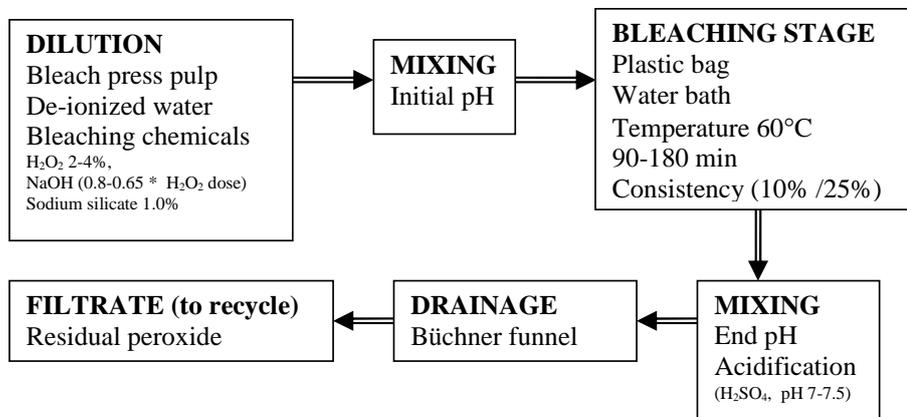


Figure 6.1 Set up for preparing residual peroxide containing filtrate.

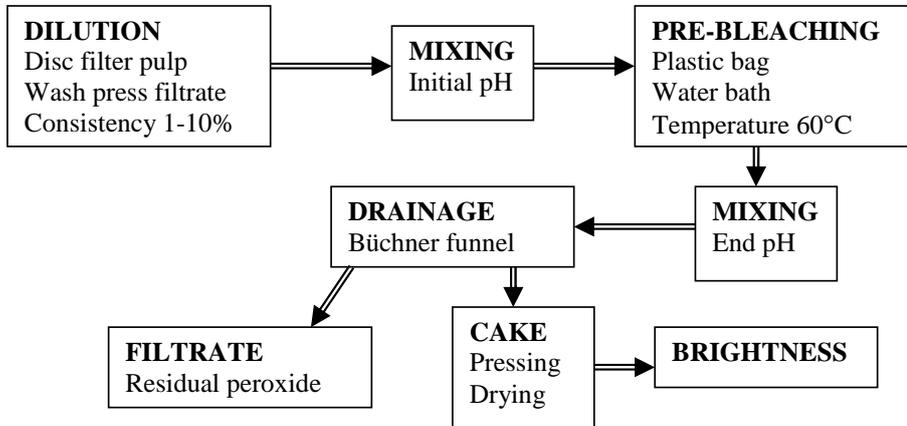


Figure 6.2 Set up for the pre-bleaching experiments.

The bleaching experiments were carried out in polyethylene bags in a water bath. A wash press filtrate containing residual peroxide was prepared for the recycling experiments as follows: alkaline peroxide bleaching at a 10% consistency and a temperature of 60°C using a mill chelated pulp obtained from the bleach press. The bleached pulp was dewatered with a Büchner funnel after bleaching. The amount of residual peroxide in the filtrate was affected by changing the peroxide dosage (2-4%) and retention time (90-180 min).

Unbleached pulp was then diluted for the pre-bleaching with a recovered Büchner funnel filtrate (simulating a wash press filtrate) and deionized water if there was a further need to adjust the consistency of the pulp. Consistencies varied from 1 to 10% in the pre-bleaching experiments. The pulp was always mixed manually in a plastic bucket. The pH was determined at the beginning and at the end of an experiment using a Metrohm 744 device. The temperature of the experiments was typically 60°C. The brightness of the pulp was determined from a pulp cake (grammage 700-800 g/m²) with an Elrepho 2000 spectrophotometer device from the filter paper side after pressing and drum drying. The residual peroxide was determined with the KCL method 214:85 /53/ and the peracetic acid concentration using the following titration method:

Measure 10ml H₂SO₄ solution, some ice and few drops of MnSO₄ into the flask. Add a certain amount of filtrate and titrate using KMnO₄ solution until the color is a light rose. The color has to remain at least 10 seconds. Add 10 ml KI solution to the flask and let the mixture be at a standstill in dark approximately three minutes. Titrate with Na₂S₂O₃ solution until the mixture is colorless, use starch solution as an indicator. PAA concentration can be calculated as follows:

$$Paa(g/l) = \frac{A \times B \times 76,05}{2 \times V} \quad (7)$$

where, A is the consumption of Na₂S₂O₃ solution, ml
 B is the concentration of Na₂S₂O₃ solution, M
 V is the volume of the added filtrate, ml

The dissolved organic compounds of the filtrate were determined according to the standard SFS-EN 1484 by using the TOC analyzer Shimadzu 5050A. All chemical dosages presented in this thesis are calculated as 100% concentrations on b. d. pulp.

It was observed that the measurement of brightness from the Büchner funnel pulp cake was affected by the pulp consistency in the drainage. The higher the consistency, the greater was the divergence between parallel brightness measurements. The effect of the consistency on the reliability of brightness measurements is shown in Figure 6.3

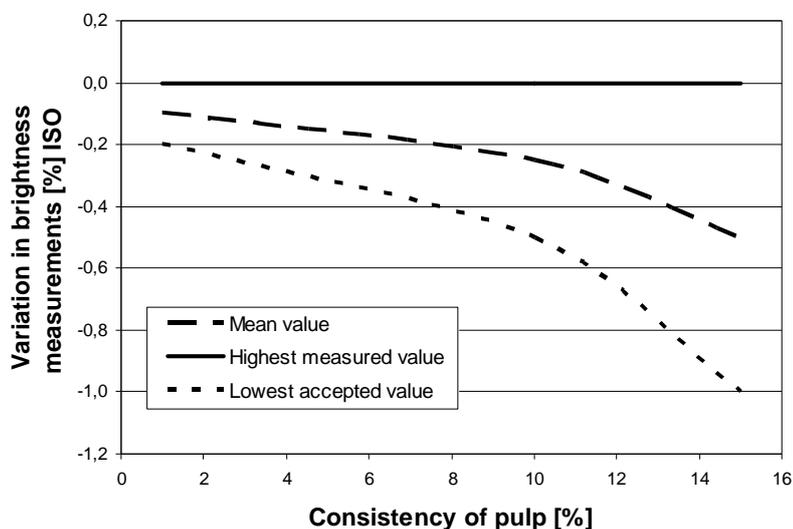


Figure 6.3 Reliability of the brightness measurements.

The main problem in brightness measurements was the uneven surface of the cake. If the consistency of pulp was high, it was possible that some of the measurements provided brightness levels that were too low. For that reason, the brightness values presented are mean values from at least six measurements from two different cakes. If the value of a single measurement was exceptionally low compared to the mean value, it was discarded.

6.3 Results

6.3.1 Basic variables

Peroxide dosage and pulp consistency

The peroxide dosage and the consistency of pulp are typically very critical factors concerning conventional peroxide bleaching. Figures 6.4 and 6.5 show how these two factors affect the brightness of the pulp in the pre-bleaching stage. Figure 6.6 describes the consumption of recycled peroxide in the neutral pre-bleaching stage.

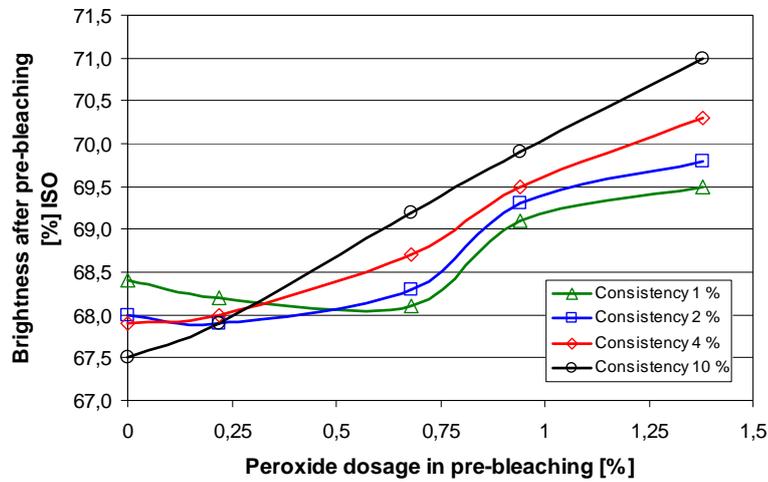


Figure 6.4 Effect of peroxide dosage on pulp brightness at different consistencies in pre-bleaching. (Disc filter pulp, temperature 60°C, pH 6.5-7, retention time 60 min.)

Figure 6.4 demonstrates that the increase in brightness is almost linear when the peroxide dosage is increased at a 10% pulp consistency. At low consistencies, the washing efficiency has a greater effect on pulp brightness than the peroxide dose. It should be kept in mind that additional dilution was carried out with deionized water at low consistencies. However, the most important issue affecting brightness is the peroxide dosage.

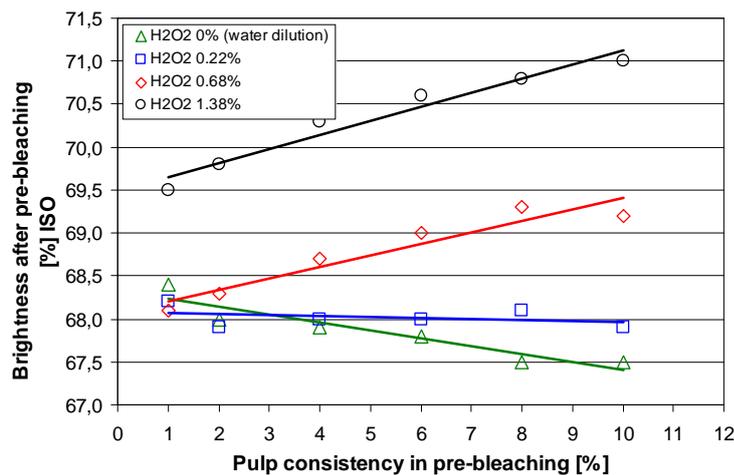


Figure 6.5 Effect of consistency on pulp brightness in pre-bleaching. (Disc filter pulp, temperature 60°C, pH 6,5-7, retention time 60 min.)

Without recycled peroxide an increase of the consistency will decrease brightness because of reduced washing efficiency, Figure 6.5. Peroxide charge of 0,2% will compensate this kind of darkening. At higher peroxide dosages the increased consistency is beneficial because of higher peroxide concentration.

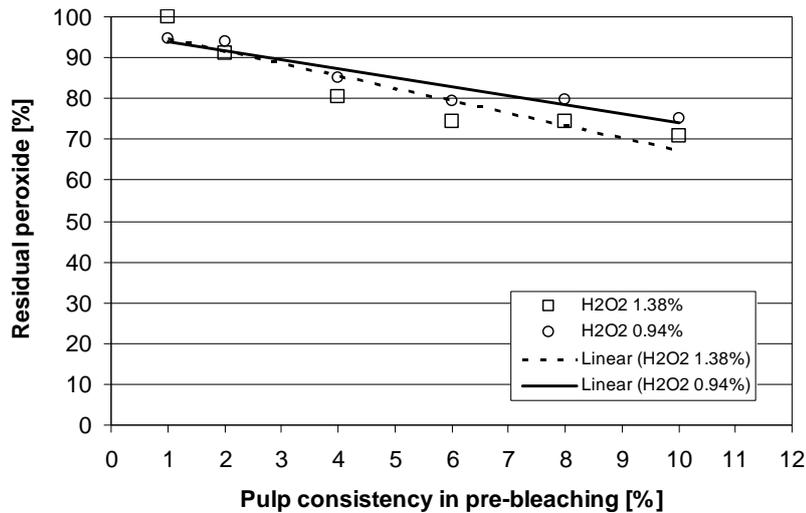


Figure 6.6 The effect of pulp consistency on the peroxide consumption in pre-bleaching stage. (Disc filter pulp, temperature 60°C, pH 6.5-7, retention time 60 min.)

Also the consumption of peroxide increases when the consistency of the pulp is high; see Figure 6.6. At low consistencies the consumption of peroxide is negligible. Due to the neutral conditions, the overall consumption and decomposition of peroxide is naturally relatively low. About 10-30% of recycled peroxide will decompose during the one-hour neutral pre-bleaching stage.

The fundamentals of bleaching conditions are the same in pre-bleaching as in the actual alkaline HC peroxide bleaching stage. The consistency of the pulp and the peroxide dosage should be maximized for effective pre-bleaching. Together these two variables act as the most important factor – peroxide concentration. The following figure shows how an increase in peroxide concentration either by increasing the peroxide dosage or by increasing consistency affects the brightness of pulp.

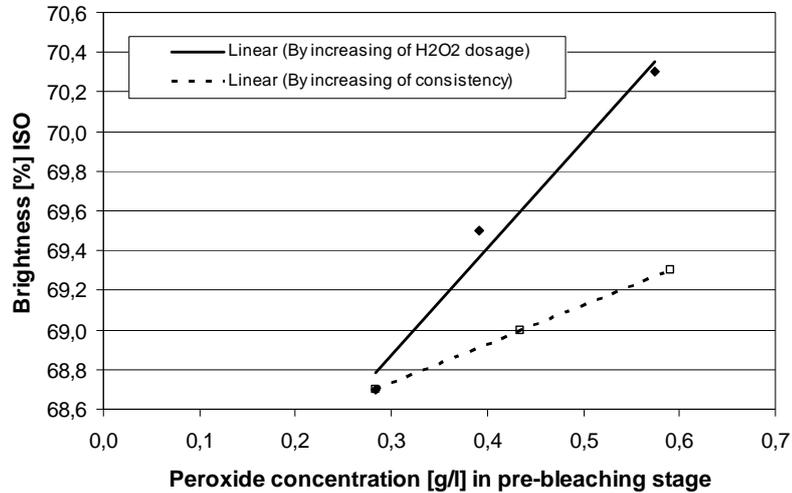


Figure 6.7 Effect of peroxide concentration on pulp brightness in pre-bleaching. (Disc filter pulp, temperature 60°C, pH 6.5-7, retention time 60min, pulp consistency 4-8%.)

From the results of Figure 6.7 one may see that the effect of the peroxide dosage is dominating compared to the effect of pulp consistency. Based on these results, it can be concluded that recycling residual peroxide prior to the disc filter is not advisable because of low consistencies. Also the residual alkali might disturb the chelation of metals if the wash press filtrate is recycled prior to the disc filter.

pH

Peroxide can be activated by adding NaOH if the dosage of recycled peroxide in pre-bleaching is relatively high. Figure 6.8 illustrates how the increased initial pH affects the brightness in the pre-bleaching stage.

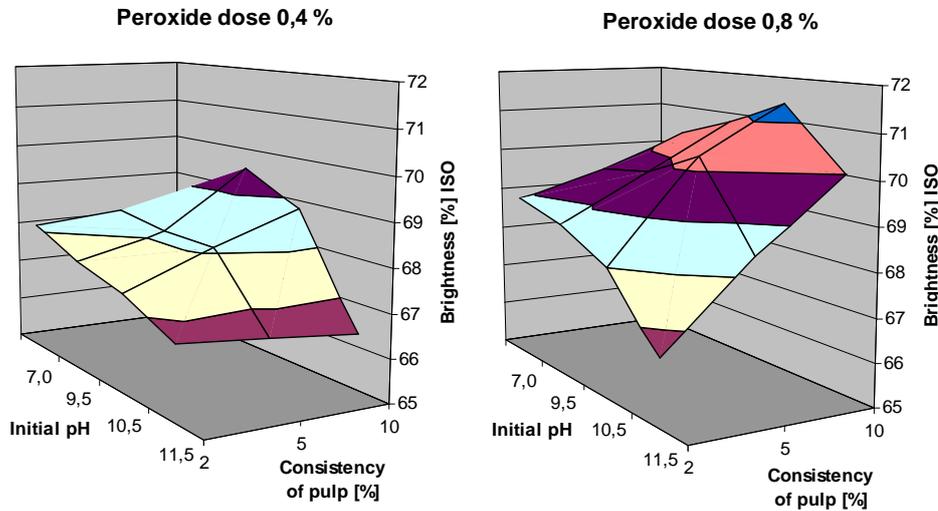


Figure 6.8 Effect of initial pH on pulp brightness in pre-bleaching.
(Disc filter pulp, temperature 60°C, retention time 60 min.)

From the left-hand side illustration in Figure 6.8 it can be seen that by increasing the initial pH at a peroxide dose of 0.4%, there is not any improvement in brightness if consistency of the pulp is 5% or lower. A slight increase in brightness can be seen if the initial pH is increased to 9.5 and the consistency of the pulp is 10%. Raising the initial pH over 9.5 will start to decrease the brightness again.

From the right-hand side illustration in Figure 6.8 it can be seen that a higher peroxide dose supports the increase in pH in the pre-bleaching stage. Again, at higher consistencies the improvement in brightness is greater. If the pH is raised above 9.5, the reaction mechanism will be the same as in the alkaline bleaching stage. Overall, it could be said that if the peroxide dose is under 1% in the pre-bleaching stage, the activation of peroxide with sodium hydroxide is questionable. Brightness would increase without additional alkali almost as much as with it. Moreover, it would increase chemical costs. The effect of alkali addition on pH levels is presented in Figure 6.9.

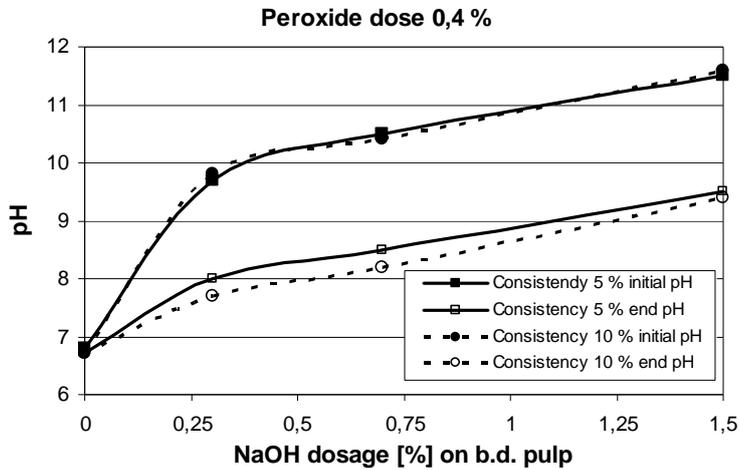


Figure 6.9 Effect of alkali on pH values in pre-bleaching stage.
(Disc filter pulp, temperature 60°C, retention time 60 min.)

The consistency of the pulp does not play a remarkable role in the pH value at the pre-bleaching stage. Only a 0.2% NaOH charge is needed to increase the pH from 7 to 9. During a one-hour retention time in pre-bleaching, the pH will drop approximately two units if the pH is increased to 10 or higher. The increase in pH will consume peroxide as can be seen in Figure 6.10.

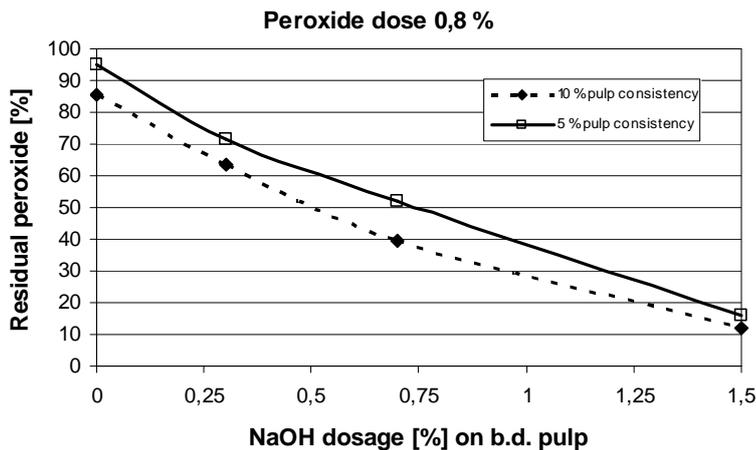


Figure 6.10 Effect of alkali and consistency on peroxide consumption in pre-bleaching.
(Disc filter pulp, temperature 60°C, retention time 60 min.)

Based on the results displayed in Figure 6.10, it can be said that the peroxide consumption is quite linear with the NaOH dose in the pre-bleaching stage. At a higher consistency, more peroxide is consumed because of a higher concentration of bleaching chemicals, as in the normal alkaline peroxide bleaching stage.

Temperature and retention time

The two basic variables in bleaching are temperature and retention time. Figure 6.11 shows how these factors affect pulp brightness in the pre-bleaching stage.

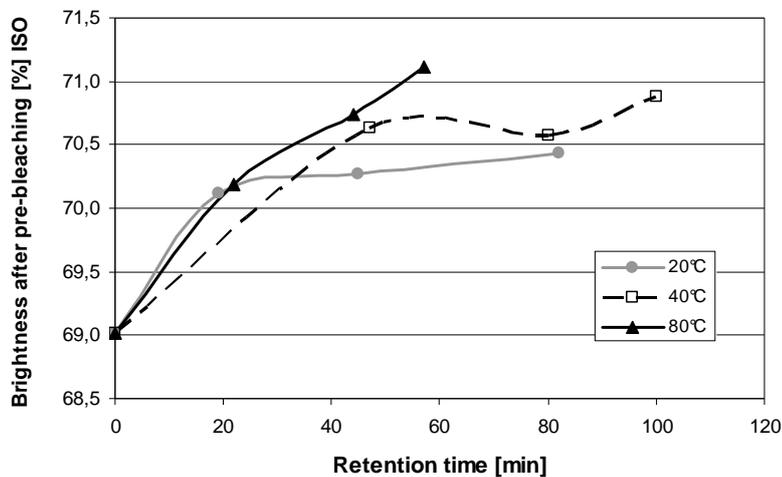


Figure 6.11 Effect of temperature on pulp brightness in pre-bleaching. (Disc filter pulp, temperature 60°C, peroxide dose 1.1%, consistency 7.5%, pH 6.3)

The rapid brightness gain at the beginning of pre-bleaching is not dependent on the temperature; see Figure 6.10. During the first 20 minutes of the retention time, the development in brightness is similar at both 20 and 80°C. After a rapid beginning, the effect of temperature on brightness is emphasized. The brightness increases much more slowly at 20°C than 80°C. The brightness increase at 40°C is somewhere between 80 and 20°C. Figure 6.12 shows how a very long retention time with the activation of peroxide affects the pulp brightness in the pre-bleaching stage.

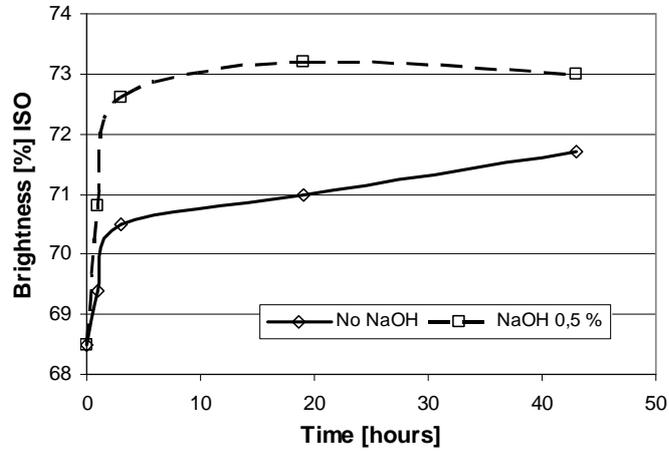


Figure 6.12 Effect of long retention time on brightness of pulp in pre-bleaching. (Disc filter pulp, temperature 60°C, consistency 8%, peroxide dose 0.7% , initial pH 6.3 and with added NaOH 10.1)

Brightness will increase continuously when the retention time is increased in the pre-bleaching stage; see Figure 6.12. With NaOH addition, the maximum brightness level is achieved more rapidly. At the end of the 45 hour experiments, the gap of the brightness was a bit over 1% ISO units for NaOH activated pre-bleaching. Added NaOH increases dissolving in the pre-bleaching stage, which is not a desirable effect regarding effluents and yield; see Figure 6.13.

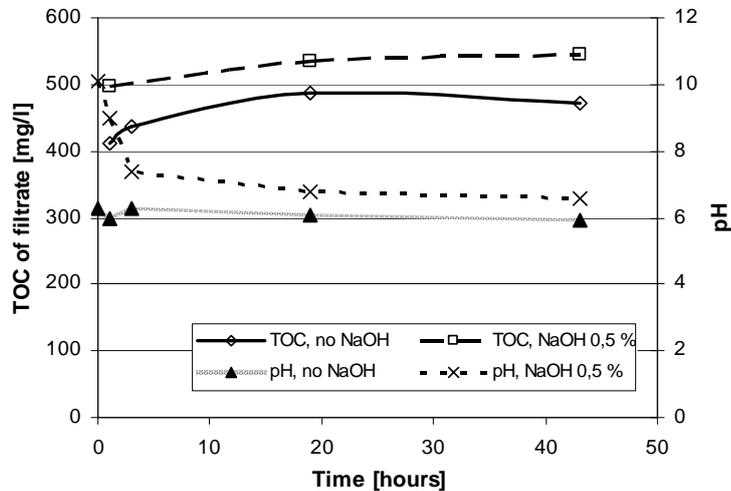


Figure 6.13 Effect of a long retention time and NaOH on the amount of dissolved organic compounds in pre-bleaching. (Disc filter pulp, temperature 60°C, consistency 8%, peroxide dose 0.7%, initial pH 6.3 and with added NaOH 10.1)

The TOC is increased by 10-15% because of added sodium hydroxide. A very long retention time will also increase the TOC by 10%. At the end of the long retention time, the pH is dropped to 7 if NaOH is added. In conclusion, it can be said that the pre-bleaching stage does not necessarily need a high temperature or a long retention time, but the effect of these two factors on brightness is beneficial.

6.3.2 Fines in recycling

Aim

A typical comment when discussing brightening caused by the recycling of wash press filtrate is that it must be due to the fines that are circulated with residual peroxide. The wash press filtrate may contain a large amount of fines which have gone through the alkaline peroxide bleaching stage. It has been thought that these fines might be the reason for the increase in brightness in recycling. Fines should increase also the light scattering. The aim of this experiment was to determine the role of recycled fines on brightness in the pre-bleaching stage.

Materials and methods

The pulp used in this experiment was taken from a Finnish SGW mill using Norway spruce as raw material. Unbleached pulp was obtained from the MC tower after the disc filter. The consistency of the pulp was approximately 9%. Wash press filtrate was taken from the wash press filtrate tank. The dry matter content of the wash press filtrate was 0.87 g/l. The pulp was mill chelated with DTPA.

The experiments were carried out in polyethylene bags in a water bath. Unbleached pulp was diluted for the pre-bleaching with the wash press filtrate. The pulp was mixed manually in a plastic bucket. The pH was determined at the beginning and at the end of each experiment. The temperature in the experiments was 60°C. The equipment, chemicals and methods for measuring brightness, the pH and residual peroxide were the same as mentioned before. The Kajaani FS-100 fiber length analyzer was used to determine the length distribution of fiber and fine material in the wash press filtrate.

The effect of fines on brightness was tested both at the mill site and at the university in laboratory experiments. Disc filter pulp was diluted with wash press filtrate with and without fines. Fines were removed by filtering the wash press filtrate with a Büchner funnel before using it in the dilution of the unbleached pulp. Figure 6.14 shows how fines affect the brightness of pulp in the pre-bleaching stage.

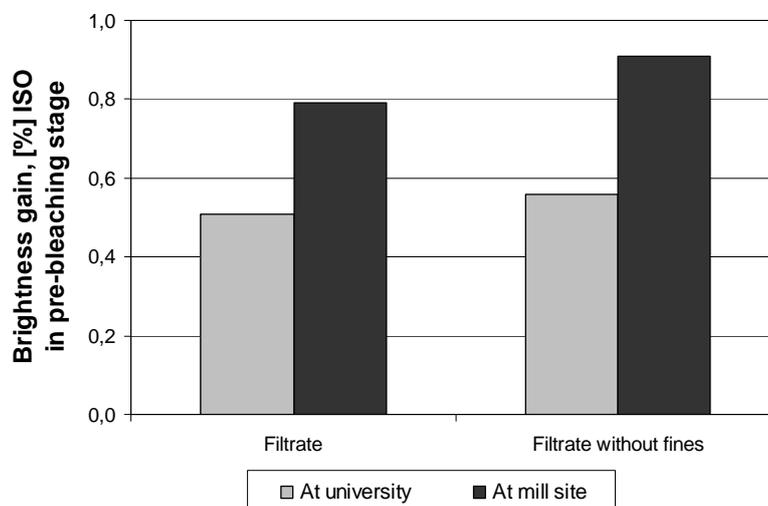


Figure 6.14 Effect of recycled fines on pulp brightness in pre-bleaching. (GW, temperature 60°C, consistency 5%, pH 6.5-7, peroxide dosage 0.4%, amount of fines 0.7% of dry pulp)

Fines were not the reason for the increase in brightness in pre-bleaching, as can be seen from Figure 6.14. The brightness remains at the same level regardless of the presence or absence of fines. Experiments conducted at the university gave a lower brightness level, but the difference between the original filtrate and the filtered filtrate was roughly the same regarding brightness. Therefore, it can be concluded that the increase in brightness must be due to chemical reactions. The brightness of the fines was 74.9% ISO. The amount of fines compared to the total amount of pulp is so low that the brightness is not affected by the recycled fines.

6.3.3 Fresh versus recycled peroxide

It was assumed that the reason for the brightness increase is not peroxide itself but perhaps some peracetic acid formed in alkaline peroxide bleaching. To shed light on the overall behavior of fresh and recycled peroxide, a comparative study was conducted on a laboratory scale. Recycled peroxide for the experiments was prepared as described above. Deionized water was used in pulp dilution when fresh peroxide was used in the pre-bleaching stage. The results are presented in Figure 6.15.

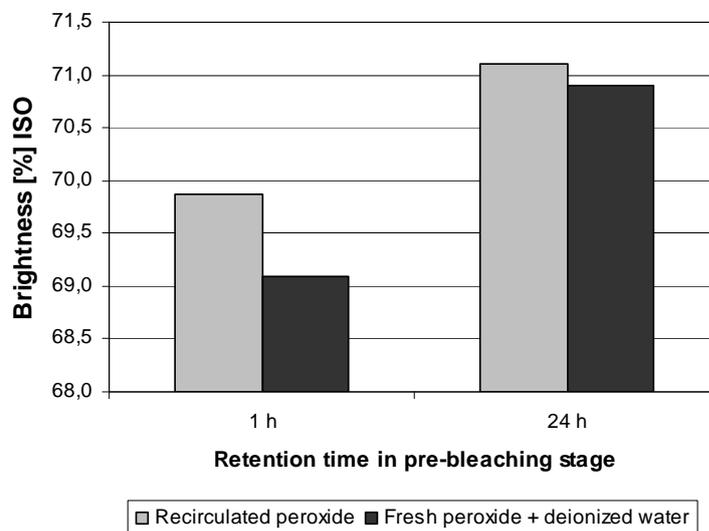


Figure 6.15 Effect of recycled vs. fresh peroxide on brightness of pulp in pre-bleaching stage. (Disc filter pulp, temperature 60°C, consistency 8%, peroxide dose 0.6%)

It was observed that the brightness of pulp increases in the case of recycled peroxide more rapidly than in the case of fresh peroxide. After a very long retention time, fresh peroxide will reach the same brightness level as recycled peroxide. It seems that in alkaline peroxide bleaching, a substance is formed that would react quite rapidly with unbleached pulp. Another explanation could be the residual alkali that is recycled together with peroxide. In conclusion, we can say that recycled peroxide is more effective because of its faster reactions, but what matters in the end is the amount of peroxide.

6.3.4 *In situ* peracetic acid in pre-bleaching

To determine the role of peracetic acid in pre-bleaching, the formation of PAA was studied in the alkaline bleaching stage. A small amount of peracetic acid was observed to remain after the bleaching; see Figure 6.16

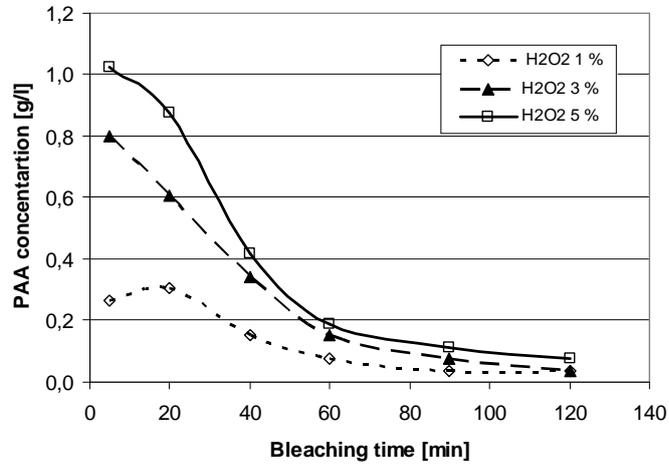


Figure 6.16 Formation of peracetic acid in alkaline peroxide bleaching. (temperature 60°C, consistency 10%, NaOH dosage 65% of added peroxide, silicate 1.0%)

From Figure 6.16, it can be seen that the formation of PAA is very effective at the beginning of the alkaline bleaching stage. The increase in chemical dosages also increased the formation of PAA. At the end of bleaching, the PAA concentration was almost constant – between 0.05 and 0.1 g/l. Figures 6.17-6.20 demonstrate how the peroxide dose, NaOH dose, consistency and temperature affect the formation of PAA.

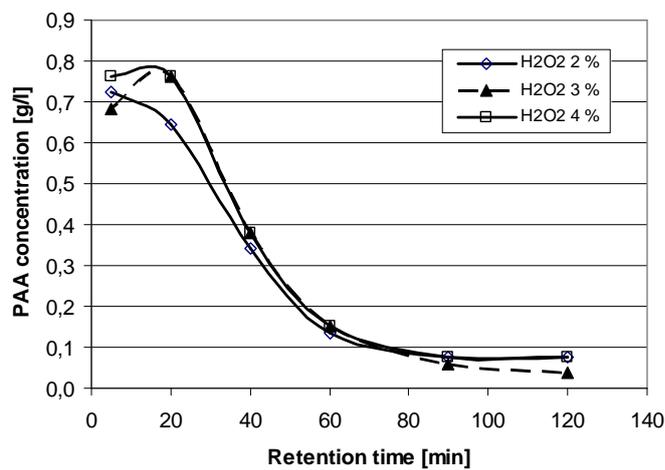


Figure 6.17 Effect of peroxide dose on formation of peracetic acid in alkaline peroxide bleaching. (temperature 60°C, consistency 10%, NaOH 2.0%, silicate 1.0%)

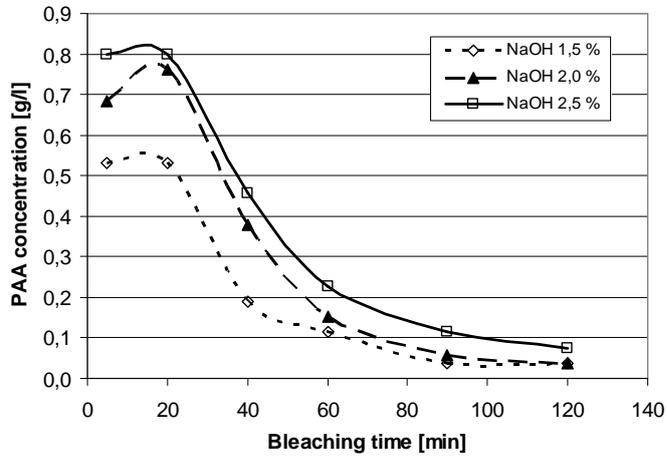


Figure 6.18 Effect of sodium hydroxide dose on formation of peracetic acid in alkaline peroxide bleaching. (temperature 60°C, consistency 10%, H₂O₂ 3.0%, silicate 1.0%)

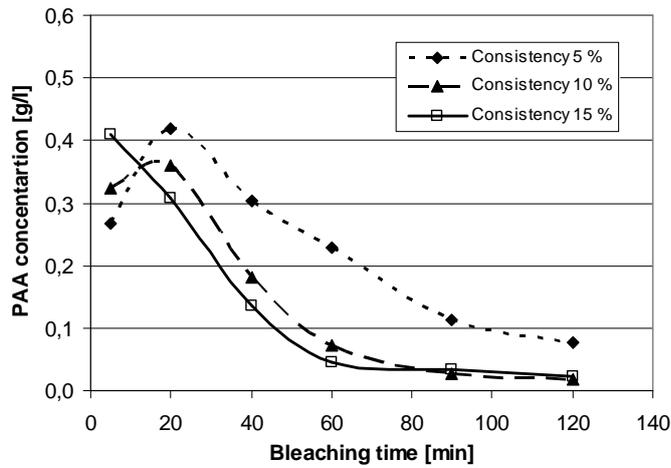


Figure 6.19 Effect of bleaching consistency on formation of peracetic acid in alkaline peroxide bleaching. (temperature 60°C, consistency 10%, H₂O₂ 3.0%, NaOH 2.1%, silicate 1.0%)

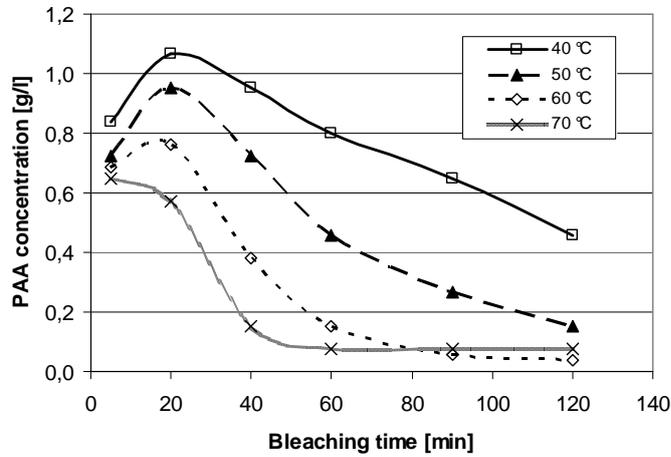


Figure 6.20 Effect of bleaching temperature on formation of peracetic acid in alkaline peroxide bleaching. (temperature 60°C, consistency 10%, H₂O₂ 3.0%, NaOH 2.1%, silicate 1.0%)

Sodium hydroxide as a deacetylating agent seems to be a dominant variable in the formation of PAA in alkaline peroxide bleaching; see Figure 6.18. NaOH through HO⁻ and HOO⁻ will release the acetic acid and PAA from the acetyl groups of hemicelluloses. The effect of peroxide at a constant NaOH concentration is minor but it is obvious that there has to be at least some peroxide present; see Figure 6.17. The amount of peroxide, however, is not so important. Fast formation on PAA indicates that in situ PAA is formed straight from the acetylic groups, not from the acetic acid. Basic variables such as temperature and consistency affect the reaction rate of the PAA formed. Increased temperature and consistency enhance the consumption of PAA in the alkaline bleaching stage.

In conclusion, it can be stated that in typical HC bleaching a great amount (0,5-1,0% as a dosage on b. d. pulp) of peracetic acid will be formed, but it will decompose or be consumed during the bleaching so that the PAA concentration remaining in the wash press filtrate is very low. Based on the results above, the recycled PAA as the dosage in the pre-bleaching stage could vary from 0.05% to 0.1% in dry pulp. The PAA concentration was measured also in the pre-bleaching stage, and the results are presented in Figure 6.21.

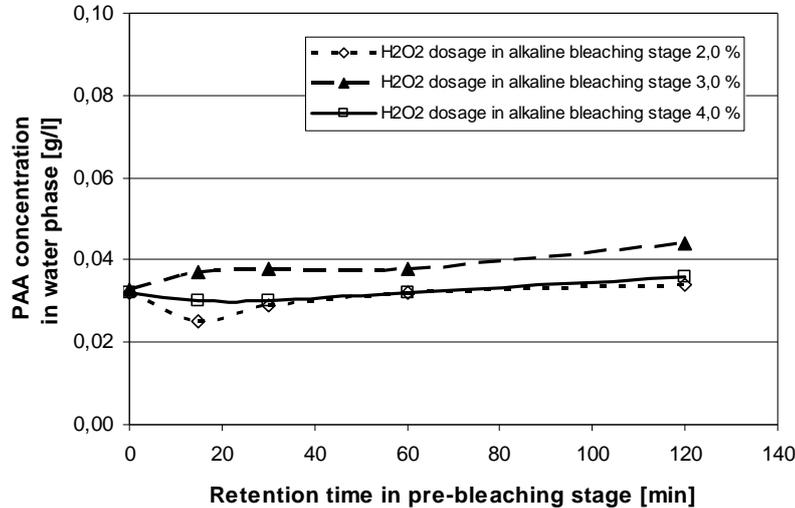


Figure 6.21 Concentration of PAA in pre-bleaching at different bleaching levels. (temperature 60°C, consistency 8%, pH 6.7-7.2, H₂O₂ 0.85-1.4%)

The bleaching efficiency of the alkaline peroxide bleaching stage has no effect on the concentration of PAA in the pre-bleaching stage – see Figure 6.21 – because the concentration of PAA in the recycled filtrate is at the same level. The concentration of PAA is at quite a constant level despite the retention time. In addition, the concentrations are so low that reliable measurement by titration was difficult. The calculated dosages of PAA in the pre-bleaching stage at an 8% consistency varied between 0.04 and 0.05% on dry pulp. It is still questionable whether this could be the reason for the faster brightness gain compared to pure peroxide.

6.3.5 Metals

Several metal ions are very harmful especially in the alkaline peroxide bleaching of mechanical pulps. Metal ions catalyze the decomposition of peroxide and the formation of radicals, as stated earlier in the theory part of this study. The addition of metal (Fe, Cu, Mn, Al) aimed to maximize the amount of radicals in the pre-bleaching stage and enhance the reactions of the radicals. Figure 6.22 shows how different metals affected the brightness of the pulp in neutral conditions on the pre-bleaching stage.

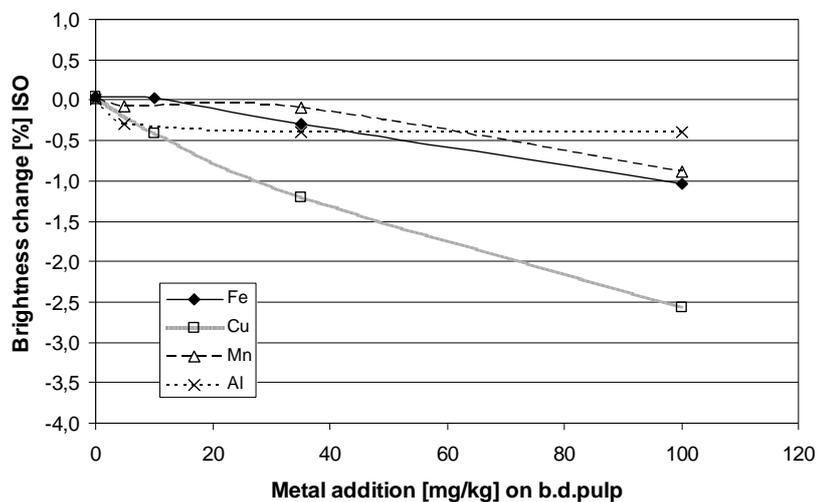


Figure 6.22 Effect of metal ions on pulp brightness in pre-bleaching. (H_2O_2 1.35%, retention time 60 min, temperature 60°C , consistency 8%, pH 6.9-7.4)

Based on the results in Figure 6.22, it can be said that none of the added metals could increase the brightness of pulp. Copper was the most harmful one and known to be a very effective catalyst in the formation of radicals. In conclusion, radicals do not work as a bleaching agents, assuming that the drop in brightness was due to the radicals. The amount of radicals is very difficult to measure and it was not even attempted in this work. The effect of metal ions on peroxide consumption in the pre-bleaching stage is presented in Figure 6.23.

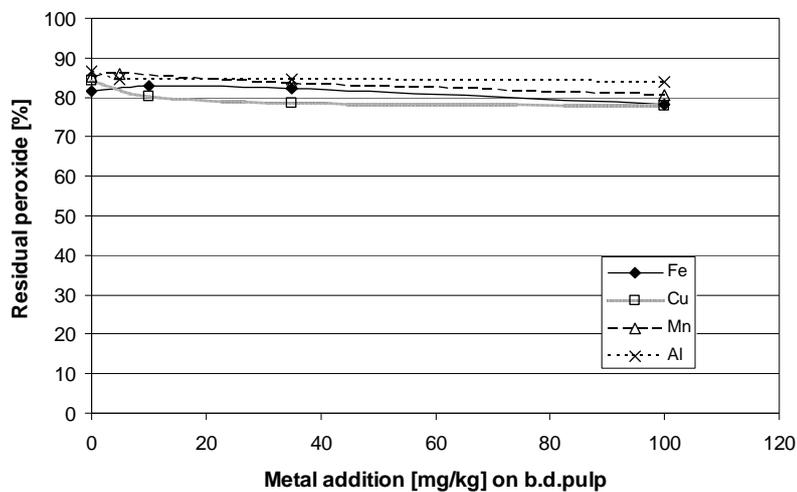


Figure 6.23 Effect of metal ions on decomposition of peroxide (H_2O_2 1.35%, retention time 60 min, temperature 60°C , consistency 8%, pH 6.9-7.4)

The effect of metal ions on the decomposition of peroxide was negligible. There was only a slight decrease in residual peroxide. These metals (Fe, Cu, Mn, Al) are not able to decompose peroxide in neutral conditions. If these metals were similarly added in alkaline peroxide bleaching, the results would be dramatic.

6.3.6 Silicate and DTPA

Also the effects of stabilizers such as silicate and DTPA were studied. The effect of silicate on pulp brightness and the consumption of peroxide is shown in Figure 6.24

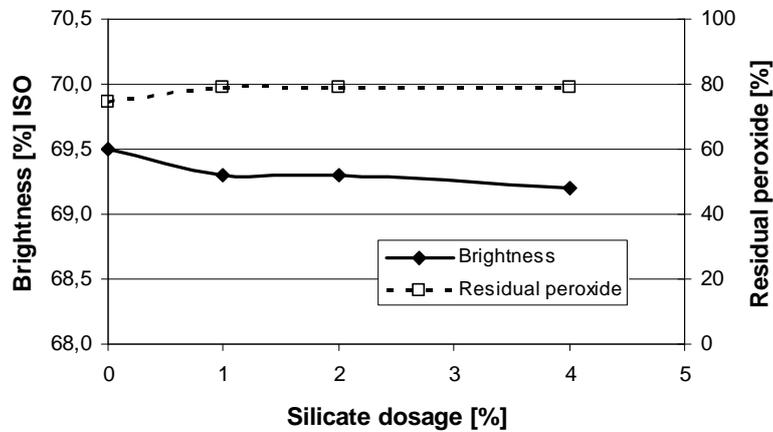


Figure 6.24 Effect of silicate on pulp brightness and peroxide consumption in pre-bleaching. (H_2O_2 0.45%, retention time 60 min, temperature 60°C , consistency 8%, pH 6.5-7)

The addition of silicate does not increase the brightness of pulp in the neutral pre-bleaching stage. Silicate had no great influence on the consumption of peroxide, either. The effect of DTPA on pulp brightness and the consumption of peroxide is shown in Figure 6.25.

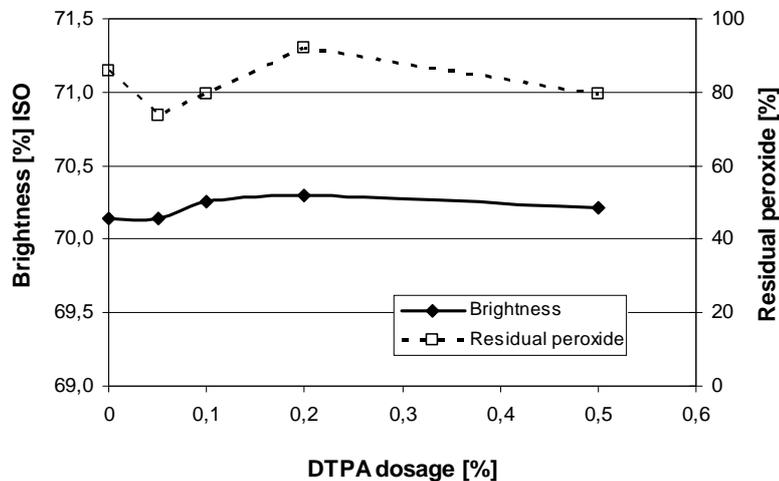


Figure 6.25 Effect of DTPA on pulp brightness and peroxide consumption in pre-bleaching. (H_2O_2 0.74%, retention time 60 min, temperature 60°C , consistency 8%, pH 6.5-7)

DTPA has no significant effect on the brightness of pulp in the pre-bleaching stage, as can be seen in Figure 6.25. The deviation in residual peroxide measurements is quite high, and based on these results, it cannot be said that DTPA would affect the peroxide consumption. It can be concluded that the role of both stabilizers, silicate and DTPA, is minor in neutral pre-bleaching conditions.

6.3.7 The effect of pre-bleaching on final brightness

Based on results discussed earlier, we can say that recycling of wash press filtrate increases brightness in the pre-bleaching stage. Figure 6.26 shows how pre-bleaching affects the final brightness of PGW.

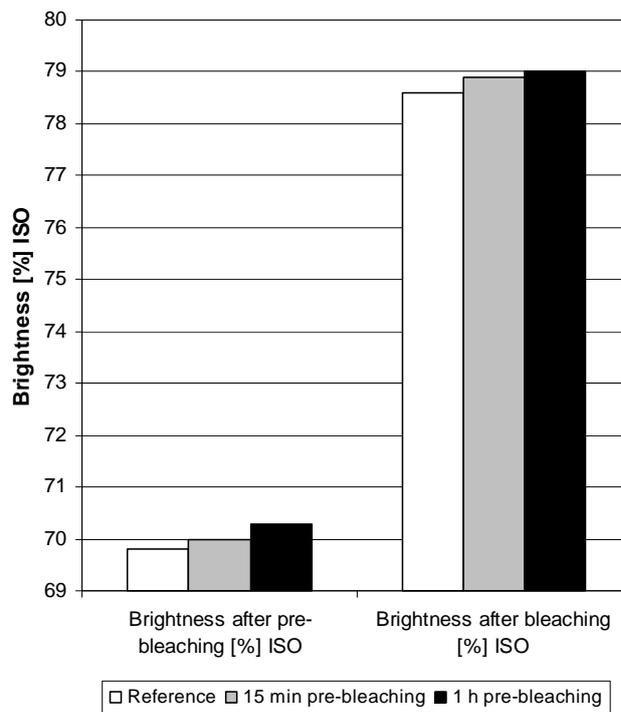


Figure 6.26 Effect of pre-bleaching on final brightness of PGW pulp. (Pre-bleaching: Peroxide dosage 0.8%, temperature 60°C, consistency 8%, retention time 15-60min. Alkaline peroxide bleaching stage: temperature 60°C, consistency 10%, retention time 120 min, H₂O₂ 3,8%, NaOH 2,5%, silicate 1.0%)

From Figure 6.26, it can be seen that the final brightness is higher with recycling. Pre-bleaching increases brightness by 0.8% ISO, and the final brightness increases by 0.4% ISO when the peroxide dosage in the alkaline peroxide stage was 3.8%.

Table 6.2. Effect of pre-bleaching on peroxide dosage needed in actual bleaching stage to achieve the same brightness level as without the pre-bleaching. Retention time in the pre-bleaching was 60 minutes.

Sample	Pre-bleaching	Bleaching	Final brightness [%] ISO
1.	no	H ₂ O ₂ 3.8%, NaOH 2,5%	78.5
2.	H ₂ O ₂ 0,8%	H ₂ O ₂ 3.8%, NaOH 2,5%	78.9
3.	no	H ₂ O ₂ 4.1%, NaOH 2,6%	78.9

In practice, this means approximately a 7% reduction in costs of bleaching chemicals. Without recycling, a 0.3% higher peroxide dosage on pulp is needed to reach the same brightness as with recycling. One should bear in mind that these laboratory experiments were done with pure dilution water and stored pulp samples. A better estimation regarding the final effect of recycling on brightness in real processes is presented in section 7, Mill experiments.

6.4 Summary of the laboratory experiments

The most important results from the laboratory experiments are summarized in the table below.

Table 6.3 Summary of results from the laboratory experiments.

VARIABLE (increase in a variable)	EFFECT ON	
	Brightness	Peroxide consumption
H ₂ O ₂ dosage	+++	
pH	+ , - *)	+++
Consistency	++	+
Temperature	+	+
Retention time	+	+
DTPA dosage	0	0
Silicate dosage	0	0
Mn content	-	0
Fe content	-	0
Cu content	--	0
Al content	0	0

+ increase

- decrease

0 no effect

*) depends on peroxide dosage and consistency

Based on Table 6.3, effective pre-bleaching requires a high peroxide dosage, high consistency and high temperature. A long retention time would be beneficial. The increase in pH depends on the peroxide dosage and consistency. If the peroxide dosage in pre-bleaching is relatively high (approximately 1,0% or higher) and the consistency is in the MC area, some sodium hydroxide can be used for the activation of the residual peroxide. Furthermore, it can be concluded that in neutral conditions the effect of metals and stabilizers on brightness is negligible.

7 MILL EXPERIMENTS

After the laboratory studies, a better estimate of the utilization of residual peroxide in real processes was needed. Therefore, mill experiments were carried out. The idea of the mill experiments was to establish how much the bleaching performance could be improved by enhancing recycling in mill conditions.

The experiments were carried out at the mill site but on a laboratory scale. Pulp samples and filtrates were extracted straight from the process and used immediately in the experiments. The conditions and chemical doses were the same as in the ongoing process except for the alkaline peroxide bleaching stage which was implemented in medium consistency due to the laboratory equipment available. The results and methods are presented at a general level in order to avoid the identification of the mills. However, general trends and effects can easily be derived from the results. Due to the high repeatability of laboratory bleachings demonstrated earlier in this study, no parallel bleaching experiments were conducted.

7.1 Aim of the mill experiments

The aim of the mill experiments was to examine how the enhanced use of residual peroxide affects the brightness, pH, metal contents and TOC prior to the alkaline peroxide bleaching stage, and the final brightness. In the first phase of the study, the current situation was analysed in outline. In that basic study of the mill experiments, the development of brightness and the amount of recycled peroxide through the process line in five different process concepts (PGW 1, PGW 2, GW, GW/TMP, BCTMP) were determined. Also the development of the pH, manganese content and TOC of the filtrates were determined.

In the second phase, the enhancement of residual peroxide utilization was tested. The basic idea of the enhancement arrangements can be seen in Figure 7.1. In every case, instead of disc filter filtrate, more wash press filtrate was used in the dilution of pulp before the bleach press. The change would increase the peroxide dose in the MC pre-bleaching stage. This was found to be the only reasonable and simple way to utilize residual peroxide. This kind of change would also be easy to implement.

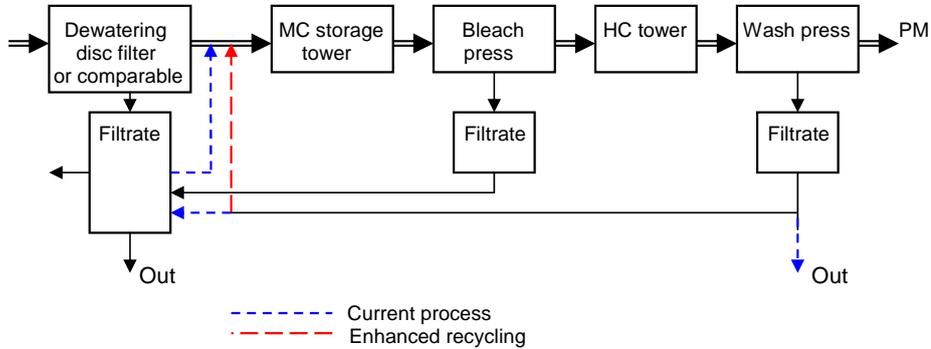


Figure 7.1 Rearrangements for a more effective utilization of residual peroxide.

In Figure 7.1, the blue dashed line illustrates the current situation and the red dashed line enhanced recycling. To some extent, residual peroxide was already recirculated, but in most cases, there was much room for improvement in recirculation.

7.2 Processes

7.2.1 PGW 1

The first PGW process was a typical grinding process where the use of residual peroxide was in no important role. Wash press filtrate with residual peroxide was either taken straight out from the process, or some of it was recycled to the filtrate tank of the disk filter. From the disc filter filtrate tank it was spread out over the process, as can be seen from Figure 7.2.

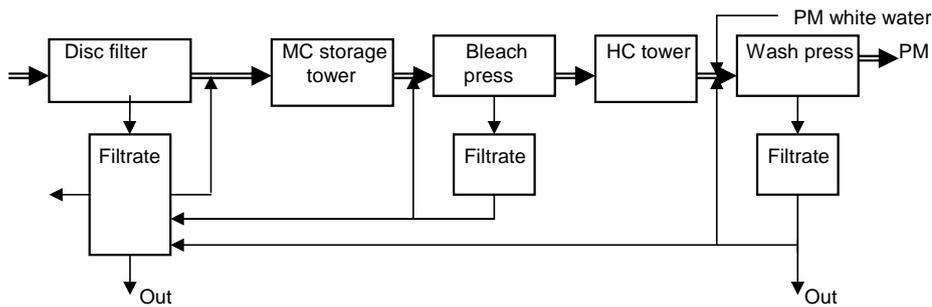


Figure 7.2 The PGW 1 process.

In this PGW 1 process, which produces a brightness of approximately 80% ISO, bleached pulp was diluted with both PM white water and wash press filtrate. As a result, approximately 60% of the dilution water was wash press filtrate. This means that the amount of recyclable wash press filtrate is not very high, but the high peroxide concentration will compensate for it. In the mill experiments, the process was changed so that the disc filter pulp and the storage tower pulp were diluted with wash press filtrate instead of disc filter filtrate; see Figure 7.3.

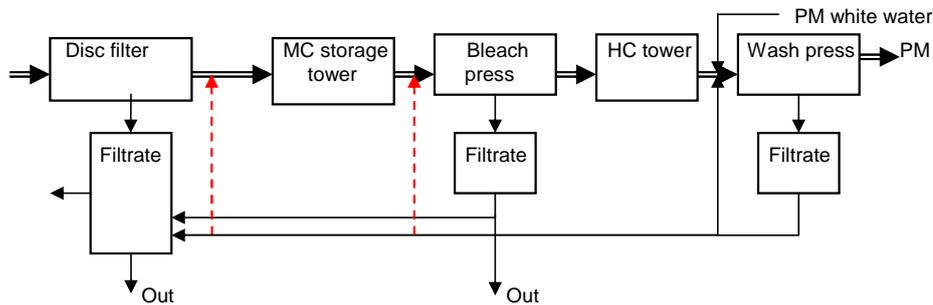


Figure 7.3 The PGW 1 process after modification.

This kind of change had a great effect on the peroxide dose and brightness in the MC stage; see Figures 7.4 and 7.5

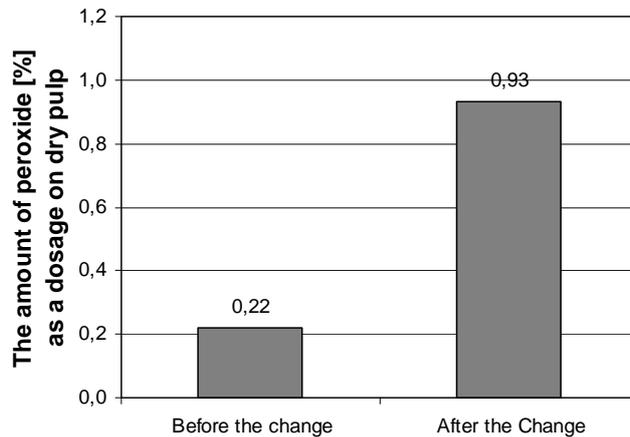


Figure 7.4 Effect of modification on peroxide dose in pre-bleaching stage, PGW 1.

As can be seen in Figure 7.4, the amount of peroxide increased clearly in the MC tower. Also the pH increased a bit. Before modification, the pH in the MC tower was 6.7, but it rose slightly above neutral due to the modification.

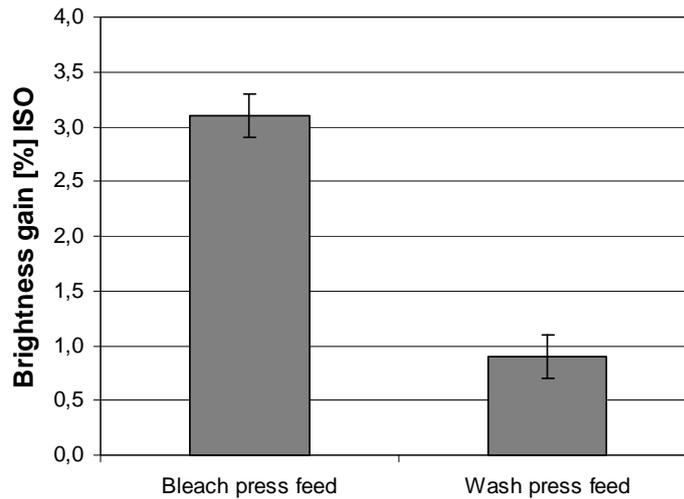


Figure 7.5 Effect of modification on brightness in PGW 1 process. Retention time in MC tower 30 min.

The brightness gain was at the expected level in the neutral pre-bleaching stage, Figure 7.5. The final brightness was increased by approximately 1% ISO unit, which is roughly one third of the brightness gain in the MC stage. This is the best estimation of the final benefit of the brightness gain in the pre-bleaching stage.

One finding from the experiment was that the TOC increased 28% due to the enhanced recycling in the MC stage. This did not have a great effect on the actual bleaching stage because of the dewatering between the MC and HC stages. A more important detail is that changes in water circulations reduced the manganese content in the bleaching stages by approximately 33%. This should have a positive affect on brightness in the alkaline HC bleaching stage. Adding sodium hydroxide to activate the residual peroxide was not found to improve the final brightness.

7.2.2 PGW 2

There was no great difference in water circulations between the first and the second PGW processes. Almost all of the wash press filtrate was recycled to the disc filter filtrate tank, and bleached pulp was diluted in practice only with PM white water. From the disc filter filtrate tank, the residual peroxide spread out over the process, as can be seen from Figure 7.6. Waste water was taken out only from the disc filter.

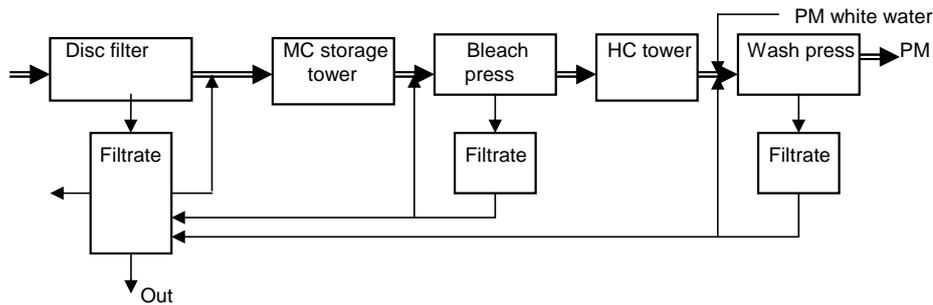


Figure 7.6 The PGW 2 process.

The process was changed so that the disc filter pulp and the storage tower pulp were diluted with wash press filtrate instead of disc filter filtrate; see Figure 7.7

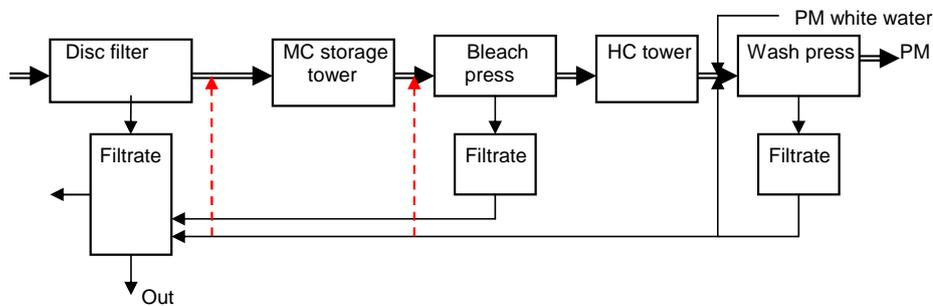


Figure 7.7 The PGW 2 process after modification.

The effect of the modification on this process was minor, which can be stated on the basis of Figures 7.8 and 7.9.

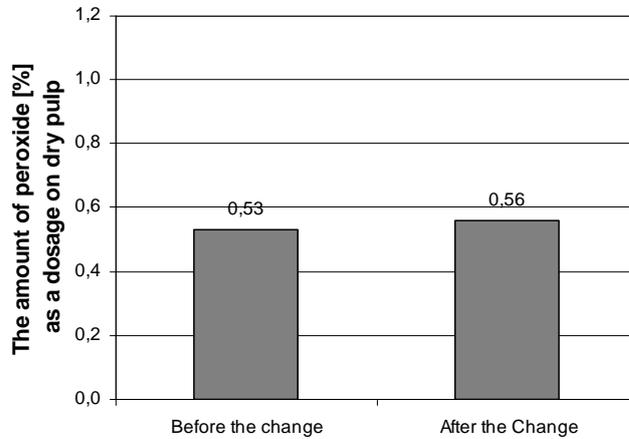


Figure 7.8 Effect of modification on peroxide dose in pre-bleaching stage, PGW 2.

The change in water circulations has practically no effect on the peroxide dose in the MC stage. This is due to the somewhat closed water circulations in the PGW mill combined with the fact that peroxide does not decompose in neutral or slightly acidic conditions. This means that there is already a great deal of peroxide in the disc filter filtrate. Because of the negligible increase in the peroxide dose, the brightness gain was presumed to be low. This can be observed from Figure 7.9.

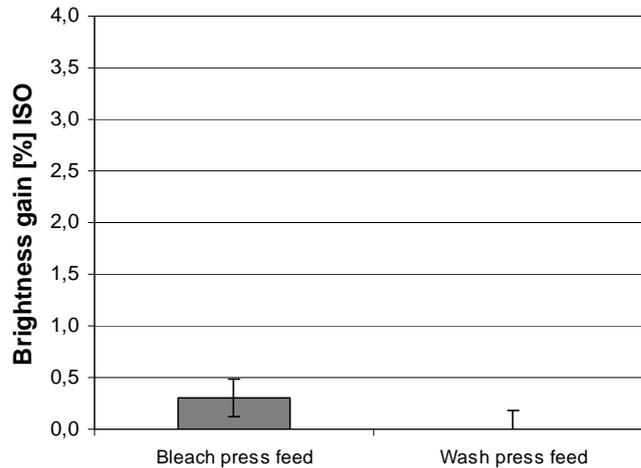


Figure 7.9 Effect of change on brightness in PGW 2 process. Retention time in MC tower 120 min.

There was no improvement in the final brightness; see Figure 7.9. Also the TOC was at a constant level in the MC stage. The only positive effect was that changes in water circulations reduced the manganese content in the bleaching stages by approximately 20%.

7.2.3 GW

The GW process was also a typical grinding process where the use of residual peroxide had not received much attention. The wash press filtrate with residual peroxide was either recycled to dilution prior to the bleach press, or used for the dilution of bleached pulp together with PM white water. Waste water was taken out from the bleach press and from the disc filter; see Figure 7.10.

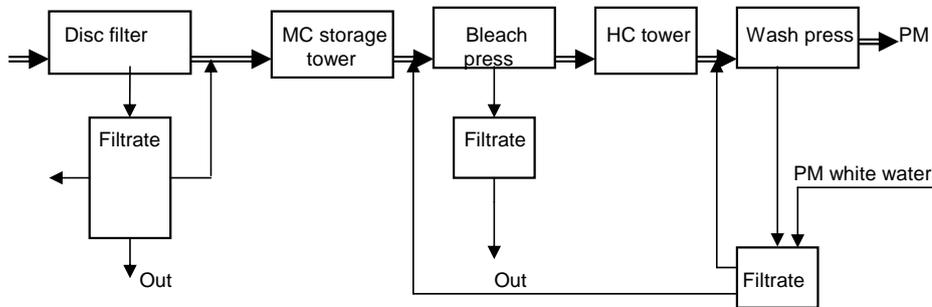


Figure 7.10 The GW process.

In this process, bleached pulp was diluted with both PM white water and wash press filtrate so that approximately 45% of the dilution water was wash press filtrate. Nearly half of the filtrate from the wash press filtrate tank was used in the dilution of bleached pulp, and half in the press showers. In the mill experiments, the process was changed so that the disc filter pulp and the storage tower pulp were diluted with wash press filtrate instead of disc filter filtrate just as in the PGW 1 and PGW 2 processes; see Figure 7.11.

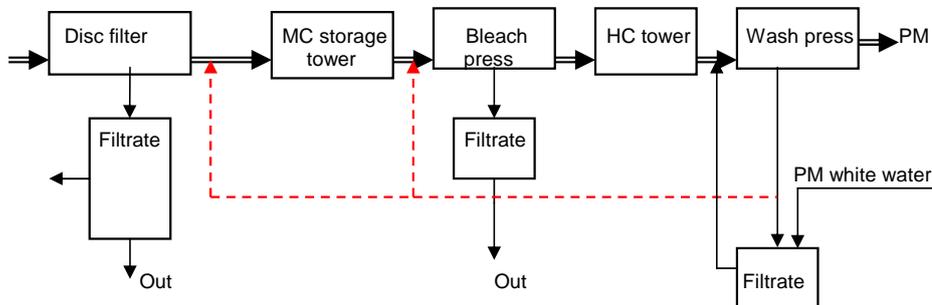


Figure 7.11 The GW process after modification.

This kind of change had no great effect on the peroxide dose because the consistency of the pulp after the disc filter was already relatively low; see Figure 7.12.

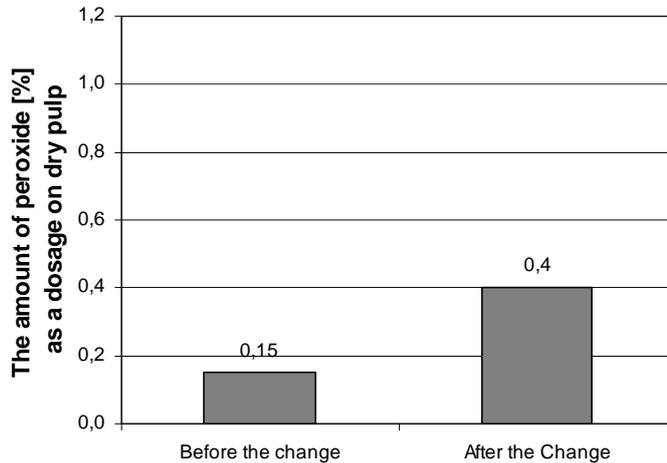


Figure 7.12 Effect of modification on peroxide dose in pre-bleaching stage.

As can be seen from Figure 7.12, the peroxide dosage achieved is not very high – only 0.4% on b. d. pulp. Also the pH increased slightly but not above 7. The effect of the modification on brightness was positive; see Figure 7.13.

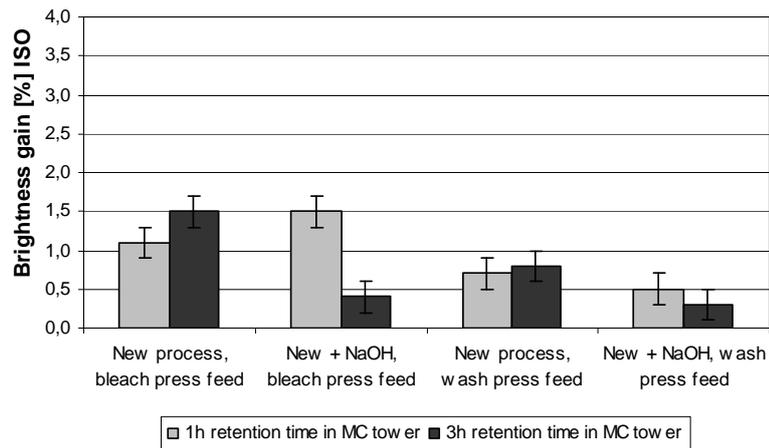


Figure 7.13 Effect of change on brightness in GW process. NaOH dose in MC stage was 0.15% on b. d. pulp when added.

The brightness gain was as high as expected. The brightness was more than 1% ISO unit higher in the bleach press. The long retention time was also advantageous in the MC stage. The sodium hydroxide added increased the brightness with a one hour retention time. With a longer, three hour retention time, however, the brightness was reduced. After the alkaline peroxide bleaching stage, the brightness was from 0.7 to 0.8% ISO units higher than in the previous process. Adding a small amount of NaOH in the MC stage decreased the final brightness slightly. In conclusion, it can be stated that if the peroxide dose is low in the MC stage, there is no need to try to activate the peroxide with sodium hydroxide. If sodium hydroxide was not added, the TOC increased by 19% due to the enhanced recycling of wash press filtrate. The sodium hydroxide enhanced the dissolution only slightly due to the low dosage. The manganese content was reduced in the bleaching stages by nearly 17%. As stated above, this should have a positive effect on brightness in the alkaline HC bleaching stage.

7.2.4 GW/TMP

This process was interesting because of its process concept, which differed from the previous one. In this process, groundwood and thermomechanical pulp were mixed together before the bleach press. Wash press filtrate with residual peroxide was either recycled into the dilution after the HC tower together with PM white water or into the dilution of TMP prior to the MC tower; see Figure 7.14.

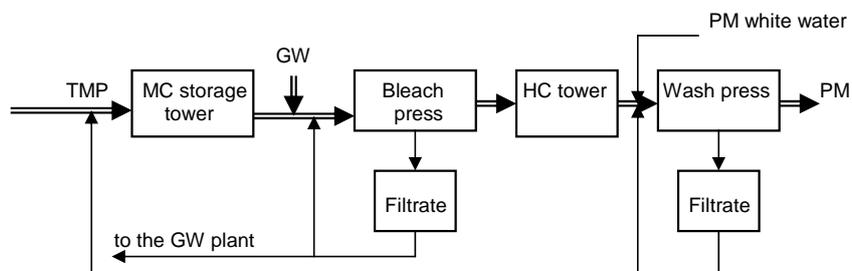


Figure 7.14 The GW/TMP process.

In this process, bleached pulp was diluted after the HC tower so that more than half of the dilution water was wash press filtrate. The volume of recyclable wash press filtrate was not very high, but this was compensated by the higher peroxide concentration in the wash press filtrate. The process was modified by diluting both the GW and the TMP into a lower

consistency than the TMP alone in the MC tower. The aim of this measure was to maximize the pre-bleaching performance in the MC stage. The mixture of the pulps was diluted only with the wash press filtrate by using a 50% higher filtrate volume; see Figure 7.15.

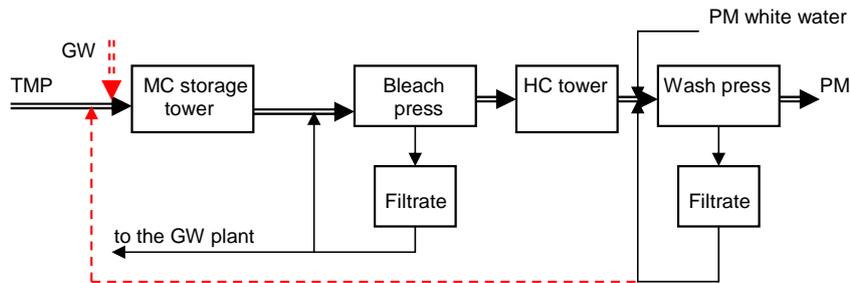


Figure 7.15 The GW/TMP process after modification.

After the first circulation, the residual peroxide was re-circulated to the GW plant as bleach press filtrate. The effect of the modification on the peroxide dose and brightness is shown in Figures 7.16 and 7.17.

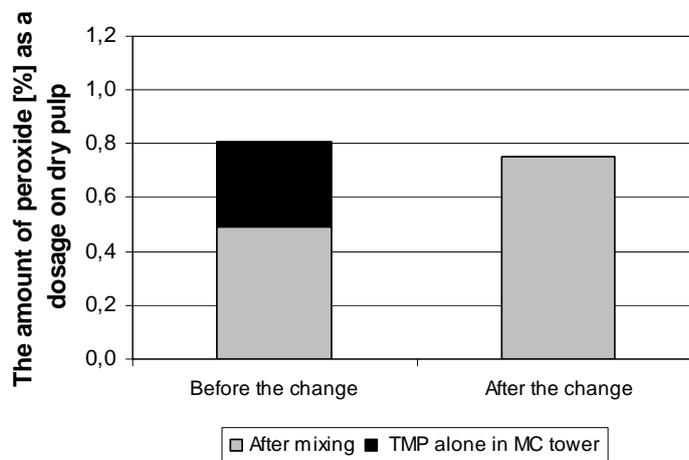


Figure 7.16 Effect of modification on peroxide dose in pre-bleaching stage.

As shown in Figure 7.16, the amount of peroxide increased by approximately 40% in the pulp mixture after the modification. Another important matter concerning bleachability is that after the modification, the whole pulp mixture got a longer retention time in the MC tower. The modification had no effect on the pH of the pulp mixture.

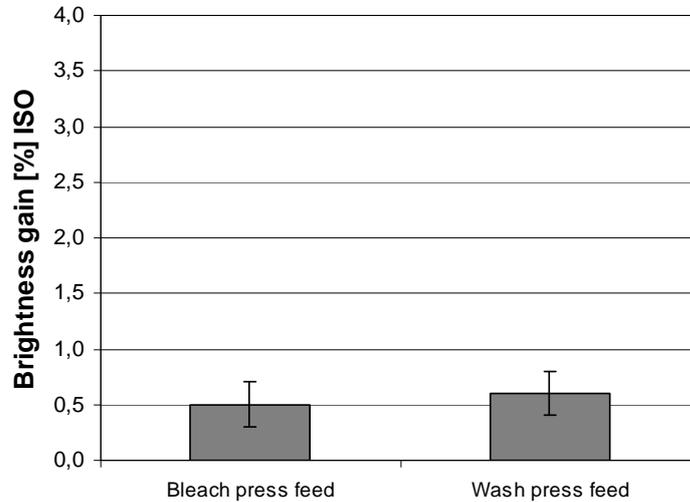


Figure 7.17 Effect of modification on brightness in GW/TMP process. Retention time in MC tower 120 minutes.

In contrast, compared to the previous processes, the brightness gain was at the same level after the alkaline peroxide bleaching as after the pre-bleaching stage, or even slightly higher. The brightness was approximately 0.5% ISO units higher compared to the previous process. The modification did not affect the TOC of the bleach press filtrate, but the manganese content in the bleaching stages was reduced by 24% due to the modification. Peroxide consumption was nearly 20% in the MC stage.

7.2.5 BCTMP

At the end of the process, close to the bleaching stages, there are no great differences in water circulations between the BCTMP process and the other previous processes. The greatest differences are at the beginning of the process. Regarding the water usage towards the end of the process, the dilution after the HC tower was done with a mixture of wash press filtrate and fresh water; see Figure 7.18. The amount of fresh water used in this dilution was very low. Most of the dilution water was taken from the wash press filtrate tank. Due to the dilution rate and high peroxide dose in the HC stage, the peroxide concentration in the wash press filtrate was very high and, at the same time, the amount of recyclable wash press filtrate was very low.

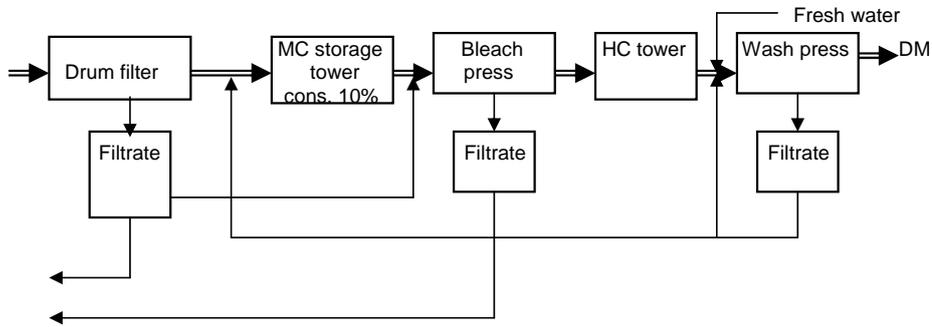


Figure 7.18 The BCTMP process.

The process was changed by slightly increasing the amount of fresh water used after the HC tower. This made it possible to recycle more wash press filtrate and residual peroxide to the dilution before the MC stage. The pulp consistency of the MC tower was decreased so that there was no need to use a drum filter filtrate in the dilution after the MC tower; see Figure 7.19.

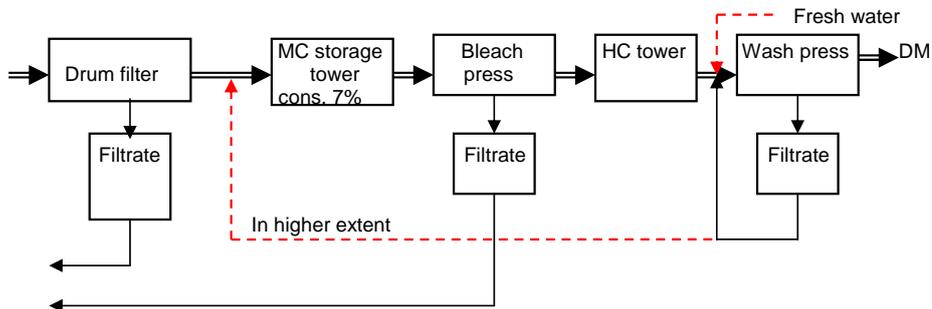


Figure 7.19 The BCTMP process after modification.

Due to the modification, the consistency of the pulp in the MC tower was decreased from 10 to 7%. The effect of the modification on the peroxide dosage is shown in Figure 7.20.

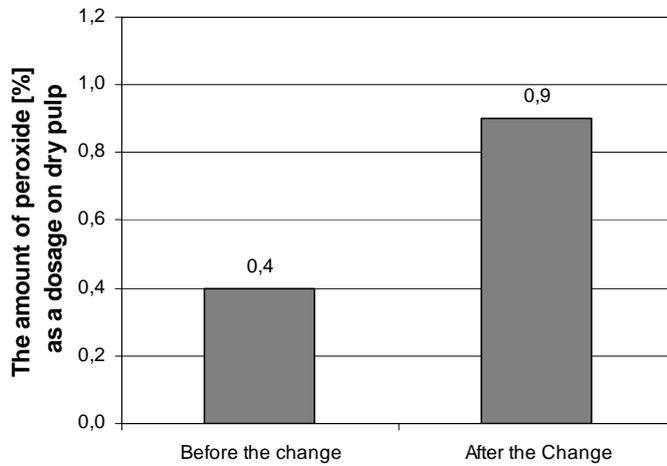


Figure 7.20 Effect of modification on peroxide dose in pre-bleaching stage.

The peroxide dosage more than doubled because of the modification. Also the pH, which was already above neutral, increased slightly in the MC stage. The TOC was at the same level, but as seen before, there was a clear reduction in the manganese content. The effect of the modification on brightness is shown in Figure 7.21.

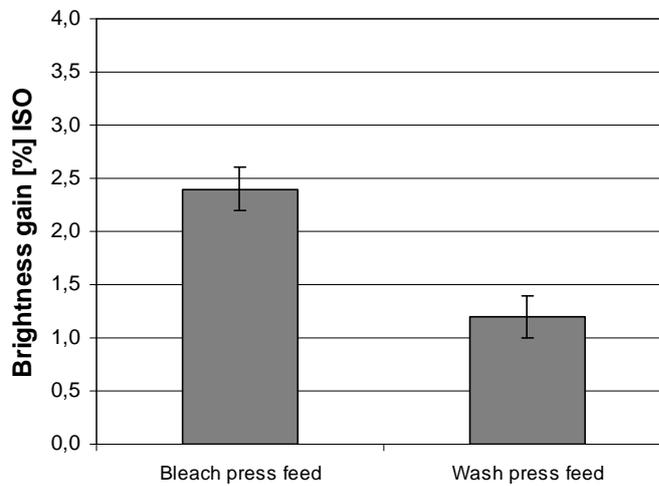


Figure 7.21 Effect of modification on brightness in BCTMP process. Retention time in MC tower 20 minutes.

Brightness was increased by over 2% ISO in the MC stage and over 1% ISO after the alkaline bleaching stage. As before, nearly 50% of the brightness gain achieved in pre-bleaching was seen furthermore in the wash press feed.

7.3 Summary of the mill experiments

Figure 7.22 represents the effects of enhanced recycling on peroxide dosages in the MC stage and brightness before and after the alkaline peroxide bleaching stage.

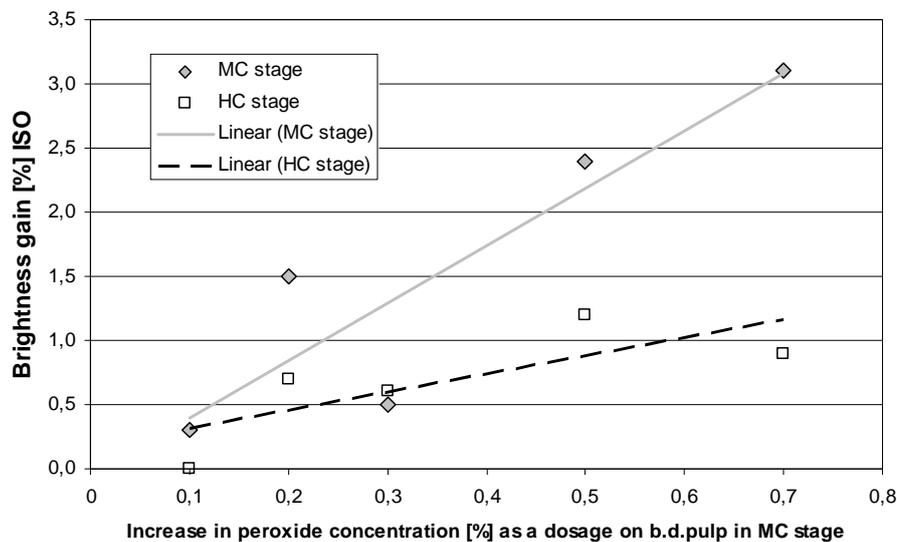


Figure 7.22 Effect of enhanced recycling on brightness.

The increase in peroxide dosage was case-specific. Doses in the current situation were between 0.2 and 0.5% on b. d. pulp, and after the modification, the doses were between 0.4 and 0.9% on b. d. pulp. In cases with the relatively highest increase in peroxide doses, the brightness gain was the greatest. In the MC stage, the brightness gain varied from 0 to 3% ISO units. After the alkaline peroxide bleaching stage, the typical gain was 1% ISO unit or less. It can roughly be said that one third of the brightness gain achieved prior to the alkaline peroxide bleaching stage can be seen in the final brightness. In one case, PGW 2, the recycling was already at a level that could not be improved any further. Table 7.1 shows how the pH, TOC and manganese contents are affected by enhanced recycling.

Table 7.1. The effect of enhanced recycling on pH, TOC and Mn content in pre-bleaching stage.

Process description	pH in MC stage		Increase in TOC [%] in water phase	Reduction of Mn content [%]
	In current process	After modification		
PGW 1	6.7	7.2	28	33
PGW 2	7.1	7.4	1	21
GW	6.1	6.7	19	17
GW/TMP	6.2	6.1	0	24
BCTMP	8.8	9.1	3	19

A comparison of results in Table 7.1 shows that particularly in the cases where recycling was increased the most, the TOC in water phase also increased. This is due to the dissolved organic compounds that are released in the alkaline peroxide bleaching stage into the wash press filtrate. There were three cases where recycling had no effect at all on the TOC. This can be explained by the fact that in these cases, the dissolved compounds have already been recycled prior to the disc filter even before the modification.

The pH was slightly increased by the enhanced circulation of the wash press filtrate. This effect was easiest to see in cases where the pH was nearly neutral. Rearrangements had a significant effect on the manganese content in pre-bleaching stages. The Mn content decreased in all cases by approximately 15-30%. This was due to the lower manganese content of wash press filtrate compared to the disc filter filtrate.

7.3 Conclusions

The aim of the mill experiments was to clarify how the enhanced use of residual peroxide affects the brightness, pH, Mn content and TOC prior to the alkaline peroxide bleaching stage, and final brightness.

In almost every mill, it was possible to enhance the use of residual peroxide as a pre-bleaching agent. The most simple way to enhance recycling was to optimize water circulations and to dilute disc filter pulp with wash press filtrate. In the MC stage, the brightness gain varied from 0 to 3% ISO units due to the enhanced recycling. A comparison of the change in peroxide doses and manganese contents in the MC pre-bleaching stage with the results of the simulation model (section 8) reveals that the results were very well in line with each other.

As a combination of a higher initial brightness and a lower manganese content, a typical gain in the final brightness was 1% ISO unit or less after the alkaline peroxide bleaching stage. This change does not seem remarkable, but as generally known, the last percentage is the most expensive and difficult to achieve. For this reason, cost savings might become quite high especially with high brightness mechanical pulps.

In general, it can be said that there were no differences between the behaviour of different types of processes (GW, PGW, TMP and BCTMP). Enhancement of recycling led to a similar conclusion.

SIMULATION

8 SIMULATION OF WATER CIRCULATIONS

As demonstrated in previous sections, it is possible to enhance the use of residual bleaching chemicals by rearranging water circulations. In addition to the effective use of bleaching chemicals, the control of harmful substances such as transition metals has been a critical factor in successful bleaching. These harmful metals are typically controlled by adding chelating agents such as DTPA or EDTA to the pulping process, but also carefully arranged water circulations can be very helpful. Therefore, it must be born in mind that in order to achieve as effective and economic process as possible, we have to handle several variables at the same time. One very useful tool for this purpose is simulation. Every process is a compromise between different variables, but these variables can rather easily be controlled by choosing a way to arrange water circulations.

The main aim of this simulation study is to observe how water circulations should be arranged in order to achieve effective recycling of residual peroxide and as small manganese content as possible in the alkaline peroxide bleaching stage using the **BALAS** simulation tool.

8.1 Simulation model

The simulation model is based on a typical pressurized ground wood (PGW) process. Five different water circulation cases (A to E) are compared to each other at a constant water usage level. The consistency profile is the same in all cases except for case E with a cut-off press. Otherwise, only water circulations are changed. The basic process is shown in Figure 8.1.

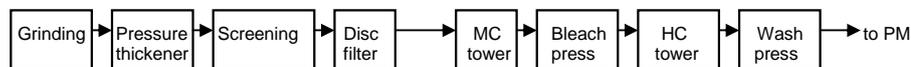


Figure 8.1 Basic process of simulation.

Assumptions for simulation:

1. Manganese is well chelated (100% in water phase after grinding)
2. Peroxide dosage 3.0% on dry pulp in bleaching
3. Consistency of pulp after disc filter 12%
4. Peroxide consumption:
 - 70% of added peroxide is consumed in bleaching
 - 30% of recycled peroxide is decomposed before the disc filter and
 - 15% of recycled peroxide is decomposed in the MC (pre-bleaching) stage

The production rate of the process line was set to 300 b. d. tons a day with a standardized PM water usage of 10 m³/t (35,8 l/s). Reject handling was excluded from the simulation to simplify the process because it would not have had a remarkable effect on the results. In addition, commonly used twin wire presses with showers to clean the wires were chosen for the simulation.

8.1.1 Case A

Case A is a typical and traditional counterflow process, where no attention is paid to the utilization of residual peroxide. The wash press filtrate is circulated prior to the disc filter where the consistency of pulp is low, and therefore, the pulp is not brightened considerably.

The complexation of manganese is usually done at the very beginning of the process because the main source of transition metals is the wood raw material itself. In practice, this means that the manganese content is highest at the beginning of the process. Because of this, in terms of manganese content, a good option is to remove waste water from the process from the hot loop, as in **Case A**. In **Case A**, half of the waste water is removed from the hot loop and the rest from the disc filter clear filtrate tank. The advantage of taking waste water from the disc filtrate is that clear filtrate does not contain fibers, which means that fiber loss is minor.

Peroxide bleached pulp is diluted after the HC tower by using half PM white water and half wash press filtrate. The rest of the PM white water is used in shower waters in grinding. Other issues that should be pointed out from **Case A** is that disc filter filtrate, which has a relatively high manganese content, is used for the dilution of the disc filter pulp itself and also in the shower water of the bleach press and the wash press. This will have a negative effect on the

manganese content and bleaching performance in HC peroxide bleaching. A flowsheet of **Case A** with a consistency profile is shown in Figure 8.2.

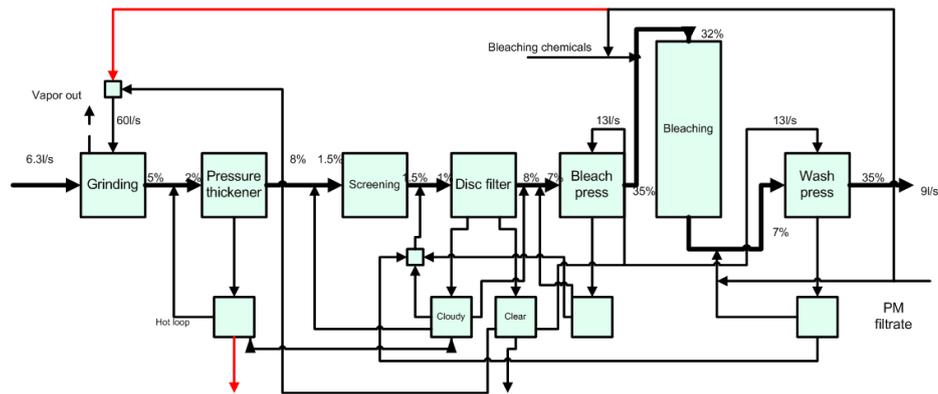


Figure 8.2 Flowsheet of **Case A**.

8.1.2 Case B

Case B differs from **Case A** mostly with regard to the utilization of residual peroxide. In **Case B**, wash press filtrate (residual peroxide) is recycled instead of disc filter filtrate to the dilution of disc filter pulp, which makes it possible to increase brightness in the MC pre-bleaching stage (pulp storage tower before the bleach press).

In **Case B**, waste water is not taken from the hot loop, which means that the manganese content is quite high until the water reaches the disc filter. For this reason, **Case B** also represents typical TMP (thermomechanical pulp) and GW (groundwood) processes. In **Case B**, half of the waste water is removed from the bleach press filtrate tank and the rest from the disc filter clear filtrate tank. By taking waste water from the bleach press, one can ensure that the residual alkali and dissolved compounds from the HC bleaching stage do not disturb the complexation of manganese at the beginning of the process. If the pH of the process rises above neutral at the beginning, it might have a hazardous effect on the chelation efficiency of manganese /54/.

PM white water is added to the process as in **Case A**. Peroxide bleached pulp is diluted after the HC tower by using half PM white water and half wash press filtrate. The rest of the PM white water is used in shower water in grinding. Also in **Case B**, disc filter filtrate is used in the shower water of the bleach press and wash press. A flowsheet of **Case B** is shown in Figure 8.3.

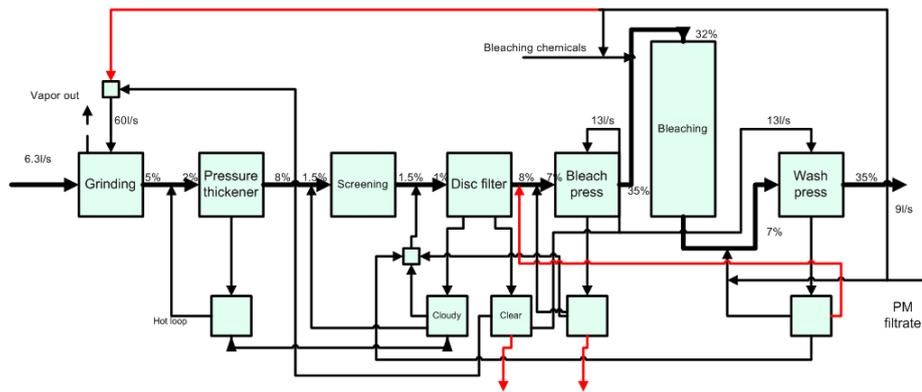


Figure 8.3 Flowsheet of **Case B**.

8.1.3 Case C

In **Case C**, the intent was both to utilize residual peroxide in the MC stage as in **Case B** and to avoid the convection of manganese to the alkaline HC peroxide bleaching stage. This was carried out by using wash press filtrate for the dilution of disc filter pulp and by replacing the disc filter filtrate with PM white water (which does not contain large amounts of manganese) in the showers of the bleach press and wash press. In **Case C**, half of the waste water is removed from the hot loop, which was an advantageous choice in terms of manganese content, and the rest from the bleach press filtrate tank.

PM white water is added to the process as in **cases A** and **B** with the exception that the showers of the bleach press and wash press also use PM white water. A flowsheet of **Case C** is shown in Figure 8.4.

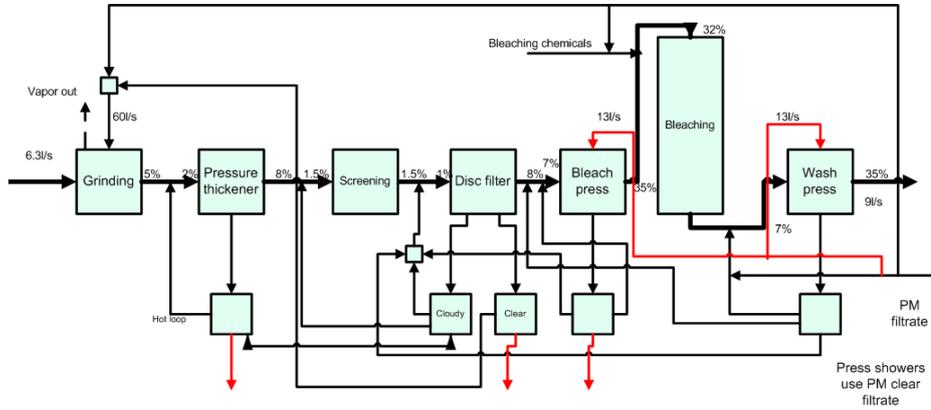


Figure 8.4 Flowsheet of **Case C**.

8.1.4 Case D

Case D is quite similar to **Case C**. The only changes can be found in the bleach press showers and the shower water in grinding. In **Case D**, the bleach press uses its own filtrate in the showers. In grinding showers, the water used is disc filter clear filtrate. PM white water is added into the dilution of bleached pulp as in the other cases, and also into wash press showers. Furthermore, the rest of the PM white water is used in dilution between the screening and disc filter. With this kind of change, it is possible to arrange the countercurrent flow from the disc filtrate to grinding, and to concentrate the manganese as much as possible into the hot loop circulation. Waste water is removed just as in **Case C**. A flowsheet of **Case D** is shown in Figure 8.5.

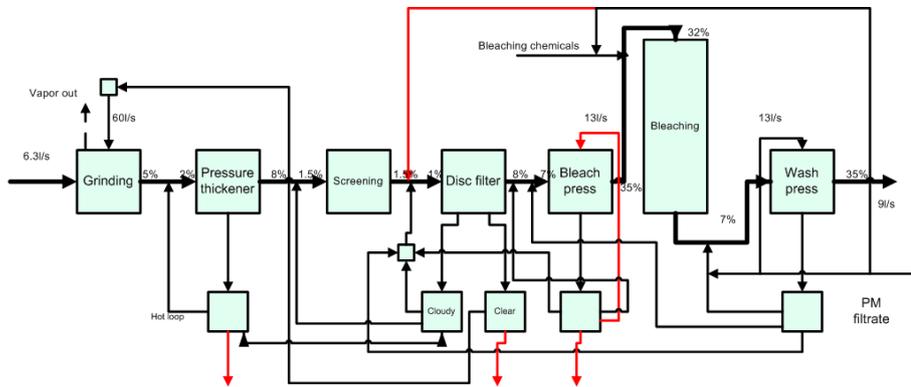


Figure 8.5 Flowsheet of **Case D**.

8.1.5 Case E

Case E differs from the other cases because of an additional cut-off press placed after the disc filter. The cut-off press allows maximizing the utilization of residual peroxide because the consistency in the MC pre-bleaching stage is higher. Furthermore, the cut-off press efficiently prevents the convection of manganese to the bleaching stages. Otherwise, water circulations are quite close to those in **Case D**. PM white water is added to the dilution of bleached pulp and also to wash press showers. The rest of the PM white water is supplied to the disc filter clear filtrate tank. In **Case E**, waste water is removed just as in **cases C** or **D**. A flowsheet of **Case E** is shown in Figure 8.6.

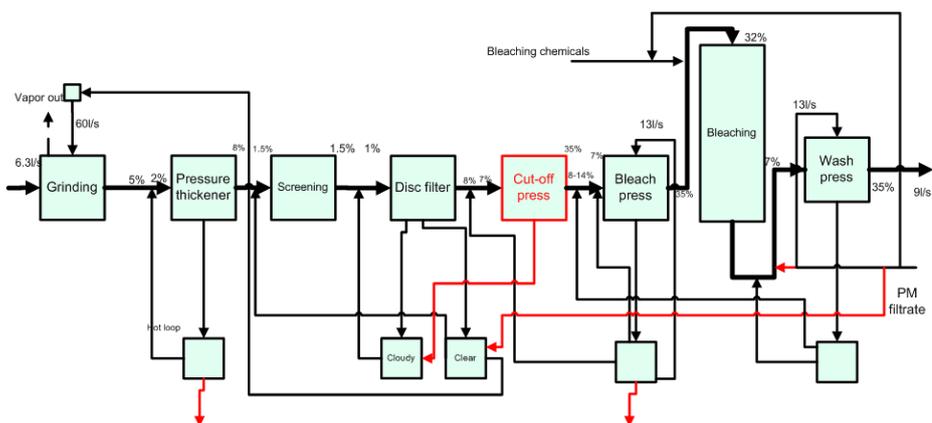


Figure 8.6 Flowsheet of **Case E**.

By using the cut-off press, water circulations can be divided effectively into two sections. Both sections have their own functions in terms of bleaching efficiency. The function of the first section from grinding to the cut-off press is to chelate the manganese to the water phase and remove it from the process. The function of section two is to use bleaching chemicals as well as possible to maximize bleaching performance and brightness gain cost-effectively.

Main differences regarding simulation cases are summarized into the table 8.1

Table 8.1 Summary of the main differences between the simulation cases A to E.

Case	Waste water out from			Recycling of wash press filtrate			PM white water usage					Bleach press shower water		
	Hot loop	Disc filter	Bleach press	Prior to the disc filter	After the disc filter	Additional cut-off press	After the HC bleaching	Grinding showers	Prior to the disc filter	Wash press shower water	Clear filter filtrate tank	Disc filter filtrate	PM white water	Bleach press filtrate
A	X	X	-	X	-	-	X	X	-	-	-	X	-	-
B	-	X	X	-	X	-	X	X	-	-	-	X	-	-
C	X	-	X	-	X	-	X	X	-	X	-	-	X	-
D	X	-	X	-	X	-	X	-	X	X	-	-	-	X
E	X	-	X	-	X	X	X	-	-	X	X	-	-	X

8.2 Simulation results

The simulation results deal with the effectiveness of residual peroxide utilization and minimizing the manganese contents in the bleaching stages. These two factors have a remarkable effect on bleaching efficiency and bleaching chemical costs. Especially the concentration of residual peroxide in the MC pre-bleaching stage is examined, as well as the amount of manganese in the alkaline peroxide bleaching stage. The following results verify how much can be done by choosing the appropriate water circulation arrangements.

8.2.1 Residual peroxide

To maximize the utilization of residual peroxide, it should be recycled to a specific pre-bleaching stage. The most reasonable location for a pre-bleaching stage in a typical PGW, GW, TMP or BCTMP process is immediately after the disc filter, before the bleach press and the alkaline HC bleaching stage. Prior to the disc filter, consistencies are usually too low for effective pre-bleaching. Figure 8.7 shows simulation results on how water circulations affect the peroxide dose in the pre-bleaching stage.

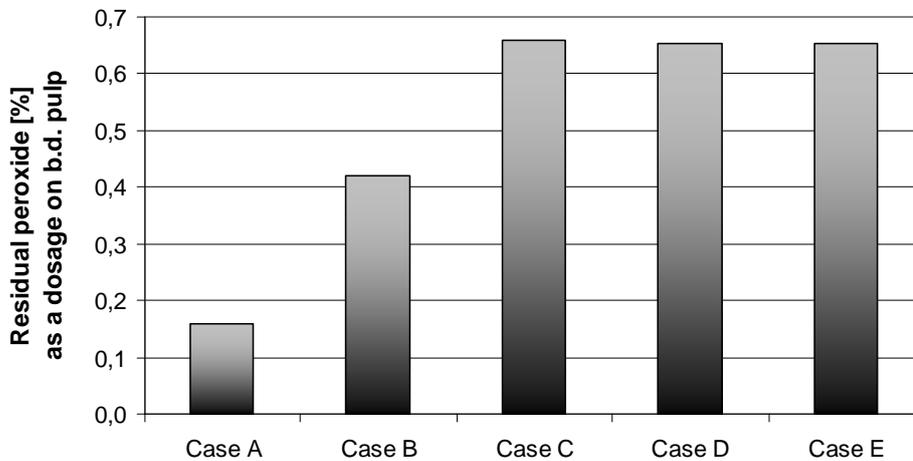


Figure 8.7 Simulated peroxide doses in MC pulp storage tower.

It is easy to discover that by enhancing recycling, the residual peroxide dose will increase; see Figure 8.7. In **Case A**, residual peroxide was recycled prior to the disc filter, which can be seen as a low peroxide dose in the pre-bleaching stage. By recycling the wash press filtrate to the dilution of disc filter pulp, the peroxide dose is more than doubled in the MC stage. In addition to that, the change in shower waters further increases the peroxide dose in **cases C** and **D** so that the dose is about 0.65% on b. d. pulp. Similar doses have been measured also in real processes.

In **cases A to D**, the consistency of pulp in MC tower is constantly 8%, but in **Case E** at the same water usage, the consistency of pulp is 14% because of an additional cut-off press before the MC stage. The effect of the consistency on the pre-bleaching efficiency can be perceived as a higher peroxide concentration; see Figure 8.8.

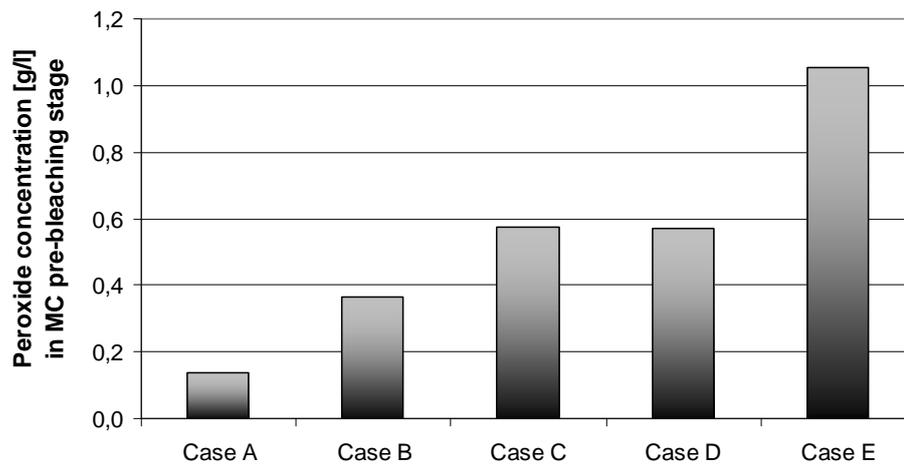


Figure 8.8. Simulated peroxide concentrations in MC pulp storage tower.

The results in Figure 8.8 explain why it would be reasonable to add a cut-off press into the process. Effective recycling with a cut-off press, **Case E**, will increase the concentration of peroxide in the MC stage significantly. The bleaching response of recycling in terms of final brightness was reported by Lippert /2/ to be approximately 2% ISO with very similar conditions. In a basic case, **Case A**, residual peroxide is circulated prior to the disc filter, which causes a very low peroxide concentration in the MC stage; see Figure 8.8.

The results shown above are simulated at a constant water usage level, 10 m³/t of PM white water fed into the process. This raises the question of how the peroxide concentration would change in the MC stage if the amount of water available was something else than that given above. Figure 8.9 describes the situation where the amount of PM white water used increases.

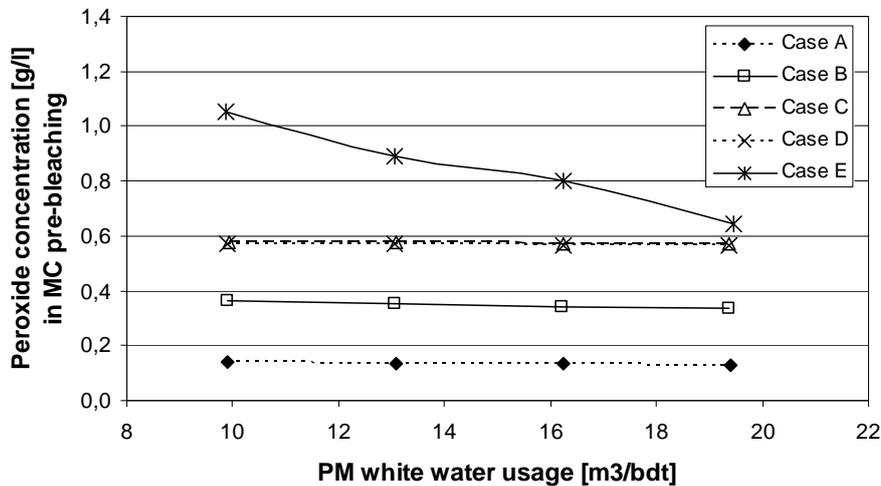


Figure 8.9. Effect of increased water usage on peroxide concentrations in MC pulp storage tower. In cases A to D, make-up water is used prior to the disc filter. In case E, half of the make-up water is utilized in the dilution of bleached pulp and all of the wash press filtrate tank overflow is used in the MC stage.

In **Case E**, the consistency of the pulp decreases in the MC stage while water usage is increased, because half of the make-up water is used in the dilution of bleached pulp and all of the wash press filtrate tank overflow is used in the dilution of pulp after the cut-off press. In **cases A to D**, make-up water is used prior to the disc filter, which does not have a remarkable effect on the pre-bleaching stage. In other words, in **Case E** when the amount of water used was increased, the consistency of the pulp and also the peroxide concentration decreased in the MC stage. The consistency of pulp in **Case E** decreased from 14% to 8%, which is exactly the same as in all other cases. This is the reason why the concentration of peroxide is at the same level in **case E** as in **cases C and D** when 19.4 m³/t PM white water was used.

8.2.2. Manganese

Manganese is known to be the most harmful transition metal ion in the alkaline peroxide bleaching of mechanical pulps. It is very important to keep the manganese content as low as possible in alkaline peroxide bleaching to ensure maximized bleaching performance. Because the effect of manganese is minor in neutral conditions in the MC stage, the inspection of manganese contents is focused on the alkaline HC peroxide bleaching stage.

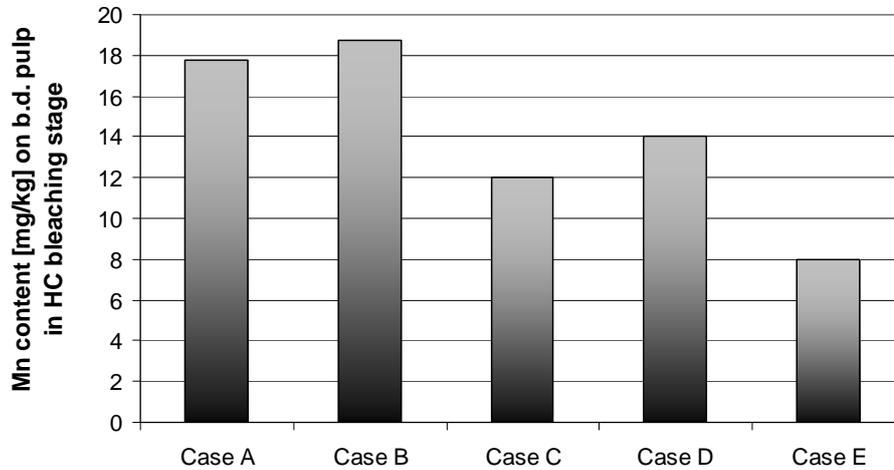


Figure 8.10. Simulated manganese ion contents in alkaline HC peroxide bleaching.

A comparison of cases A and B in Figure 8.10 leads to the idea of opening the hot loop circulation. The manganese content is a bit lower in Case A because half of the waste water is removed from the hot loop where the metal content is the highest. In cases B to D, the disc filter pulp was diluted with wash press filtrate which contains less manganese than the disc filter filtrate itself. This should decrease the manganese content in the bleaching sequence. Nevertheless, opening the hot loop compensates for the advantage that can be achieved by using wash press filtrate instead of disc filter filtrate in the dilution of disc filter pulp.

It is also easy to detect from Figure 8.10 that by using PM white water instead of disc filter clear filtrate in the bleach press and wash press showers, the reduction of manganese content in the HC bleaching stage is remarkable, as in Case C. This kind of rearrangement minimizes convection of manganese over the disc filter. In Case D, the manganese content is a bit higher compared to Case C. This is because the bleach press showers use their own filtrate instead of PM white water. This allows concentrating the manganese into its own circulation.

Regarding manganese contents, Case E is clearly the best. The convection of manganese over cut-off press in Case E is very limited. The manganese content in this case is less than half of that in cases A and B and two thirds of that in cases C and D. The effect of the Mn content reduction observed on bleaching performance in alkaline peroxide bleaching stage is

remarkable. This is another reason why the cut-off press investment might be reasonable. Of course, if disc filter filtrate is used in the bleach press and wash press showers, this advantage will be lost.

Again, the results shown above are simulated at a constant water usage level, 10 m³/t of PM white water fed into the process. The question now is how the manganese content would change in the alkaline HC peroxide bleaching stage if the amount of water available was something other than the above. Figure 8.11 describes the situation where the PM white water usage is increased.

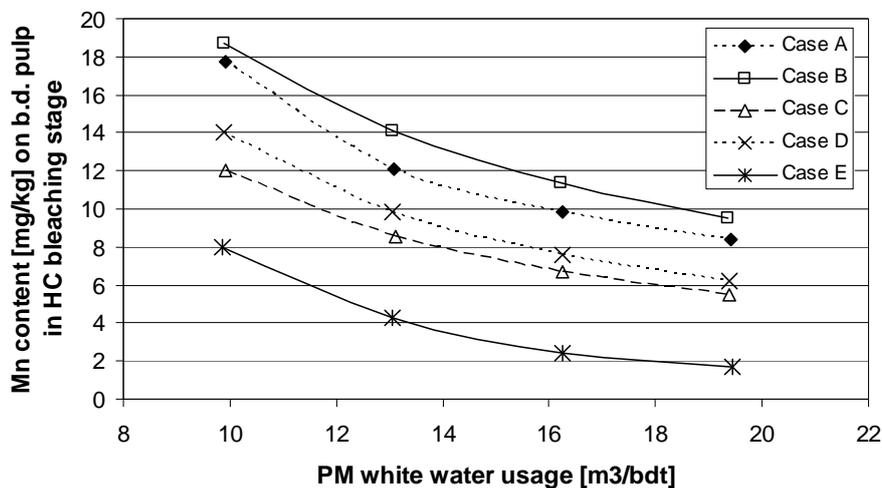


Figure 8.11. Effect of increased water usage on manganese contents in HC peroxide bleaching stage. In cases A to D, make-up water is used prior to the disc filter. In Case E, half of the make-up water is used for the dilution of bleached pulp and all of the wash press filtrate tank overflow is used in the MC stage.

It is easy to conclude from Figure 8.11 that the amount of water available has a great effect on the manganese content through the whole process. The manganese content is decreased if more water is available. However, **Case E** stands out clearly from the other cases because of the cut-off press. A rough estimation is that in **Cases C** and **D**, 50% more PM white water is needed than in **Case E** to achieve the same manganese content in the alkaline bleaching stage, and in **Cases A** and **B** twice as much PM white water is needed as in **Case E**.

8.3 Summary

The aim of simulation study was to investigate on how water circulations should be arranged in order to recycle residual peroxide effectively and to achieve as small a manganese content as possible in the alkaline peroxide bleaching stage using the **BALAS** simulation tool.

Based on the simulation results:

1. Residual peroxide can be utilized very effectively if

- the disc filter pulp is diluted only with wash press filtrate before the MC storage tower.
- an additional cut-off press is placed immediately after the disc filter and pulp is diluted only with wash press filtrate. This may even lead to better results than the former measure. The consistency of pulp will increase, which will have a significant effect on the peroxide concentration in the MC stage.

2. Manganese content in the HC alkaline peroxide bleaching stage can be reduced if

- the disc filter pulp is diluted only with wash press filtrate before the MC storage tower.
- disc filter clear filtrate is not used in the bleach press and wash press showers. Instead, the showers use either PW white water or a filtrate of their own.
- an additional cut-off press is placed after the disc filter, and pulp is diluted only with wash press filtrate.
- waste water is also removed from the hot loop (PGW process).

In conclusion, water circulations need to be divided into two sections. Both of these sections have their own purpose. Section one: manganese removal. Section two: brightening of pulp. This division is presented in Figure 8.12.

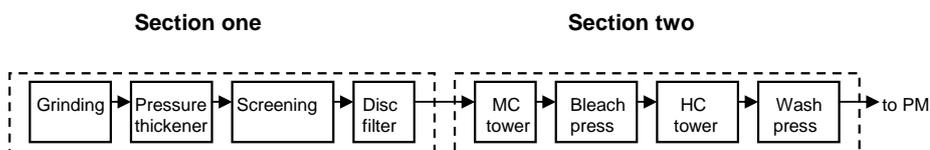


Figure 8.12. Division of water circulations in PGW process.

9 PROFITABILITY ASSESSMENT

Based on the results presented in this study, it seems to be quite obvious that economical profitability can be achieved by rearranging water circulations and recycling residual peroxide. As stated before, each process is unique, but general trends are quite easy to identify also from these results. Figure 9.1 presents the effect of the brightness gain in the pre-bleaching stage on the final brightness. It is the best estimation based on all of the laboratory and mill experiments presented in this thesis.

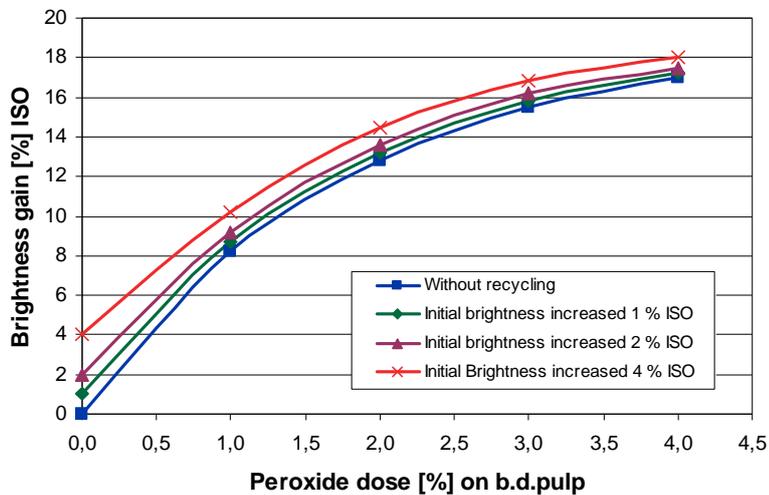


Figure 9.1 The effect of brightness gain in pre-bleaching stage on final brightness

It is clear that the higher the initial brightness is, the higher will also the final brightness be; see Figure 9.1. HC bleaching with high peroxide charges will reduce the benefit achieved in the pre-bleaching stage. This figure should give a realistic picture of how the brightness gain achieved in pre-bleaching affects the peroxide dosage needed in the alkaline peroxide bleaching stage. Based on Figure 9.1 and the results of the mill experiments, cost savings were estimated for the processes examined in the mill experiments; see Table 9.1.

Table 9.1 Estimation of cost savings based on results of mill experiments. Chemical prices used in the calculations: H₂O₂ 500 eur/t, NaOH 300 eur/t. Sodium silicate dosage assumed to be constant.

Process description	Effect on final brightness [%] ISO	Cost savings [%] in bleaching chemicals (H ₂ O ₂ and NaOH)	Approximated cost savings [EUR/ yr] if 100 000 tons b. d. pulp were produced
PGW 1	+ 0.9	9	250 000
PGW 2	0	0	0
GW	+ 0.7	9	200 000
GW/TMP	+ 0.6	10	200 000
BCTMP	+ 1.2	16	400 000

Based on the results in Table 9.1, great savings can be achieved by rearranging water circulations. Currently, the typical capacity of a mechanical pulping plant is between 200 000 and 300 000 tons, which in practice means possible savings between 500 000 and 1 000 000 euros per year. Figure 9.2 illustrates the overall situation concerning the possibilities to save bleaching chemical costs by more effective recycling of residual peroxide.

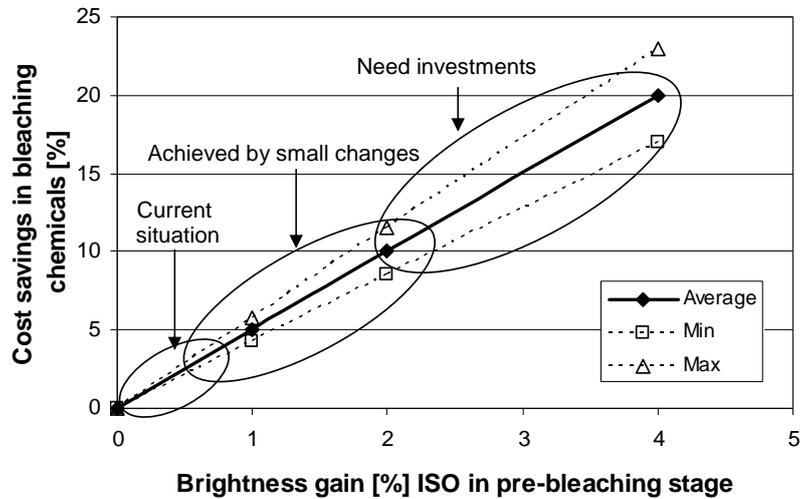


Figure 9.2 Effect of brightness gain in pre-bleaching stage on final brightness.

Figure 9.2 represents realistic possibilities for savings in bleaching chemicals through the recycling of residual peroxide. The overall situation is such that especially in older mills, water circulation arrangements should be improved a great deal to maximize their bleaching chemical usage. It is quite common that for some reason a small part of the residual peroxide is recycled prior to the bleaching stage, but not for this purpose. Brightness prior to the alkaline peroxide bleaching stage could be increased 1-3% ISO units and the final brightness 0.5-1% ISO units with minor changes. An investment in a special MC stage with an additional press would improve the bleaching efficiency even more. Instead of losing the residual chemicals, cost savings might rise up to 20%.

10 CONCLUSIONS

The amount of water available is usually restricted, which leads to a situation where a complete understanding of the process including water circulations and the influence of dissolved water components is essential. The main aim of this thesis was to introduce and examine the possibilities for the efficient use of residual peroxide by means of water circulation rearrangements.

In this thesis, it was shown that with optimum recirculation of residual peroxide the final brightness can be improved or chemical costs can be decreased. From scientific perspective, it was important to discover that recycled peroxide was even more effective pre-bleaching agent compared to fresh peroxide. This must be due to the peracetic acid in wash press filtrate that has been formed in alkaline bleaching stage. Even short retention time was adequate and the activation of residual peroxide using sodium hydroxide was not necessary.

There are several practical possibilities to use residual peroxide in bleaching. A modern mechanical pulping process line consists of defibration, screening, a disc filter, a bleach press, HC peroxide bleaching and a wash press. The most advisable way to utilize residual peroxide in one-stage HC process is to recycle wash press filtrate into the dilution of disc filter pulp (MC pre-bleaching stage). Recycling of residual peroxide prior to the disc filter is not recommended because of low consistencies. An arrangement such as this would be beneficial in terms of reduced convection of manganese to the alkaline peroxide bleaching stage. Manganese originates from wood material and is removed to the water phase already in the early stages of the process. For this reason, it would be beneficial to divide water circulations into two sections. Both of these sections have their own purposes. Section one: enhanced manganese removal. Section two: efficient brightening of pulp.

The water circulations can be divided into two sections if the disc filter pulp is diluted only with wash press filtrate before the MC storage tower. The situation is even better if an additional cut-off press is placed directly after the disc filter, and pulp is diluted only with the wash press filtrate. The consistency of pulp will increase, which will have a significant effect on the peroxide concentration in the MC stage. In terms of manganese content, it is essential

to avoid the use of disc filter filtrate in the bleach press and wash press showers. An additional cut-off press would also be beneficial for this purpose.

As a combination of a higher initial brightness and lower manganese content, the typical brightness gain is approximately 0.5-1% ISO units after the alkaline peroxide bleaching stage. This change does not seem to be remarkable, but as generally known, the last unit is the most expensive and difficult to achieve. The estimation for cost savings is not unambiguous. For example in mill case GW/TMP, a 0.6% ISO higher final brightness gave 10% savings. With a hypothetical 200 000 ton annual production, this means that the mill could save more than 400 000 euros per year in bleaching chemical costs. In general, it can be said that there were no differences between the behaviour of different types of processes (GW, PGW, TMP and BCTMP). The enhancement of recycling suggested nothing to the contrary. However, one has to remember that the possibility to utilize residual peroxide in older mills depends largely on the process equipment, the amount of water available and the existing pipeline connections. In brief, it can be said that each process is unique, and the same solutions cannot be applied in all cases.

REFERENCES

1. Lindholm, C.A., Bleaching, Mechanical pulping, Papermaking Science and Technology, Book 5, Sundholm, J. (Ed.), Fapet Oy, Jyväskylä, 1999, pp. 313-325.
2. Lippert, G.V., Mill experience in a PGW bleach plant using high consistency and medium consistency technology, 1991 International Mechanical Pulping Conference, 2-5 June 1991, Minneapolis, USA, pp. 171-175.
3. Lachenal, D., de Choudens, C., Bourson, L., Bleaching of mechanical pulp to very high brightness, *Tappi J.*, **70**(1987)3, pp. 119-122.
4. Abbot, J., Ault, K., Vanderaa, S., Wright, P., Reagent recycling in peroxide bleaching, *Appita* **45**(1992)6, pp. 393-396.
5. Parker, M., Mackie, D., Benefits of washing mechanical pulp, International Mechanical Pulping conference, Quebec, Canada, 2-5 June 2003, pp. 133-139.
6. Jäkärä, J., Aksela, R., Benign and effective, *Pulp Pap. Int.*, **48**(2006)1, pp. 28-31.
7. Colodette, J.L., Dence, C.W., Rothenberg, S., Factors affecting hydrogen peroxide stability in the brightening of mechanical and chemimechanical pulps, Part III: Hydrogen peroxide stability in the presence of magnesium and combinations of stabilizers, *J. Pulp Pap. Sci.* **15**(1989)2, pp. J45-J51.
8. Prasakis, J., Sain, M., Daneault, C., Metal management improves peroxide bleaching of TMP, *Tappi J.*, **79**(1996)10, pp. 161-166.
9. Lidén, J., Öhman, L.O., On the prevention of Fe- and Mn-catalyzed H₂O₂ decomposition under bleaching conditions, *J. Pulp Pap. Sci.*, **24**(1998)9, pp. 269-276.
10. Gupta, V.N., Effect of metal ions on brightness, bleachability and colour reversion of groundwood, *Pulp Pap. Can.*, **71**(1970)18, pp. 69-77.
11. Yang, W., Ni, Y., Oxygen formation during peroxide bleaching of a thermomechanical pulp and its relationship to bleaching performance. *IPPTA* **12**(2000)3, pp. 1-6.
12. Ju, Y., Ni, Y., Ohi, H., Further understanding of the manganese-induced decomposition of hydrogen peroxide, *J. Pulp pap. Sci.*, **26**(2000)3, pp. 90-94.
13. Qiu, Z., Ni, Y., Improving peroxide bleaching by decreasing manganese induced peroxide decomposition, *Pulp Pap. Can.*, **102**(2001)7, pp. 44-47.
14. Evans, T.D., Kutney, G.W., Peroxide bleaching of mechanical pulps. Part 1. Alkali darkening-the effect of caustic soda, *Svensk papperstidning*, **88**(1985)6, pp. R78-R82.
15. Wekesa, M., Ni, Y., Further understanding of the chemistry of Mn-induced peroxide decomposition, 11th International symposium on wood and pulping chemistry, Nice, France, 11-14 June 2001, vol. III, Poster presentations, pp. 429-434.
16. Colodette, J.L., Dence, C.W., Rothenberg, S., Factors affecting hydrogen peroxide stability in the brightening of mechanical and chemimechanical pulps, Part I: Hydrogen peroxide stability in the absence of stabilizing systems, *J. Pulp Pap. Sci.*, **14**(1988)6, pp. J126-J131.

17. Johns, D.T., Utilization of chelate to optimize the hydrogen peroxide bleaching process, Appita 50th Annual General Conference, 6-10 May 1996, Auckland, New Zealand, pp. 237-241.
18. Colodette, J.L., Dence, C.W., Factors affecting hydrogen peroxide stability in the brightening of mechanical and chemimechanical pulps, Part IV: The effect of transition metals in Norway Spruce TMP on hydrogen peroxide stability, *J. Pulp Pap. Sci.*, **15**(1989)3, pp. J79-J82.
19. Heikkilä, M., Vuorinen, T., Decomposition of hydrogen peroxide in catalytic cycle, 2000 International pulp bleaching conference, Halifax, Nova Scotia, Canada, 27-30 June 2000, pp. 155-160.
20. Andersen, I., Johnsen, K., Metal distribution in thermomechanical pulp, 27th EUCEPA conference - Crossing the millenium frontier, emerging technical and scientific challenges, Grenoble, France, 11-14 Oct. 1999, pp. 305-309.
21. Ni, Y., Court, G., Li, Z., Mosher, M., Tudor, T., Burt, M., Improving peroxide bleaching of mechanical pulps by enhanced chelation process, *Pulp Pap. Can.*, **100**(1999)10, pp. 51-55.
22. Basciano, C.R., Heimbürger, S.A., Importance of chemical pretreatment on the hydrogen peroxide brightening of mechanical pulps, 76th Annual Meeting of the Technical Section, Canadian Pulp and Paper Association, Montreal, 30 Jan.-2 Feb. 1990, pp. A7-A18.
23. Manchester, D.F., Pitcher, J.M., Whitning, P., Factors affecting the use of chelating agents to aid the brightening of mechanical pulps, CPPA, 70th Annual Meeting, Technical Section, 2-3 February 1984, Montreal, Quebec, pp. B339-B348.
24. Colodette, J.L., Dence, C.W., Rothenberg, S., Factors affecting hydrogen peroxide stability in the brightening of mechanical and chemimechanical pulps, Part II: Hydrogen peroxide stability in the presence of sodium silicate, *J. Pulp Pap. Sci.*, **15**(1989)1, pp. J3-J9.
25. Liimatainen, H., Haikkala, P., Lucander, M., Karojärvi, R., Tuovinen, O., Grinding and pressure grinding, Mechanical pulping, Papermaking Science and Technology, Volume 5, Sundholm, J. (Ed.), Fapet Oy, Jyväskylä, 1999, pp. 107-156.
26. Tienvieri, T., Huusari, E., Sundholm, J., Vuorio, P., Kortelainen, J., Nystedt, H., Artamo, A., Thermomechanical pulping, Mechanical pulping, Papermaking Science and Technology, Volume 5, Sundholm, J. (Ed.), Fapet Oy, Jyväskylä, 1999, pp. 159-221.
27. Lindholm, C.A., Kurdin, J.A., Chemimechanical pulping, Mechanical pulping, Papermaking Science and Technology, Volume 5, Sundholm, J. (Ed.), Fapet Oy, Jyväskylä, 1999, pp. 223-249.
28. He, Z., Ni, Y., Zhang, E., Further understanding on the formation of anionic trash during peroxide bleaching of a spruce TMP, International Mechanical Pulping Conference, Quebec, Canada, 2-5 June 2003, pp. 125-131.
29. Basta, J., Holtinger, L., Wackerberg, E., Metal management, mechanical versus chemical pulp bleaching, 1996 Pulping conference, Nashville, USA, 27-31 Oct. 1996, Book 1, pp. 23-28.

30. Qiu, Z., Ni, Y., Peroxide pre-treatment under acidic conditions to improve peroxide bleaching of mechanical pulps, *Pulp Pap. Can.*, **102**(2001)7, pp. 44-47.
31. Hook, J., Wallin, S., Optimization and control of two-stage peroxide bleaching, 1989 Pulping conference, Seattle, USA, 22-25 Oct. 1989, Book 1, pp. 267-275.
32. Froass, W.C., Factors affecting mechanical pulp brightening when peroxide liquor is recycled, 1992 Pulping conference, Boston, USA, 1-5 Nov. 1992, Book 3, pp. 899-910.
33. Berger, M.I., Meier, J., Suss, H.U., Schmidt, K., Two-stage peroxide bleaching - Method of choice for mechanical pulps, 1989 Pulping conference, Seattle, USA, 22-25 Oct. 1989, Book 1, pp. 249-255.
34. Lachenal, D., Bourson, L., Lachapelle, R., Two-stage peroxide bleaching of mechanical pulp, CPPA, 75th Annual Meeting, Technical Section, Montreal, Canada, 2-3 Feb. 1989, Preprints B, pp. B193-B196.
35. Lougheed, M., Presley, J.R., The upgrading of a bleach plant: Mill experience with a two-stage bleach plant retrofit, 1989 Pulping conference, Seattle, USA, 22-25 Oct. 1989, Book1, pp. 261-265.
36. Haveri, M., Washing of peroxide bleached groundwood pulp, Master of Science Thesis, Lappeenranta University of Technology, 1999, 177 pages.
37. Lönnberg, B., Svedman, M., Jakara, J., Nyman, J., PGW grinding with peroxide in shower water, 18th International Mechanical Pulping Conference, Oslo, Norway, 15-17 June 1993, Poster presentations, pp. 143-153.
38. Pan, G.X., Spencer, L., Leary, G.J., A comparative study on reactions of hydrogen peroxide and peracetic acid with lignin chromophores, *Holzforschung*, **54**(2000)2, pp. 144-152.
39. Sjögren, B., Danielsson, J., Engstrand, P., Gellerstedt, G., Reitberger, T., Zachrisson, H., The importance of radical reactions for brightness increase in hydrogen peroxide bleaching of mechanical pulps, International Symposium on Wood and Pulping Chemistry, 22-25 May 1989, Raleigh, NC, USA, pp.161-166.
40. Kang, G.J., Ni, Y., The Formation of Peracetic Acid and Its Impact on Peroxide bleaching of Mechanical Pulps, 11th International Symposium on Wood and Pulping Chemistry, Nice, France, 11-14 June 2001, pp. 351-355.
41. He, Z., Ni, Y., Zhang, E., Comparison of Oxalate Formation from Spruce TMP: Conventional Peroxide Bleaching Process Versus the P_M Process, *J. Pulp Pap. Sci.*, **29**(2003)12, pp. 391-394.
42. Laitinen, R., Toivonen, J., Yleinen ja epäorgaaninen kemia, kahdeksas painos, Otatieto, Karisto Oy, Hämeenlinna, 1994
43. Li, Z., Ni, Y., Heiningen, A.R.P., Incorporation of peracetic acid into brightening of groundwood pulps, *Pulp Pap. Can.*, **98**(1997)5, pp. 34-37.
44. Brasileiro, J.B., Colodette, J.L., Piló-Veloso, D., De Oliveira, R.C., Bleaching of eucalyptus kraft pulp with peracids – the effect on pulp characteristics, *Appita J.*, **55**(2002)6, pp. 461-467.

45. Jääskeläinen, A-S., kraft pulp bleaching with peroxyacetic acid and other peroxy compounds, Doctoral Thesis, Helsinki University of Technology, Laboratory of Forest Products Chemistry, Helsinki, 1999, 149 pages.
46. Abbot, J., Hobbs, G.C., The influence of metal ions on two-stage peroxide bleaching of radiata-pine TMP, *J. Pulp Pap. Sci.*, **18**(1992):2, pp. 67-70.
47. Lachenal, D., Nguyen Thi, N.B., Chirat, C., Soria, L., Optimum use of H₂O₂ in kraft pulp delignification, *Pap. Puu*, vol. 79, no. 4, 30 May 1997, pp. 252-256.
48. Nilvebrant, N-O., Stenman, D., Importance of hydroxyl radicals during hydrogen peroxide bleaching, 12th International symposium on wood and pulping chemistry, Madison, USA, 9-12 June 2003, vol. I, pp. 97-100.
49. Johnson, S.E., Optimal use of hydrogen peroxide, *Tappi J.*, **77**(1994)7, pp. 262-264
50. Hobbs, G., Abbot, J., The role of radical species in peroxide bleaching processes, 46th Appita Annual General Conference, 30 March - 3 April 1992, Launceston, Australia, pp. 99-106.
51. Gierer, G., Jansbo, K., Reitberger, T., Formation of hydroxyl radicals from hydrogen peroxide and their effect on bleaching of mechanical pulps, *J.Wood Chem. Tech.* **13**(1993)4, pp. 561-581.
52. Guay, D, Cole, B.J.W., Fort, R.C., Genco, J.M., Hausman, M.C., Mechanisms of oxidative degradation of carbohydrates during oxygen delignification, 10th International symposium on wood and pulping chemistry, Yokohama, Japan, 7-10 June 1999, pp. 222-226.
53. Anon. (1985) The hydrogen peroxide content of a bleaching solution. KCL Method No. 214: 85.
54. Tamper, J., Manganese in peroxide bleaching of mechanical pulp, Master of Science Thesis, Lappeenranta University of Technology, 2003, 78 pages.

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Tamper, J., Hietanen, T., Manner, H., Optimization of pre-bleaching conditions and water usage in peroxide bleaching of mechanical pulps, 38th Annual ABTCP Conference, São Paulo, 17-20 October 2005.

Tamper, J., Hietanen, T., Manner, H., Residual Peroxide as an Efficient Bleaching Chemical for Groundwood Pulp, 16th PTS-Symposium on the Chemical Technology of Papermaking, Munich, Germany, 15-17 September 2004.

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