

STUDIES ON WASHING IN KRAFT PULP BLEACHING

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IN KRAFT PULP BLEACHING**

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Abstract

Washing during kraft pulping can be divided into two separate areas each with its own distinct features: namely brownstock washing and washing in bleaching. Research interest has so far concentrated mostly on investigating brownstock washing and factors affecting its efficiency. Pulp washing in bleaching, however, has been practically neglected. The basic phenomena are the same as in brownstock washing, but there are differences which have not been taken into consideration to a sufficient extent. This less explored area is the focus of this research.

In this thesis, it is shown that brownstock washing and pulp washing between bleaching stages are distinct areas with their own specific features. They differ for example in terms of the composition and molecular size of the impurities in the pulp suspension. Various process conditions, pH, temperature and so on cause further differences between washing in bleaching and brownstock washing.

The removal of specific compounds can be clearly affected by the appropriate selection of wash liquor. It is shown that the dynamic behaviour during washing is different for different compounds and depends on the properties of the wash water. The key element is to find the most harmful compounds in specific positions in bleaching and on the basis of that finding, to determine the most suitable wash liquor system.

Chemical oxygen demand (COD) is a widely used method for evaluating the washing result, but as a collective measurement variable it does not describe the actual compounds that cause the "loss" of bleaching chemicals. Studies have shown that many compounds contribute to COD load but ultimately most of them have no real effect on the bleaching result. A suggestion for more precise definition of wash loss is offered than COD.

Keywords: bleaching, chlorine compounds, COD, softwood, wash loss

Dedicated to my marvellous sisters Katja, Kirsi and Mari

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This research work was carried out at the University of Oulu in the Department of Process and Environmental Engineering during the period 1999-2004. In 1999-2002 I worked as a researcher in the Fibre and Particle Engineering Laboratory on the Fundamentals of Pulp Washing projects I and II. The rest of the experimental work was done in the Industrial Environmental Engineering Unit during the period July 2002 - June 2003. Since then I have been working at Oy Metsä-Botnia Ab and the finalising of the last publication and construction of the thesis has been done in addition to my daily work.

I am most grateful to the supervisors of my thesis, Professor Olli Dahl from Helsinki University of Technology (previously working as a special researcher in the Industrial Environmental Engineering Unit at the University of Oulu) and Development Manager, Docent Kari Ala-Kaila from the Metsä-Botnia Rauma mill. Olli, I could not have done this thesis without you and I want to thank you for setting me off on this journey. You started this marathon and it has been extremely nice to work with you and under your supervision. I am also deeply indebted to you Kari. I am sure that I would not have been able to finish this work without your guidance and advice. There should be more supervisors like you. Special thanks also to Research Director, Docent Hannu Kuopanportti (now at YTI Research Centre, Mikkeli) and Professor Jouko Niinimäki from the Fibre and Particle Engineering Laboratory, University of Oulu for your words of advice.

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Oulu, November 2005

Mervi Sillanpää

List of original articles

This thesis is based on the following articles:

- I Sillanpää M, Ala-Kaila K, Tervola P & Dahl O (2001) A view of pulp washing in bleaching. *Paperi ja Puu* 83(1): 45-49.
- II Sillanpää M, Sankari M, Dahl O & Ala-Kaila K (2003) Real wash loss compounds in peroxide bleaching of softwood kraft pulp. *Appita Journal* 56(5): 397-400.
- III Sillanpää M, Ala-Kaila K, Sankari M & Dahl O (2003) Behavior of certain components in the vacuum drum washer after the first D stage in ECF bleaching. *Tappi Journal* 2(9): 18-21.
- IV Sankari M, Sillanpää M, Ala-Kaila K & Dahl O (2004) Use of secondary condensates from black liquor evaporation as process water in D₀ bleaching. *Pulp & Paper Canada* 105(5): 36-40.
- V Sillanpää M, Dahl O & Ala-Kaila K (2005) Leaching of chlorine compounds and metallic elements after the first chlorine dioxide bleaching. Accepted for publication in *Paperi ja Puu*.

The first publication summarizes the present knowledge of pulp washing in bleaching. The review emphasized the differences between pulp washing in bleaching and brown stock washing being written by the author and modified in co-operation with the co-authors.

The second publication was written by the present author. The experimental work was made by Dr Minna Sankari.

The real behaviour of certain components on mill scale was studied in the third publication. The experimental work and writing were carried out by the author. The planning of the experimental work was done together with Dr Kari Ala-Kaila and Prof. Olli Dahl.

The present author was the second author in the fourth publication. The author also made the final modifications to the article before publication.

The experimental work and writing of the fifth publication were carried out by the author. The planning of experimental work was carried out together with the co-authors.

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1 Introduction

1.1 Background

Washing during kraft pulping can be divided into two separate areas, each with its own distinct features, namely brownstock washing and washing in bleaching. The main purposes of brownstock washing are to remove dissolved organic and inorganic substances that would contaminate the pulp during subsequent steps in the process and to recover the maximum amount of spent chemicals with the minimum dilution. Efficient washing improves the recovery of spent chemicals, reduces the consumption of reagents in the subsequent bleaching, and essentially limits effluent load from the plant.

The aim of washing in bleaching is to remove both dissolved organic and inorganic matter, which will disturb the subsequent bleaching stage and enhance the consumption of bleaching reagent. As the optimum chemical conditions in successive bleaching stages vary, one very important purpose of washing is to render the conditions more suitable for the next bleaching stage. This may include modifying the pH, the metal content of the pulp and the temperature. Thus, an additional aim of washing is also to serve as chemical conditioning and a heat exchanger during the purification procedure.

During the past decade, environmental concerns have created new pressures to reduce effluent loading from kraft pulp bleaching. Pulp mills also have intrinsic needs to cut down their use of water and reduce effluents. Efficient and rational water use provides improved heat balance and chemical recovery. Intrinsic and extrinsic demands have forced both pulp mills and the related engineering industries to develop and optimise pulping process equipment to meet these demands. Improved pulp washers and washing systems connected with the introduction of oxygen-based reagents have in particular provided considerably improved tools for the reuse of process water and have thereby essentially reduced effluent discharge or even allowed the implementation of a closed water circulation system in kraft pulp bleaching.

This ongoing trend has placed increasing requirements on pulp washing, particularly in the interstage washing in bleaching. Less fresh water is used for pulp washing, but at the same time the quality and cleanliness of the pulp should remain high. The more closed the water re-circulation system is, the dirtier the wash water will be during

bleaching, probably resulting in an increased reagent consumption and poorer pulp quality. Since more expensive bleaching chemicals are used and the loss of bleaching chemicals is not acceptable, more specific washing is needed.

Regarding the vast amount of effluent discharged from a bleaching plant, there are good opportunities to gain substantial economic savings by optimising the wash procedure. Research interest has so far been concentrated mostly on investigating brownstock washing and factors affecting its efficiency. In contrast, pulp washing in bleaching has been practically neglected, although it is an economically important field and offers many interesting research topics. The basic phenomena are the same as in brownstock washing, but there are differences, which have not been taken into consideration to a sufficient extent. In this thesis, I wanted to focus my research on this less explored area.

1.2 The research challenge

The following list includes the most important driving forces behind this thesis and the reasons for undertaking it:

1. *To focus attention on pulp washing in bleaching.* Brownstock washing and pulp washing between bleaching stages are distinct areas and they have their own specific features. Research that clarifies and points out the differences is required.
2. *To highlight the special characteristics of pulp washing in kraft pulp bleaching.* What is the effect of the quality of the wash water and how can the washing result be described reliably? Furthermore, the transient behaviour of specific components, such as different chlorine species, during washing is of general interest.
3. *The lack of an appropriate wash loss measurement method.* Chemical oxygen demand (COD) is a widely used method to evaluate the washing result. However, as a collective measurement variable it does not depict accurately enough the actual compounds that cause the “loss” of bleaching chemicals.

1.3 Hypothesis

The research reported here was based on the following main hypothesis:

The special characteristics of pulp washing in bleaching deviate from those of brownstock washing. This special nature is more pronounced with regard to the quality of wash liquor, the reaction products and the concept of describing the washing result.

1.4 Research environment

This study was based on laboratory- and mill-scale tests and the research environment selected was dependent on the phenomena to be studied. Although it is very interesting

and challenging to examine the real situation on mill scale, the basic phenomena needs to be studied on laboratory scale. In laboratory tests, conditions and compounds were selected so as to describe the real situation in the mill as accurately as possible.

Bleaching is a very extensive research area, so in order to keep this research in reasonable proportions only softwood kraft pulp was used in experiments. Furthermore, bleached softwood kraft pulp constitutes over half of the produced bleached pulp in Finland (Metsäteollisuuden tuotanto Suomessa 2003). It is reasonable to assume that by enhancing the development of washing in softwood bleaching, the solutions can most probably be applied in hardwood bleaching, too.

There are various bleaching chemicals in use and chlorine dioxide is only one of the most frequently used bleaching agents. The chlorine dioxide bleaching stage was selected, because it is one of the most effective and widely used in different bleaching sequences. It also produces effluents, which contain compounds that can raise difficulties both for the environment and production processes.

The peroxide stage can effectively compensate for the chlorine dioxide bleaching stage especially at the end of the bleaching sequence. Therefore, it is interesting to compare these two bleaching stages especially when characterising wash loss compounds.

2 Brownstock washing versus washing in a bleach plant

2.1 Basic phenomena in washing

A pulp-water suspension consists of two main phases: the free liquor phase and the fibre phase. The fibre phase includes wood fibres and the liquor entrained inside the fibre and in close contact with the fibres. The entrained liquor can be assumed to behave as an immobile liquor phase, which is connected to the free liquor through a mass transfer resistance. (Ala-Kaila 1998.) The free liquor is quite easily removed during washing but the entrained liquor can be removed only by diffusion or by capillary force. These both are slow processes and they are dependent on the time, temperature and the chemical composition of wash water.

Washing is based on five basic processes: dilution, mixing, dewatering, diffusion and displacement. All the washers apply all or some of these processes in their washing arrangement. The simplest way to perform washing is to dilute the fibre suspension with wash water, mix the suspension and then filter or press the liquor out of the suspension. The other washing principle is based on displacing the free liquor from a pulp mat with wash water. These principles are used in different combinations in industrial pulp washers. In practise, several machines or operations are connected in series so that wash water is travelling counter-currently to the washed pulp. This principle ensures an adequate washing result with a moderate amount of wash water.

2.1.1 Counter-current washing systems in bleaching

The effluent load from bleaching is greatly dependent on the washing system and the amount of effluent is nowadays about 5-70 m³/Adt (Towers & Turner 1998). Most of the wash water applied in bleaching is not fresh water; on the contrary, it originates mainly from the drying machine and the condensates from black liquor evaporation.

Most washers and washing systems have several washing stages. The best possible washing result is achieved when every washer and stage applies clean water as wash water. Because this principle is very water consuming, it is not utilised in modern

washing systems. Normally, wash water circulation is organised in a counter-current manner, where the cleanest wash water is routed to the final washing stage. The filtrate of the final washer is re-used in the previous washer. Wash water flows and pulp move in opposite directions which enables us to keep the wash water consumption at a reasonable level without sacrificing the washing result.

The main counter-current washing systems in kraft pulp bleaching involve three different wash water circulation systems: direct counter-current, jump-stage and/or split flow washing. Figure 1 shows the principle of direct counter-current washing, in which fresh water is mainly used only in the last washer.

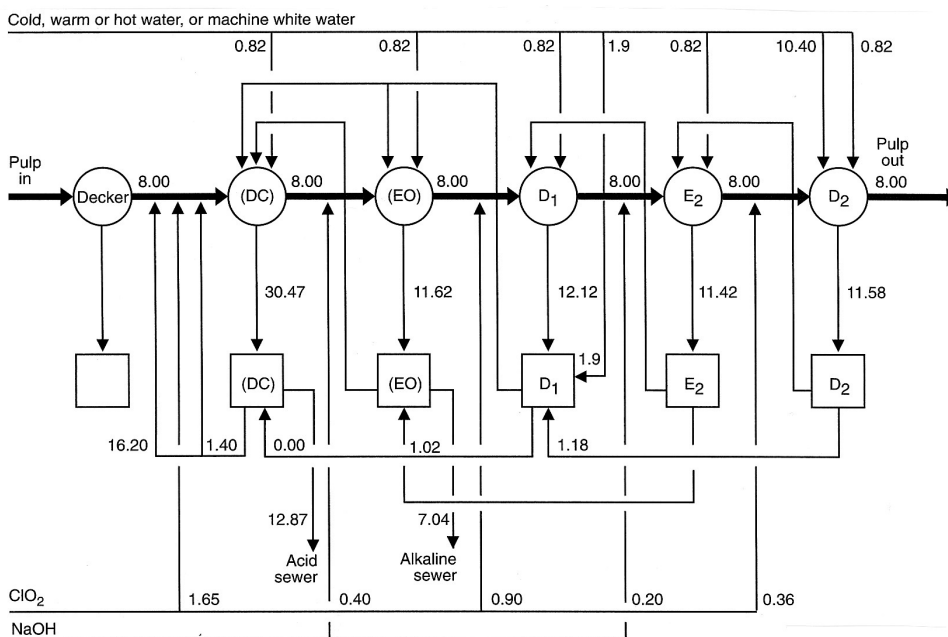


Fig. 1. Flowsheet for direct counter-current washing system (all flows in m³/adt). (Histed *et al.* 1996.)

According to the jump-stage counter-current washing principle, the acidic and alkaline filtrates are kept separate and filtrates from the later stages are used as wash water in the previous stages of the bleach plant (Fig. 2). Fresh water is introduced into the last alkaline and acidic washers.

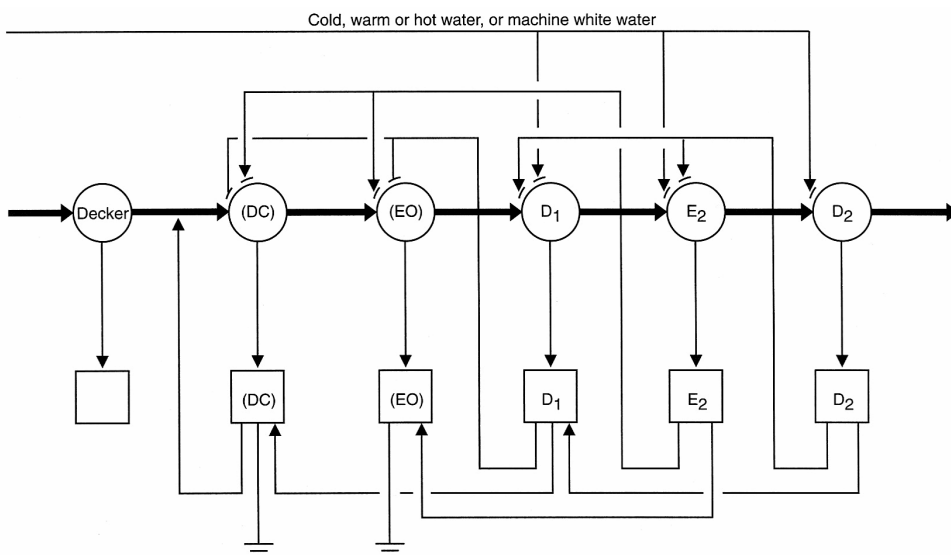


Fig. 2. Flowsheet for jump-stage counter-current washing system. (Histed *et al.* 1996.)

In the split-flow washing system, the pulp is washed both with alkaline and acidic filtrate (Fig. 3). With this system, the pulp is washed first with water similar to the stage it is leaving and then with water similar to the stage it is entering. (Singh 1979.)

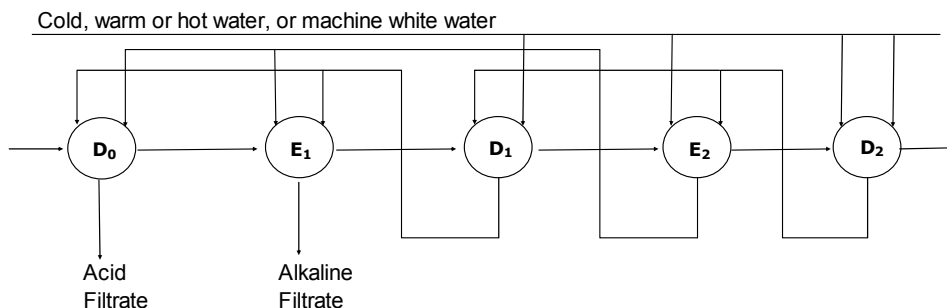


Fig. 3. Flowsheet for split-flow counter-current. (Singh 1979.)

A combination of the jump-stage and split-flow washing principles is the most common approach in pulp bleaching today (Fig. 4) Direct counter-current washing produces almost the same effluent load, but this method has an obvious risk of precipitation problems. However, these challenges can be totally or at least partly avoided by using the split-flow and jump-stage principles. (Dahl 1999.)

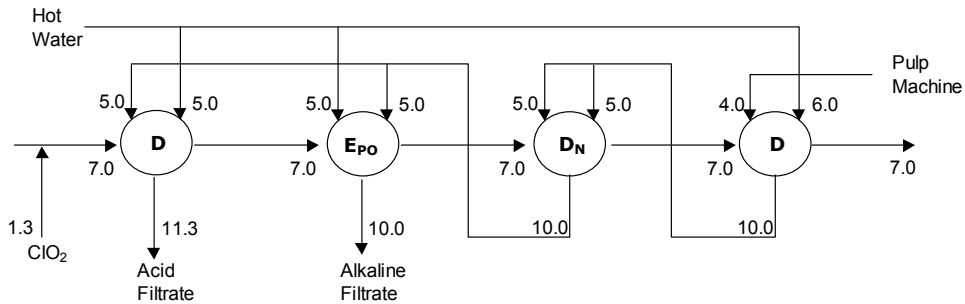


Fig. 4. One flowsheet for split-flow and jump-stage counter-current washing in a modern kraft bleach plant, unit of numbers m³/ADt . (Carter & Gleadow 1994.)

Typical water usage with various washing principles is shown in Table 1.

Table 1. Typical water usage and resulting effluent discharge in the (DC)(EO)DED bleach plant sequence (Histed et al. 1996).

Filtrate system	Effluent discharge [m ³ /ADt]	
	Theoretical	Actual
Direct counter-current	13-15	15-25
Jump-stage counter-current	23-25	30-40
Split-flow counter-current	23-25	30-40
Split-flow-jump-stage counter-current	11-15	12-25

2.1.2 Fractional washing

Modern washing implementations offer new opportunities for improving the control of washing and the washing result. These new approaches and principles provide many benefits: limited carry-over between bleaching stages, improved metal removal, and the possibility to reduce fresh water and steam consumption and reduced bleaching chemical consumption (Joronen *et al.* 1998, Ala-Kaila 1997b, Tervola *et al.* 1993, Steffes *et al.* 1995).

As far as bleaching is concerned, the latest development steps are fractional washing (Tervola *et al.* 1993) and wash presses (Steffes *et al.* 1995). In fractional washing, the filtrates can be divided into two or three fractions having different chemical properties. The principle of fractional washing is presented in Fig. 5.

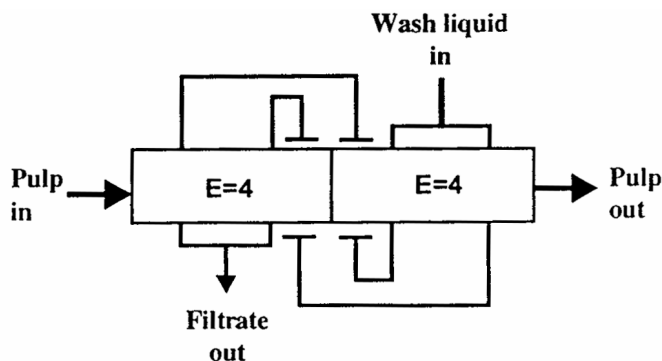


Fig. 5. Principle of fractional washing. (Joronen, Löppönen, Pikka & Vilpponen 1998.)

Since organic and inorganic compounds have different leaching behaviour during washing, this behaviour could be applied in a more advanced way in fractional washing. Ala-Kaila (1997b) observed that fractional washing is especially beneficial in the removal of quick-leaching components such as metal ions and small molecules. The use of particular wash water could be designed in a way that certain impurities are removed, because an inorganic or organic material needs different kinds of conditions. Our leaching experiments (Sillanpää *et al.* 2005) showed that the time scale of leaching is quite small and most of the impurities are removed during the first couple of minutes. Furthermore, pulp also reacts very rapidly, for example, to pH changes (Sillanpää *et al.* 2001, Ala-Kaila 1999b, Ala-Kaila & Alén 1999a). With fractional washing, it is also possible to increase the recycling ability of the active process chemicals (Ala-Kaila & Poukka 2003).

When one is aware of the most harmful impurities continuing with the pulp from washing to the next bleaching stage, washing can be designed in a way that supports the removal of these impurities.

2.2 Composition of alkaline and acidic filtrates

The main purpose of washing in the bleaching process is the same as in brownstock washing: to remove harmful impurities from the pulp. These washing systems differ, however, in terms of the composition and molecular size of the impurities in the pulp suspension. Although the precise composition of the effluents is dependent on both constant and alternating factors (Fig. 6), some general characterisations can be made. In brownstock washing, the filtrate is alkaline and rich in organic substances of a fairly large molecular size. According to Sjöström and Alén (1999), most of the lignin in kraft black liquors is of high molecular weight. Broadly speaking, organic compounds constitute two-thirds of the dry matter in pine and birch kraft black liquor and inorganic compounds, one-third.

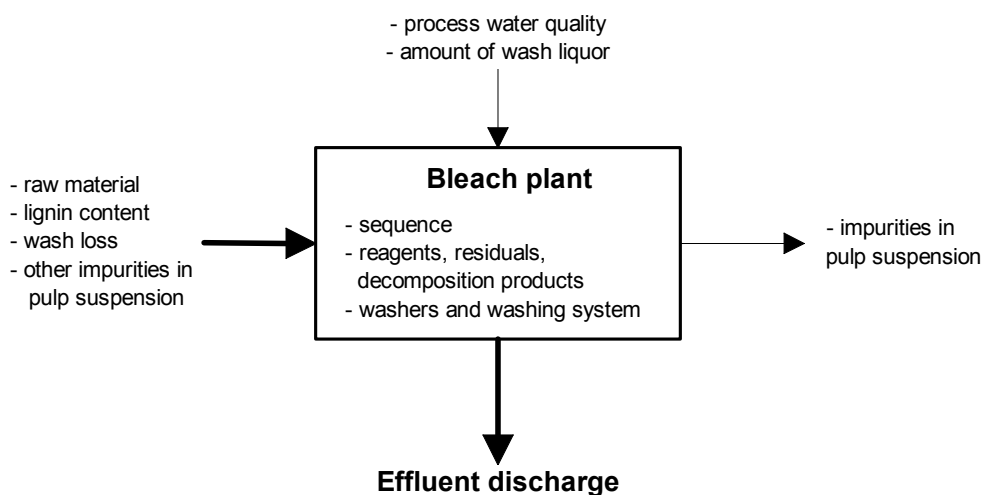


Fig. 6. Main factors affecting effluent discharge from kraft pulp bleaching. (Dahl 1999.)

Usually, two distinct filtrates exist in bleaching: alkaline and acidic. The chemical composition of the bleaching effluent depends greatly on the incoming wood raw material, the bleaching sequence and the precise conditions under which the bleaching stages are performed (Pakkanen & Alén 1998). As in brownstock washing, the alkaline filtrate is rich in organic substances, whereas the acidic filtrate contains a lot of inorganic material. A clear difference in the molecular weight distribution has been detected between the alkaline and acidic effluents from an ECF plant. Bryant *et al.* (1998) observed that the alkaline effluent contained a significantly higher proportion of high molecular weight substances than the acidic effluent, and that the lignin present in the acidic effluent had a much lower molecular weight than that in the alkaline effluent. Sågfors and Stark (1996) obtained similar results with acidic and alkaline filtrates from four mills pulping hardwood and softwood mixtures, and their results showed that the alkaline effluent contained 65-75% of high molecular weight material and the acid-stage effluent of just 20%. Altogether, in contrast to brownstock washing, organic compounds constitute one-third of the dry matter in bleaching effluents and inorganic compounds two-thirds.

2.3 Process conditions

Various process conditions provide further differences between washing in bleaching and brownstock washing. In bleaching, the process temperature can be adjusted from 30°C to 120°C and acidity from pH 2 to pH 13 (Patrick 1991), while in brownstock washing the temperature normally varies from 50 to 120°C and the pH is always higher than 10.5 to keep organic material soluble. These dramatic changes in conditions during the bleaching sequence, mainly in acidity, can affect the organic and inorganic impurities in an

unpredictable manner. This is something that has not received enough attention, especially the dynamic nature of these phenomena. It is possible, for example, that large modifications in acidity may precipitate or dissolve both organic and inorganic substances, especially metal compounds. One example of the effect of process conditions on deposit-forming can be seen in Fig. 7.

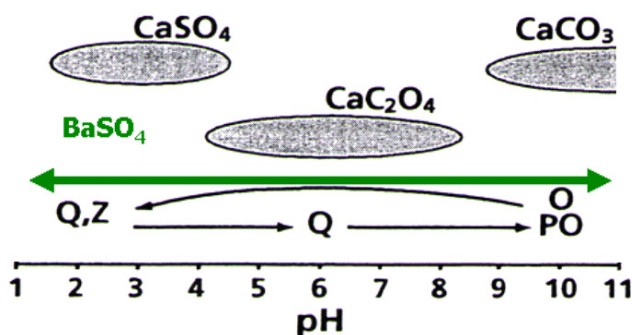


Fig. 7. Effect of solution pH on deposit-forming. (Germgård & Steffes 1996.) Barium sulphate was added later in Fig. 7.

Whether alkaline or acidic, the pulp also affects the functioning of washers, which could have draught problems or plugging problems due to deposits. When wash water circulations are being planned in a mill, these differences in operating conditions (pH, temperature, ion concentrations) have to be taken into account. Different process conditions (pH, temperature, chlorine species, etc.) also partly dictate the material selection in process equipment. In brownstock washing we do not have to consider the above mentioned problems to the same extent.

2.4 Is washing necessary in bleaching?

The purpose of washing between the bleaching stages is explained above, but is it really necessary? Its necessity can be demonstrated by examining what happens if the impurities are present in the next bleaching stage. Nivelon *et al.* (1996) showed that the consumption of bleaching chemicals in ECF and TCF bleaching was 20% to 50% higher when there was a carry-over of organic substances. Fiskari *et al.* (1999) also noted that bleach plant closure and inefficient washing resulted in a dramatic increase in the consumption of bleaching chemicals.

The first two bleaching stages are the most important ones, because they remove most of the lignin and inorganic material from the pulp (Dence & Reeve 1996). Therefore, efficient washing in the first two washers provides good chemical and economically profitable conditions for bleaching. Inefficient washing increases the consumption of bleaching chemicals in the following stages and reduces pulp brightness.

Furthermore, the importance of washing depends on the bleaching chemical applied in the next bleaching stage. Pulp washing between the ozone and chlorine dioxide stages is

not necessary and it is possible to reduce the need for chlorine dioxide in the AD stage by means of acid treatment without interstage washing (Henricson 1997, Chirat & Lachenal 1997, Fuhrmann *et al.* 1998, Pikka & Vehmaa 2002). An ozone stage, on the other hand, can be quite sensitive to impurities as Vuorinen *et al.* (1997) have proved. For example, filtrate from the A-stage is very detrimental in the subsequent ozone stage and washing is beneficial between the A and ozone stages. Since ozone reacts very sensitively with dissolved organic solids (Lindholm & Malkov 1997), only a low carry-over of these solids can be tolerated in bleaching sequences that employ this chemical. This leads to an increased demand for efficient washing before the ozone stage.

Beside transition metals, reduced sugars have also been observed to retard peroxide bleaching and accelerate the catalytic decomposition of hydrogen peroxide, so their removal requires good washing (Heikkilä *et al.* 2000). On mill scale, it has been observed that the bleaching efficiency of the peroxide stage is reduced due to reactions with circulated dissolved material (Fuhrmann *et al.* 2000).

After the final D-stage, washing is essential to minimise the carry-over of corrosive material into the pulp dryer or paper machine and to minimise the brightness reversion of the pulp in storage towers.

An illustrative table (Table 2) is presented below, which describes the primary and secondary washing objectives both in brownstock area and in bleaching (Lunn 2000). It clarifies the differences and presents the compounds, which make washing in bleaching especially necessary.

Table 2. Washing objectives (removal of...) (Lunn 2000).

Washing location	Primary	Secondary
Before O2 delignification	organics	Mn, Cu, Fe
Before the bleach plant	organics sodium	alkalinity
D0 stage	organics Ca, Si, Mn	acids
EOP stage	organics	pitch
D1 stage	acids	organics
E2 stage	alkalinity	
D2 stage	chlorides	

3 Release and resorption of material in washing

The free liquor in a pulp suspension is quite easily removed during washing but the removal of entrained liquor is a slow process and depends, for example, on time and chemical conditions. Even though the time scale would be long enough for impurities to be removed through diffusion, process conditions can cause the resorption of impurities. Depending on the situation, this resorption can be beneficial, detrimental or of no effect. The following sections deal with the release and resorption of organic and inorganic compounds during washing, focusing on the behaviour of COD and different chlorine compounds. Their dynamic nature and the effect of wash water quality are the key points.

3.1 Behaviour of organic material in a pulp suspension

Lindholm *et al.* (1996) found that an ozone stage in TCF bleaching releases mainly lignin, whereas alkaline stages such as E, P and PO, dissolve large proportions of non-ligneous material in addition to lignin. Part of this dissolved organic material from the alkaline bleaching stages is precipitated and adsorbed back onto the fibres when the filtrate is acidified in the ozone stage. They concluded that when ozone-bleached pulp is gently neutralised before interstage washing, considerable amounts of organic material, mainly lignin, seem to be released from the fibres. It should be noted that these are results of laboratory trials and that ozone has proved in practice not to be a very selective bleaching chemical.

Acidification of O, P and PO stage filtrates in the absence of pulp has not been observed to precipitate organic material to any significant extent. Lindholm and Malkov (1997) discovered that more than 50% of the dissolved organic material might be resorbed onto the fibres in the presence of pulp. These results indicate that acidification performed before washing may also be used for the resorption of non-lignin material (carbohydrates) after the E, P and PO stages, and could in this way increase the bleaching yield. Most of the resorbed material is non-lignin material, but also some lignin is resorbed. Acidification pH is the key factor how resorption of lignin can be controlled.

The behaviour of dissolved organic material from kraft pulp is a highly dynamic process, and its importance has been emphasised by Ala-Kaila *et al.* (1996, 1997a).

Washing is usually a fast process, and these authors maintain that the dynamic character of the chemical phenomena taking place in pulp-water suspensions should be taken into account when aiming at the efficient removal of organic material.

The behaviour of organic material during washing was studied after chlorine dioxide bleaching of softwood kraft pulp (Sillanpää *et al.* 2005). Leaching of organic material was measured as an increase in free liquor COD, which is a sum parameter for all compounds reacting with potassium dichromate in acidic conditions. The leaching of COD clearly occurred in two steps; an initial fast phase followed by a much slower phase. Two steps have also been detected in the leaching of organic material in brownstock washing and post-oxygen washing (Ala-Kaila *et al.* 1996, Trinh & Crostogino 1987). Alkaline media were more effective in leaching than acidic or neutral, but the result of leaching with neutral filtrate was only slightly poorer. The rate of leaching during the slower phase seemed to be a little higher with alkaline and neutral leaching filtrates than with acidic filtrate.

3.2 Inorganic compounds

Metals have been known to play an important role in bleaching (Lachenal *et al.* 1998, Hobbs & Abbot 1991, Gellerstedt & Pettersson 1982, Dahl *et al.* 1998) and their function and influence have been studied extensively, but there are still many open questions concerning the behaviour of certain metals in bleaching. A traditional theory for the behaviour of metals in pulp-water suspensions is based on Donnan's law (Towers & Scallan 1996, Ala-Kaila 1999b). This simple theory successfully describes the partitioning of common soluble metal ions such as sodium, calcium, magnesium and manganese between the wood fibres and the surrounding liquor. But Donnan's law, as many other theories, is based on a state of equilibrium, which is hard to achieve at least in pulp washing, because the reaction times are very short, only a few minutes. Towers and Scallan (1996) assumed that all mobile ionic species are completely ionised and completely soluble over the entire pH range which is not true for every metal (e.g. copper and iron, at least). Another approach to explain the behaviour of metals in pulp suspension is based on the aquatic chemistry of ions, a viewpoint that allows the solubility of metals and their reaction kinetics to be taken into account. Räsänen (2003) developed in his thesis a new model which is a combination of the Donnan's model with a complexation model. This model facilitates realistic modelling of ion exchange in pulp suspensions.

The extensive laboratory experiments of Bryant and Edwards (1994) indicated that manganese bound to the pulp is at its minimum under acidic conditions, 1.5-2.5 pH, when all the manganese is in soluble form. The amount of manganese bound to the pulp increases as the concentration of hydrogen ions decreases, but remains approximately constant above pH 6.5. Bryant and Edwards concluded that it is likely that as manganese leaves the ion exchange sites it will precipitate onto the surface of the fibre and remain associated with the fibre but in a different form. In alkaline resorption experiments, acid pretreated pulp was mixed with sodium hydroxide to reach a pH of 11.5. Their results

suggested that the redeposition of manganese, magnesium and calcium is an equilibrium process and the amount of resorbed metal strongly depends on the sodium concentration.

Oxygen-based bleaching reagents (hydrogen peroxide, ozone and peracetic acid) are highly sensitive to the presence of even very low concentrations of transition metals. A metal chelating stage and effective pulp washing are therefore usually employed in TCF sequences prior to the peroxide stage. Metal removal can be accomplished by pre-treatment with an acid or a chelating agent. Lapiere *et al.* (1997) observed that the pH of the solution determines the degree of metal removal, either by increasing the solubility of metal salts adsorbed on the pulp or by enabling a more complete ion exchange. Ala-Kaila and Alén (1999a), studying the dynamic response in pH and the behaviour of certain chemical elements in pulp-water suspensions, showed that an addition of acid to oxygen-alkali delignified pulp clearly increases the amounts of metallic components in the free process liquor around the fibres, whereas a caustic addition to an acidic pulp-water suspension will increase the amounts of Na, K, and Si in the free process liquor but reduce those of Mg, Ca, Ba and Mn. The essential changes in the concentrations of most elements in these leaching experiments took place within 30 seconds of pH adjustment.

Presley *et al.* (1997) and Hill *et al.* (1997) used a new strategy for metals control that destroys the sites on the pulp fibres to which transition metals are attached. This is done at pH 3 and a relatively high temperature, over 80°C. Zhang *et al.* (1998) investigated the impact of washing efficiency on the performance of the peroxide stage after a metal removal stage and noted that washing efficiency has an implied effect on pulp brightness, with distilled water giving a better brightness than tap water. Washing efficiency nevertheless has a greater impact on pulp brightness than does the quality of the wash water.

Thus, some metals such as manganese can be harmful in bleaching, whereas others like magnesium can be beneficial. Because the efficient removal of harmful metals in washing can enable the pulp mill to optimise the use of wash water, it is important to understand their transient behaviour in the process. We studied the behaviour of calcium, manganese and magnesium in leaching experiments (Sillanpää *et al.* 2005) and found out that at first, the concentration of these metals in leaching filtrates rapidly reached a certain level and after that rapid phase, slow leaching took over. The properties of the leaching filtrate had a substantial effect on the metal concentrations. Acidic leaching conditions led to a higher removal of metals than alkaline conditions, as expected. The leaching rates of calcium and especially manganese during the slow phase were slightly higher compared with that of magnesium. Dissolving solid particles in the fibres, such as CaCO₃, may contribute to the dynamic behaviour of the metallic elements measured. Most of the removal (on average 75%, depending on the metal and leaching filtrate) occurred during the initial fast phase, which lasted approximately two minutes. According to Ala-Kaila and Alén (1999a), when the pH of a suspension of oxygen-delignified pulp was adjusted from alkaline to acidic, the concentrations of Ca, Mg and Mn in the free liquor increased rapidly and reached steady concentrations within three minutes. Despite the almost steady concentrations, it was concluded that about 20% of the metal removal took place in the slow phase.

3.2.1 Chlorine compounds

Oxygen-based bleaching reagents have been used as partial or total replacements for chlorine dioxide, with the aim of ensuring the sufficiency of the chlorine dioxide plant or in some cases reducing the concentration of chlorine compounds in the bleaching filtrates. In the latter case, the objective may even be to circulate part of the alkaline filtrates to the brownstock washing and then to chemical recovery. This requires low levels of chlorine compounds in alkaline bleaching filtrates, because these compounds are undesirable in chemical recovery due to their major role in creating corrosion problems, their effect on plugging and environmental pollution (Salmenoja & Mäkelä 2000, Jemaa *et al.* 1997, Ulmgren P (1996).

As pulp mills are closing their water circulation (Nivelon *et al.* 1996, Miller & Lennon 1996, Vega Canovas & Maples 1995) and directing a certain part of the bleaching filtrates to brownstock washing, more knowledge of the efficiency of chlorine compound removal in washing could benefit the processing of bleaching filtrates. The bleaching filtrate recycling process, BFRTM, is one possible way to handle and circulate part of the alkaline filtrates in brownstock washing (Fig. 8). Process is based on minimisation of the concentration of chloride ions in the acidic effluent by reducing the use of chlorine dioxide in the bleaching and by removing metals before reusing the filtrates as a wash liquor in the washer after the first chlorine dioxide stage (Dahl 1999).

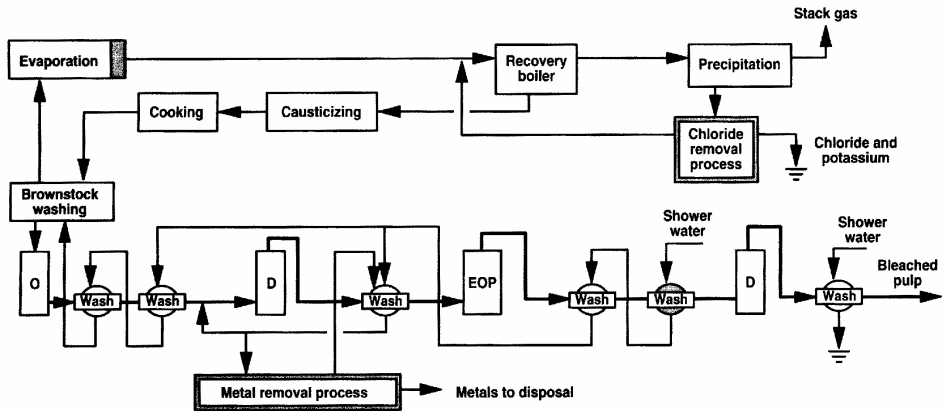


Fig. 8. Schematic flowsheet of the BFRTM process. (Maples, Ambady, Caron, Stratton & Vega Canovas 1994.)

3.2.1.1 Behaviour of chlorine on mill scale

Mill trials (Sillanpää *et al.* 2003b) illustrated that inorganic chlorine, mainly chloride, makes up over half of the chlorine load in the liquor continuing with the washed pulp from the D0 stage to the next bleaching stage. Most of the chlorine dioxide decomposed to chloride ions during bleaching, but traces of chlorate were also detected in the filtrates.

The proportion of organic chlorine increased during washing and that of inorganic chlorine decreased, which suggests that inorganic chlorine is easier to remove from pulp than organic. One explanation for the behaviour of organic chlorine may be that the use of alkaline EOP wash water leached organically-bound chlorine out of the pulp. This observation was supported by the fact that the kappa number, i.e. the lignin content of the pulp and chlorine content of the pulp clearly decreased in the washer. Before washing, the filtrate also contained chlorate, but it was either removed during washing or it reacted further and formed other chlorine compounds.

Mass balance calculations showed that the washing of different chlorine compounds was quite efficient compared with COD, TOC and sodium, which were not efficiently removed because of their high content in the second wash water. This water was carried along with the pulp to the next bleaching stage. The amount of chlorine carry-over depended on the quality of the wash water, the chlorine dioxide dosage in the preceding bleaching stage and the outlet consistency of the washed pulp. The carry-over of certain compounds can be greatly affected by the correct choice of wash water.

3.2.1.2 Leaching of chlorine compounds

As mentioned earlier, special attention should be paid to the total amount of chlorine in filtrates because of its major role in creating corrosion problems and the effect on plugging (Salmenoja & Mäkelä 2000, Tran *et al.* 1999, Klarin & Westermarck 1994). As far as the environment is concerned, some of the problematic compounds in bleaching effluents are various organochlorine compounds (Tana & Lehtinen 1996, Dallons & Grawford 1990, Bajpai 1996, Verta *et al.* 1999).

The existence and behaviour of different chlorine compounds during chlorine dioxide bleaching were investigated during the 1990s by Ni *et al.* (Ni *et al.* 1992, Ni & van Heiningen 1993, Ni *et al.* 1994a, Ni *et al.* 1994b) and Svenson *et al.* (1999). The formation of various chlorine compounds depends on many variables, such as the kappa number of the unbleached pulp, pH, temperature and chemical dosage etc. The studies concerning the distribution of inorganic chlorine species (Cl^- , ClO^- , ClO^{2-} , ClO^2 , ClO^{3-}) and the mechanism of the formation of chlorine compounds during chlorine dioxide bleaching have been used as an aid towards optimising bleaching conditions (Ni & van Heiningen 1993, Ni *et al.* 1992). Although these different chlorine species have been considered in earlier studies (Ni *et al.* 1992, Ni & van Heiningen 1993, Ni *et al.* 1994a, Ni *et al.* 1994b, Svenson *et al.* 1999, Dence 1996, Sillanpää *et al.* 2003a, Ragnar & Törngren 2002, Björklund *et al.* 2002, Söderhjelm 1990, Gunnarsson 1995), their dynamic behaviour during washing and leaching has been less clear. The understanding of this behaviour is important, because the removal of different chlorine species can then be designed more effectively. Furthermore, it is important to appreciate the effect of different leaching filtrates on the behaviour of various chlorine species in order to achieve the best possible operating conditions in washing.

In order to clarify the dynamic nature of leaching, we studied the leaching behaviour of different chlorine compounds with three different leaching liquors: alkaline, neutral and acidic. According to our studies (Sillanpää *et al.* 2005), the leaching of compounds

clearly took place in two steps; an initial fast phase followed by a much slower phase. Almost 80% of the removal occurred during the fast phase, which was two minutes for various chlorine compounds. A minor part (10-15%) of the total chlorine in the filtrate consisted of adsorbable organic compounds (AOX). Efficient washing after the first chlorine dioxide stage was able to remove most of the AOX and the slowly leaching part of AOX (20%) was removed in the next alkaline extraction stage.

The properties of the leaching filtrates had a substantial effect on the leaching result: for metals, acidic leaching conditions led to a higher removal than did alkaline conditions, and for chlorine compounds, alkaline conditions were the most effective. However, the organic chlorine in pulp was removed effectively both during alkaline and neutral leaching and it seems that an adequate washing result after the chlorine dioxide bleaching stage could be obtained with slightly milder conditions considering the alkalinity of the leaching liquor. Since the fast leaching step lasted for approximately two minutes, washers with adequate retention times could benefit from this and achieve good removal efficiency.

4 Characterisation of washing result

4.1 Washing efficiency

Generally speaking, the result of washing is a function of many variables, such as the amount of wash water, feed consistency, air entrainment, sheet formation, wash water distribution and discharge consistency (Shackford 1992). Most of these variables are interrelated, and an improvement in one variable may well have a favourable or unfavourable impact on the others. Shackford (1992) concludes that the primary objectives for achieving the best washing result are the lowest possible feed consistency, optimum mat formation with a uniform basis weight, a uniform shower liquor distribution, the highest possible discharge consistency and minimal air content in the feed to the washer.

Displacement velocity, pulp pad thickness, pulp pad consistency and operating temperature are considered to be the most important variables in displacement washing. These factors have been studied mainly in brownstock washing (Trinh *et al.* 1989, Grén & Ström 1985, Lee 1979, Grähs 1976, Hakamäki & Kovasin 1985, Eriksson & Grén 1987, Eriksson 1996, Lee 1984) but their influence is likely to be similar in bleaching. Although results appear to disagree about the magnitude and direction of some of the effects, it can be said that the beneficial effect of increased pad thickness on washing efficiency is the only effect that has not been contradicted.

The variables mentioned above all affect the washing result from an operational point of view. However, much can also be achieved with the proper selection of wash water and application position. The aim in bleaching is to minimise the amount of effluent and maximise the washing result so that the carry-over to the next bleaching stage is as low as possible. This carry-over might consume extra bleaching chemicals and thus raises the bleaching costs and lowers the bleaching result. In order to really evaluate the washing result, we need to know what are the harmful compounds which cause this extra chemical consumption in bleaching. We can evaluate the operational parameters, but for more efficient washing the issue is to clarify the concept of wash loss in bleaching.

4.2 Wash loss

A couple of methods exist for evaluating washing result and wash loss. The amount of sodium in the pulp suspension after washing has typically been used as an indicator of wash loss in brownstock washing. The disadvantage of this method is that it does not take into consideration organic and other inorganic compounds in a pulp suspension. Sodium loss is naturally not the most suitable factor by which to evaluate pulp washing in bleaching, and therefore chemical oxygen demand (COD) has partly replaced it as an indicator in both brownstock washing and especially in bleaching. As a useful method, this method also has disadvantages, as considered by Bottan (1993). For example, the time delay of analysis is quite long and it is not easy to reproduce.

The COD method only takes into account compounds which can be oxidised, and this is a cause for reasonable doubt. There can be unoxidisable material which can be harmful in bleaching whereas some of the oxidised material is not harmful at all. What would then be the most appropriate and correct method for describing wash loss in connection with bleaching? For instance, Shackford (1992) suggests that washing efficiency can be estimated by determining the quantities of bleaching by-products (e.g. NaCl) in the pulp suspension after each washing, although, as by-products are naturally dependent on the bleaching chemicals used, each bleaching stage needs its own specific criteria. The precise characterisation of wash loss could provide new information about washing and point to the most important variables that should be measured. In the best situation, the characterisation could provide one or more variables which directly indicate wash loss and can be measured continuously. Recently published papers indicate that among various chemicals causing COD in wash loss, only certain compounds have real effect on bleaching and oxygen delignification response. In oxygen delignification, certain inorganic sulphur compounds and kraft lignin had some real effect on the bleaching response and they could be called real wash loss compounds in that stage (Sankari *et al.* 2004b). In the D0 bleaching stage, the most harmful compounds among the various studied chemical compounds turned out to be different lignin fractions (Viirimaa *et al.* 2002). These results support the assumption that COD as a collective measurement is not the right variable to measure as a wash loss.

Once the fundamentals of pulp washing and the elements affecting washing performance are better known, control of washing will become more accurate. Towers and Turner (1998) discovered in their survey of bleach plant washing practices in Canadian mills that in most cases the parameters used are not the direct measurements of washing performance, and that the chemical demand in the following stage is the most frequently monitored variable, followed by mat consistency. Other possible parameters for measuring washing performance are chemical oxygen demand, fibre content of the filtrate, metals and pH.

Lunn (2000) has presented possible wash loss measurements which are applicable especially in the mill environment. COD, liquid kappa and dissolved solids describe the organic wash loss, whereas sodium, metals (Mn, Ca, Si, Fe, Cu), alkalinity and acidity can be used to depict the inorganic wash loss. These measurements have advantages and disadvantages which sometimes can reduce their suitability for describing wash loss and

washing efficiency. However, it is clear from these investigations that there is a need for a more suitable variable to monitor and control in bleach plant washers.

Wash loss is defined as the amount of washable compounds in the pulp suspension which could have been removed in washing. I propose a slightly new, more precise definition for wash loss in bleaching. This reformulated definition is as follows:

Wash loss is the amount of residual washable compounds in the pulp suspension, which cause additional chemical consumption or a decrease in the process response in the subsequent bleaching stage.

4.2.1 Wash loss compounds in chlorine dioxide bleaching

Black liquor evaporation produces a large volume of condensates. Stripped condensates are largely used in pulp mills worldwide in the brownstock washing area, in the O-stage washing area and in the recausticising cycle. Additionally, some of the condensates have the potential for use in the bleach plant (Pekkanen & Kiiskilä 1996), particularly in the EO and EOP bleaching stages. In modern pulp mills, there is a possibility to use alkaline bleach plant filtrates in brownstock and post-oxygen washing (Sävelin & Bergqvist 1997, Joronen *et al.* 1998, Liias & Merikallio 1998). This easily leads to an excess of condensates and to the question whether this surplus could be used in the D-stages.

When condensates are used in brownstock and post-oxygen washing, part of the wash water continues to the next bleaching stage and the effect of this carry-over is not clear. Although there is only a limited amount of published data concerning the effect of condensates on the bleaching of kraft pulp (Annola *et al.* 1995, Niemelä *et al.* 1999), these studies make it reasonable to assume that typical secondary condensates would not increase the consumption of bleaching chemicals. However, we wanted to check this in more detail. The aim of our experiments (Sankari *et al.* 2004a) was to determine the effects of different volatile organic compounds (VOC) on the bleaching performance in D0 bleaching. These compounds (formic acid, acetic acid, propionic acid, methanol, ethanol and acetone) are also the main components in secondary condensates. In the second part of the experiments, we studied the effect of different mill condensates on D0 bleaching.

In the volatile compound experiments, only acetic acid had some effect both on the pulp brightness and kappa number. Propionic acid had a minor negative effect on the kappa number. When the statistical deviation in the experiments was taken into account, the effects we detected were almost negligible. No effects of the VOC on pulp viscosity were detected. Many of the compounds have a high COD, but they had no clear effect on pulp properties (kappa number, viscosity or ISO brightness).

In the condensate experiments, every secondary condensate fraction lowered the pulp brightness and raised the pulp kappa number. COD characterisation results indicated that most of the COD in the condensates originated from methanol and formic acid. According to the volatile compound experiments, these components did not affect the bleaching result. Therefore, the most harmful components for bleaching were probably sulphur-based components, such as dimethyl disulphide (DMDS) and dimethyl sulphide

(DMS), which also contribute to COD in the condensates. This finding is in good agreement with the results reported by Niemelä *et al.* (1998). However, it must be remembered that condensates might also contain other compounds, which were not analysed in these experiments, but which could have affected the bleaching result. For example, fatty and resin acids are known to affect the brightness in the D0 stage (Viirimaa *et al.* 2001).

Secondary condensates can be used as process water in bleaching, but in this case the condensates should be clean enough. Traditionally, the quality of condensates has been evaluated by measuring either conductivity or the COD of the filtrates. These measurements may be adequate, but better results can be obtained by measuring the colour of the condensates as Dahl *et al.* (1998b) have earlier proposed. The colour measurement takes into account lignin and coloured sulphur compounds, but e.g. disregards colourless methanol. Lignin and methanol both contribute to COD, but are known to have the opposite effect on the bleaching result (Viirimaa *et al.* 2001, Viirimaa *et al.* 2002).

4.2.2 Wash loss compounds in peroxide bleaching

With the trend towards closed water cycles, it is even more important to understand the effect of certain components on the performance of various bleaching stages. Portions of the bleaching filtrates are often used as wash water or dilution liquors in different positions, and compounds found in these filtrates continue with the pulp to the following bleaching stage. For example, in the chlorine dioxide stage, various organic acids (formic acid, acetic acid) are formed, and lignin can decompose into dicarboxylic acids (Dence 1996). Furthermore, possible degradation products of hemicelluloses are hydroxy carboxylic acids such as lactic acid and glycolic acid (Sjöström & Alén 1996). In addition, methanol may be formed in chlorine dioxide bleaching and be carried along for example to the next peroxide stage as a wash loss as also dissolved lignin and hydrocarbons (glucose). The impurity compounds have various impacts on bleaching; some might result in additional chemical consumption or otherwise reduce the bleaching performance, whereas some might even improve the bleaching result, while others have a negligible effect (Lindholm *et al.* 1996, Lindholm & Malkov 1997, Hobbs & Abbot 1991, Pikka *et al.* 2000).

In order to evaluate the effectiveness of washing, it is essential to measure the actual compounds which cause the loss of bleaching agents, in this case peroxide. In this study (Sillanpää *et al.* 2003a), we concentrated on the compounds (formic acid, acetic acid, methanol, glycolic acid, glucose, lignin, lactic acid and succinic acid) found in real bleaching filtrates which are likely to be recycled inside the bleach plant. If the peroxide stage is preceded by a chlorine dioxide stage, which is often the case, these compounds can be found in the pulp suspension continuing to the peroxide stage. Transition metals are very detrimental to peroxide bleaching, but because this effect is quite well known these metals were not included in this study.

The peroxide stage is known to be very sensitive to operating conditions, so the design and experimental part have to be carefully planned. In these experiments, added

impurities and reactions during the hydrogen peroxide bleaching affected the final pH substantially and made the adjustment of pH extremely difficult. It seems that these impurities can affect the bleaching in at least two ways: changing the reaction conditions or consuming additional hydrogen peroxide.

The decreasing effect of lignin on brightness and its increasing effect on kappa number were both anticipated results and their inversely proportional dependence is natural. Besides lignin, only glucose had an impact on brightness and kappa number. In earlier studies, there have already been indications that reduced sugars can accelerate the catalytic decomposition of hydrogen peroxide, and that sugars might also react with peroxide, causing additional bleaching chemical consumption (Vuorinen 2002, Heikkilä & Vuorinen 2000). Therefore, the results presented in this study directly sustain the effects of sugars on peroxide bleaching.

Many chemical compounds can cause a lot of COD in bleaching, but only some of them have a real effect on bleaching performance. On the basis of this study, only lignin and glucose can be called actual wash loss compounds in peroxide bleaching, since they clearly decreased the bleaching performance of Scandinavian softwood kraft pulp. When the carry-over comprised lignin and glucose, it resulted in a lower pulp brightness and higher kappa number. Other impurities tested, i.e. formic acid, acetic acid, methanol, glycolic acid, lactic acid and succinic acid had no effects on the bleaching performance. Instead of measuring a collection of variables as COD, it could be better to measure only the lignin concentrations in the liquid part of the pulp suspension in order to estimate the actual wash loss at the end of washing.

5 Synthesis of the publications

This thesis is based on five publications dealing with washing in kraft pulp bleaching. The publications are studies covering different aspects of interstage washing in bleaching from the characterisation of real wash loss compounds to the dynamic leaching behaviour of chlorine compounds.

The first article (I) explored the current knowledge of pulp washing as a part of the bleaching process. In addition to emphasising the differences between pulp washing in bleaching and brownstock washing, it pointed out a clear need for an adequate method for wash loss measurement in bleaching.

The concept of wash loss and what are actually the real wash loss compounds in peroxide bleaching and chlorine dioxide bleaching were studied in the second (II) and fourth (IV) articles. The fourth publication focused mainly on the use of secondary condensates as process water in D0 bleaching, which is one possible way to reduce the use of fresh wash water in washing. The effect of different wash loss compounds was studied, because the use of condensates requires a deeper knowledge about wash loss compounds and their effects on bleaching.

Chlorine compounds are important wash loss compounds because they can have a damaging impact on the process and on the environment. This was the driving force behind the third (III) article, which studied the behaviour of chlorine components on mill scale. In order to better understand the dynamic nature of chlorine compounds and some metallic elements during washing and how the removal efficiency can be improved, a laboratory study concerning the leaching behaviour was conducted. The fifth (V) article presented the results of these laboratory tests in which the effect of different leaching liquors was tested.

6 Summary

The research reported here was based on the hypothesis that the special characteristics of pulp washing in bleaching deviate from brownstock washing, particularly regarding the quality of the wash liquor, the reaction products and the measurement of the washing result.

There is a good possibility to gain substantial economic and environmental savings by optimising the washing procedure in kraft pulp bleaching. Research interest has mainly concentrated on investigating brownstock washing and factors affecting its efficiency. Since pulp washing in bleaching has been practically neglected, in this thesis, the objective was to focus on this less explored area. The basic phenomena are the same as in brownstock washing, but there are differences which have not been sufficiently taken into consideration.

In this thesis, it was shown that brownstock washing and pulp washing between bleaching stages are distinct areas and that they have their own specific features. They differ for example in terms of the composition and molecular size of the impurities in the pulp suspension. Various process conditions, pH, temperature etc., cause further differences between washing in bleaching and brownstock washing. Dramatic changes in conditions during the bleaching sequence, mainly in acidity, can affect the organic and inorganic impurities unpredictably.

The removal of specific compounds can be clearly affected by selecting the wash liquor appropriately. It was shown that the dynamic behaviour during washing differs for different compounds and depends on the properties of the wash water. Even though the delays in modern industrial washers are somewhat short, from a couple of seconds to a few minutes, a large amount of impurities can be removed during washing. The key issue is to find the most harmful compounds in specific positions in bleaching and on the basis of that finding, design the most suitable wash liquor system.

Chemical oxygen demand (COD) is a widely used method to evaluate the washing result, but as a collective measurement variable it does not describe the actual compounds that cause the “loss” of bleaching chemicals. Studies have shown that many compounds contribute to the COD load but in the end, most of them had no real effect on the bleaching result. It would be more precise to measure for instance the amount of lignin than to use COD as a criterion for wash loss.

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