

JYU DISSERTATIONS 85

Jukka Pekka Isoaho

Dithionite Bleaching of Thermomechanical Pulp

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UNIVERSITY OF JYVÄSKYLÄ
FACULTY OF MATHEMATICS
AND SCIENCE

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**Dithionite Bleaching of
Thermomechanical Pulp
Chemistry and Optimal Conditions**

Esitetään Jyväskylän yliopiston matemaattis-luonnontieteellisen tiedekunnan suostumuksella
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ABSTRACT

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The study described bleaching of thermomechanical pulp (TMP) mainly by a reductive bleaching agent, sodium dithionite. The theoretical part concentrated on the elucidation of lignin-preserving bleaching of mechanical pulps by introducing general concepts and reaction mechanisms. It also discussed novel analytical possibilities to determine sulphur-containing anions originated from dithionite.

The primary objective of the experimental part was to find out relevant factors affecting achievable brightness gain in the lignin-preserving bleaching of pressure groundwood (PGW). The bleachability and brightness stability were characterised by employing brightness measurements after the sodium dithionite treatment. Observations were further confirmed by filtrate analyses and total sulphur measurements of TMP.

Reaction pathways of dithionite bleaching were studied by analysing various sulphur anions (bleach liquor and filtrates) and also the sulphur chemically bound to fibres. The effects of bleaching factors were studied mainly by designing the experiments with the Taguchi method. The new information on reactions of dithionite during the bleaching process further developed the postulated mechanism of lignin-preserving bleaching. The quantities of different sulphur constituents in filtrates and pulps after bleaching with respect to the added dithionite under laboratory-scale conditions could be presented. The efficiency of bleaching improved with an increase in temperature. Hence, temperature was the most important factor concerning the efficiency of dithionite bleaching, but it could not be extracted from other variables. The dosage and composition of dithionite grade were also significant factors and they should be optimised carefully for each mill-scale application with PGW.

Keywords: Dithionite, lignin-preserving bleaching, thermomechanical pulp, pressure groundwood

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PREFACE

The main experimental work of this thesis was conducted in the Laboratory of Applied Chemistry at the Department of Chemistry, University of Jyväskylä, from the years 1997 to 2006. Also, many paper mill environment studies have been done with co-operation partners. This research was carried out on a prolonged pathway with many unnecessary interrupts. Finally, this project is in its finale.

I would like to give my deepest thanks to my supervisor, Raimo Alén. His contribution, guidance and professional knowledge that contributed to this work was substantial. Work contribution of Jori Soininen (Vocational Education Institute of Northern Central Finland, POKE) was a very important part of my experimental work. For many years he gave valuable support to our co-operations and projects. I also wish to thank all of my colleagues and the personnel at the Department of Chemistry.

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- I Isoaho, J.P., Soininen, J. and Alén, R. (2019), Chemistry of Dithionite Bleaching. Part 1. Effect of Bleaching Variables, *submitted to APPITA*.
- II Isoaho, J.P., Soininen, J. and Alén, R. (2019), Chemistry of Dithionite Bleaching. Part 2. Comparable Study with Different Thermomechanical Pulps, *submitted to APPITA*.
- III Isoaho, J.P., Tarkkanen, S., Alén, R. and Fiskari, J. (2012), Oxidative Degradation of AOX in Softwood-Based Kraft Mill Effluents from ECF Bleaching, *Nord. Pulp Pap. Res. J.*, 27(4):707-713.
- IV Isoaho, J.P., Alén, R. and Louhelainen, J. (2006), Total Sulphur Content of Dithionite-Bleached Pulp, *Cell. Chem. Technol.*, 30(9-10):769-774.
- V Louhelainen, J., Alén, R. and Isoaho, J.P. (2005), Determination of the Total Sulfur Content in Black Liquor by X-ray Fluorescence, *J. Pulp Pap. Sci.*, 31(1):57-61.
- VI Malkavaara, P., Isoaho, J.P., Soininen, J. and Alén, R. (2000), Dithionite Bleaching of Thermomechanical Pulp: Factors Having Effects on Bleaching Efficiency, *J. Chemometr.*, 14(5-6):693-698.

Responsibility for authorship

- I The author was responsible of writing the manuscript. Experimental work and planning was conducted together with co-author Jori Soininen.
- II The author was responsible of writing the manuscript. Experimental work and planning was conducted together with co-author Jori Soininen.
- III The experimental work was done by co-author Suvi Tarkkanen. Planning of experiments and writing were done by the author.
- IV The author wrote, planned and completed the experimental work.
- V Jarmo Louhelainen was responsible of interpreting the results and writing the manuscript. Experimental work was performed by the author in collaboration with Jarmo Louhelainen.
- VI Petteri Malkavaara was responsible of writing and calculations. The author planned the experiments and was responsible for the practical laboratory work.

SUPPORTING PUBLICATIONS

Käkölä, J.M., Alén, R.J., Isoaho, J.P. and Matilainen, R.B. (2008), Determination of Low-Molecular-Mass Aliphatic Carboxylic Acids and Inorganic Anions from Kraft Black Liquors by Ion Chromatography, *J. Chromatogr. A*, 1190:150–156.

Pere, J., Isoaho, J.P., Jussila, S., Suurnäkki, A. and Alén, R. (2005), Bleaching of Mechanical Pulps: Implications of Demethylation of Pectin for Pulp Brightness, 59th Appita Annual Conference and Exhibition: Incorporating the 13th ISWFPC (International Symposium on Wood, Fibre and Pulping Chemistry), Auckland, New Zealand, Proceedings, pp. 311-315.

Louhelainen, J., Alén, R. and Isoaho, J.P. (2004), Determination of Total Sulphur Content in Black Liquor by X-ray Fluorescence, International Chemical Recovery Conference, June 6-10, Charleston, South Carolina, USA.

Malkavaara, P., Isoaho, J.P., Soininen, J. and Alén, R. (1999), Dithionite Bleaching of Thermomechanical Pulp: Factors Having Effects on Bleaching Efficiency, 6th Scandinavian Symposium on Chemometrics, SSC6, Porsgrunn, Telemark, Norway, Proceedings.

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LIST OF ABBREVIATIONS

Ara	Arabinose
BGH	Borohydride (Borol®) Generated Hydrosulphite
CSF	Canadian standard freeness
CTMP	Chemithermomechanical pulp
DBI	Direct Borohydride Injection
DDAV	Dehydrodiacetovanillone
DTPA	Diethylenetriaminepentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
FAS	Formamidine sulphinic acid
Gal	Galactose
GalA	Galacturonic acid
Glc	Glucose
GlcA	Glucuronic acid
GW (SGW)	Groundwood (pulp), stone groundwood
HPLC	High performance liquid chromatography
IC	Ion chromatography (chromatographic)
IR	Infrared spectroscopy
ISO	International Standards Organization
LWC	Light-weight coated paper, coated magazine paper
Man	Mannose
MC	Medium consistency
MDF	Medium-density fibreboard
MeGlcA	Methylglucuronic acid
MWL	Milled wood lignin
PGW	Pressure groundwood
Rham	Rhamnose
RMP	Refiner pulp
SBK	Semi-bleached kraft
SBS	Sodium bisulphite
SC	Supercalendered paper
STPP	Sodium tripolyphosphate
TMP	Thermomechanical pulp
UBS	Unbleached sulphite
UHQ	Ultra high quality
UV	Ultraviolet spectroscopy
VTT	Technical Research Centre of Finland
Xyl	Xylose

1 INTRODUCTION

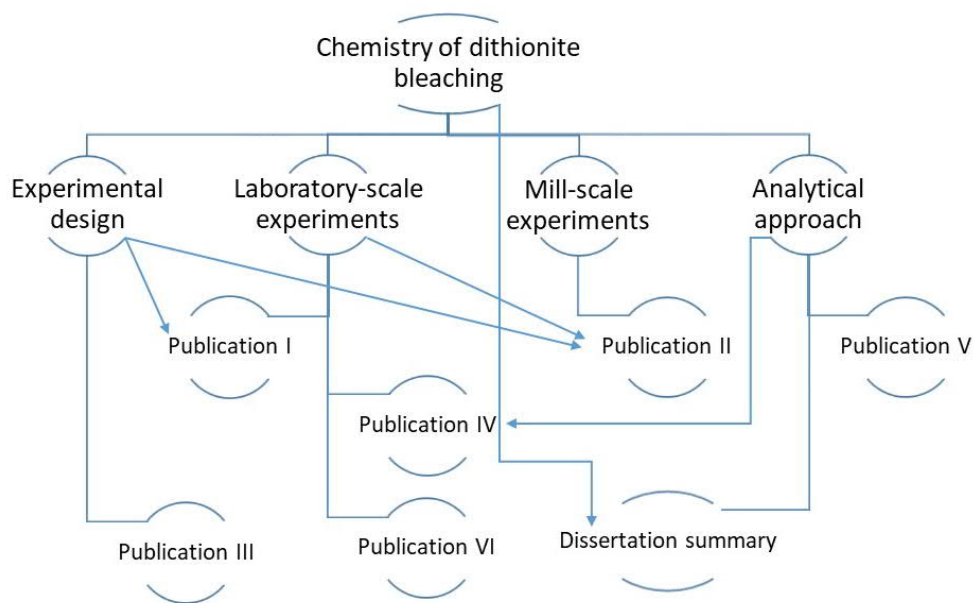
General features describing mechanical pulping processes can be challenging to visualise because of the non-uniform raw material, wood. The quality of mechanical pulping can alternate; for example, wood species, wood ages, variation within a tree stem and chemical composition of wood. Mechanical pulps, such as thermomechanical pulp (TMP), are manufactured in mechanical processes and do not use any additional chemicals for separating the fibres from the wood. Despite the high volume of energy consumed in pulping, the processes are considered as energy efficient and mechanical pulps can be produced with a high yield of 97–98%. The advantage of mechanical pulps compared to chemical pulps is to produce low basis weight paper with sufficient optical properties [Varhimo and Tuovinen, 1999].

Mechanical pulps are bleached to the target brightness, according to lignin-preserving bleaching, eliminating the colour-contributing groups, for example, by sodium dithionite. However, the attained brightness level is not permanent; the pulps tend to turn yellow during their life cycle because of the high lignin content.

Mechanical pulps are being used extensively for the manufacture of newsprint and are finding increasing acceptance in other paper grades and specialty products. However, in order, to speed up their acceptance and extend their use into fine paper products, the quality and uniformity of these pulps must be further improved. In terms of pulp quality, it is recognised that improvements are required with respect to their brightness and colour (or yellowness) as well as the rapid reversion characteristics that occur with yellowing.

This literature review is focused on lignin-preserving bleaching of mechanical pulps by introducing the general concepts, reaction mechanisms and colour reversion characteristics. The main aims of experimental research were to clarify the reaction pathways of dithionite bleaching and to clarify the most significant factors of the bleaching process. The reactions were studied both on laboratory-scale and mill-scale experiments. The principle of the reaction studies was very simple. Before every bleaching experiment, all the sulphur compounds of dithionite liquor were determined, and after bleaching, the sulphur compounds of

pulp filtrate samples were correspondingly analysed. Because the concentrations of sulphur compounds in the bleach liquor and the pulp filtrate were known, the degradation pathways of dithionite could be determined rather accurately. The scheme and general view of the experimental sub-parts of the dissertation is composed as follows:



One postulated mechanism for the degradation of sodium dithionite under bleaching conditions is illustrated in Figure 1, and this mechanism was confirmed to be accurate in the later laboratory studies. In this figure, it can be seen that the chemistry of dithionite bleaching is very complicated and includes many competing reactions. For example, depending on the efficiency of the process, various sulphur compounds can be pronounced at different concentrations in the bleaching filtrate. The same constituents with dithionite can also be present in bleach liquor and some of these ions can be found in pulps bonded to fibres. It could be concluded that sulphite is always present in filtrates if dithionite reduces chromophores. On the other hand, if the sulphate concentration increases compared to the initial level, dithionite is directly oxidised, indicating a defective bleaching system. Thiosulphate is mainly a product of thermal decomposition or inefficient bleaching. In the laboratory-scale trials, residual dithionite can also be found from filtrates; under mill conditions, dithionite degrades faster.

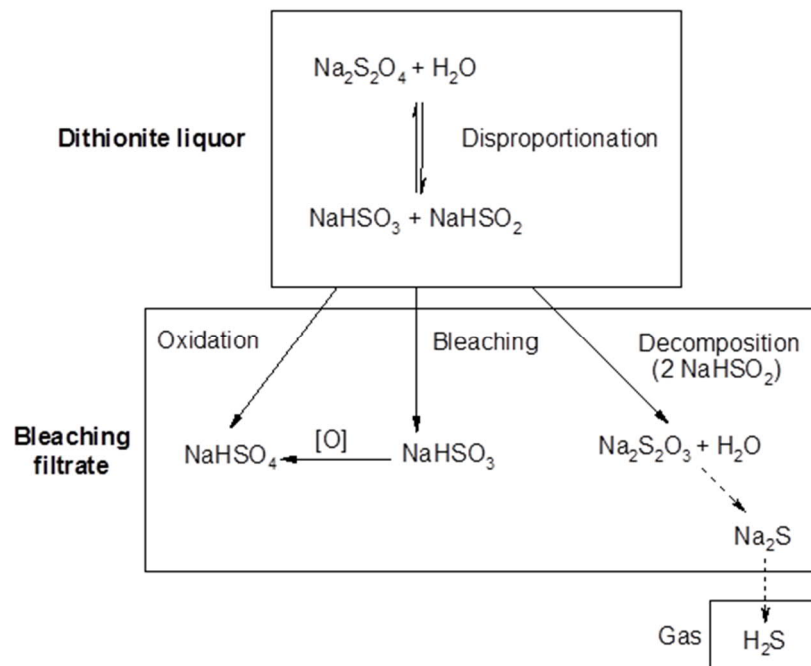


FIGURE 1 Postulated mechanism for the degradation of sodium dithionite during bleaching (modified from Auhorn and Melzer [1982]).

The Taguchi method [Roy, 2001] is typically used in the experimental design of bleaching trials because this method reduces the total number of experiments, and in some cases, the results are easily explained. In the Taguchi method, orthogonal matrixes are used for experimental design, allowing changes in several factors at the same time. Effects of different factors on the bleaching process can be separately handled by these methods because this method assumes that factors are independent. Furthermore, the percentage proportion of total effect (contribution) for each factor can be calculated and the significant factors of dithionite bleaching can be rather easily detected.

2 AIMS OF THE STUDY

The bleaching of mechanical pulps is dominated by two chemicals, dithionite (hydrosulphite) and peroxide; at present, peroxide is the prevailing system. The technical aspects of dithionite bleaching are well known, but the chemistry of the formation of detrimental products from dithionite has typically been ignored. The experimental implementation of this research was:

- To investigate bleachability from the mill aspect and the impacts of process variables in dithionite bleaching by means of laboratory bleaching using the Taguchi method (Publications I and IV).
- To clarify the decomposition of dithionite under typical paper mill conditions and optimise dithionite production unit performance (Publication II).
- Experimental implementation of the Taguchi method and process performance examination (Publication III).
- To evaluate the feasibility of dithionite to refiner bleaching and prevent corrosion problems caused by dithionite and its decomposition products (Publications I, II and VI).
- To find out which process variables should be considered with particular attention when altering or planning the process conditions at bleach plants using dithionite bleaching (Dissertation summary).

3 MECHANICAL PULPING

Wood species is the most significant criterion for mechanical pulping and pulp quality. Mechanical pulps consist of a distribution of fibres, fibre fragments and fines. Softwood species, especially the spruce family, are superior to hardwoods due to their more simple fibre morphology and chemical composition, which is the reason why they are widely used in thermomechanical pulping. In Northern Europe Norway spruce (*Picea abies*) is the most favourable raw material due to providing ideal pulp properties for different paper products: good fibre properties, low extractives content and high initial brightness. Spruce also gives excellent strength as well as optical and smoothness properties [Leask, 1987; Varhimo and Tuovinen, 1999].

One of the main reasons for using pine for mechanical pulp to a lesser extent is the high number of extractives, which can produce pitch problems in paper mills. The extractives (acetone soluble) content in pine may alternate up to 14.1%, which is measured from inner heartwood [Uusitalo, 2004]. Spruce contains considerably lower values, usually below 2.0% [Sjöström, 1993]. Pine as a raw material also attributes lower tensile and tear indexes than spruce and it requires more energy to be pulped to a given freeness due to coarser fibres. Only the poplar (*Populus*) of the hardwood species is suitable for the TMP process. However, a chemical pre-treatment of wood chips is required in order to balance the strength and optical properties of the pulp (Figure 2). The sheets from mechanical pulp have considerably higher opacity than sheets from chemical pulps and the higher fibre stiffness in mechanical and chemithermomechanical pulps leads to sheet structures giving higher bulk.

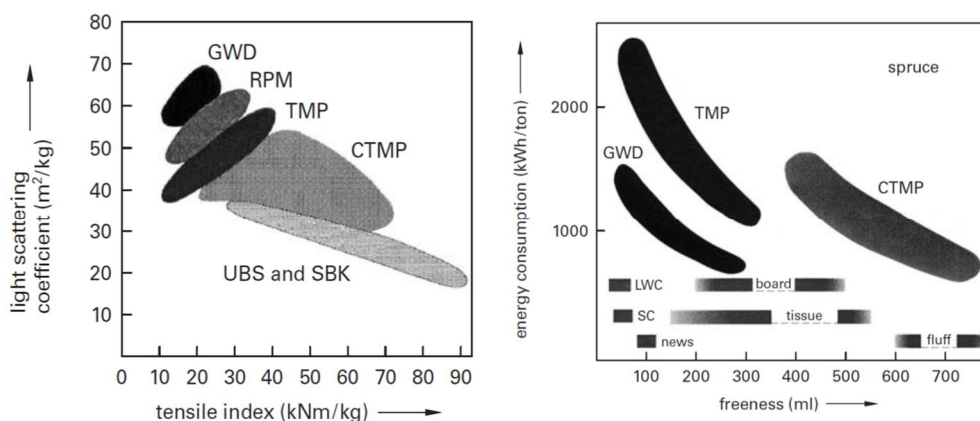


FIGURE 2 Strength, opacity and energy consumption in mechanical pulps; GWD = groundwood pulp, RPM = refiner pulp, TMP = thermomechanical pulp, CTMP = chemithermomechanical pulp, UBS = unbleached sulphite and SBK = semi-bleached kraft [Höglund, 2009].

The purpose of mechanical pulping is to detach the fibres from the wood material and loosen up their structure to make them suitable for papermaking. Material reduction in the manufacturing processes, grinding and refining, are

low; thereby, high yields of 97–98% are typical of mechanical pulping [Sundholm, 1999]. It is also remarkable that if any additional chemicals are not used, the resulting pulp contains all components of the wood raw material in about the same ratios as in wood.

The central principle in grinding is to bring the wood raw material into a cyclic oscillating stress field whereby the absorbed mechanical energy breaks down the structure of the fibrous raw material [Sironen, 1991; Smook, 1992; Salmén et al. 1999]. In grinding, debarked logs are pressed or forced against a rotating grindstone and simultaneously cleaned with a large quantity of water, which also acts as a cooling and lubricating agent. The wood blocks are oriented parallel to the axis of the stone so that the grits of the stone remove intact fibres. The fibre structure in the wood matrix is stressed cyclically in a series of shear as well as compression and decompression stages. As a result, fines and flexible fibres with good bonding characteristics are produced. In the refiner, wood chips are first disintegrated into fibres and fibre fragments; these are subsequently worked into a narrow gap between two parallel patterned refiner discs, of which either one or both rotate.

3.1 Grinding

The groundwood process is the oldest pulping process using wood as raw material [Haunreiter, 1997]. The first groundwood pulps had already been produced in the 1840s by a German, Friedrich Keller, who sold the patent rights to Heinrich Voelter. The prototype developed was a grinding machine suitable for industrial use; it was completed in 1852 [Anon., 2017].

The groundwood process consists of debarking the logs, pressing them against a rotating grindstone, and lastly cleaning and cooling grindstone with shower water (Figure 3). Groundwood pulps (GW) have for a long time been produced in non-pressurised systems and modern systems also preheat logs and use pressurised steam (PGW). Fibres and fibre fragments are torn from the wood under intensive treatment from the grits of the stone.

A number of process variants have been established for the two methods. Mainly, the preheating and processing temperatures of the wood material distinguish the different methods. For a long time, GW pulps have been produced in

non-pressurised systems. In more recent systems, the logs are preheated and processed under pressurised steam. The temperature in systems for production of pressurised groundwood (PGW) can vary from 100 °C to 140 °C [Höglund, 2009].

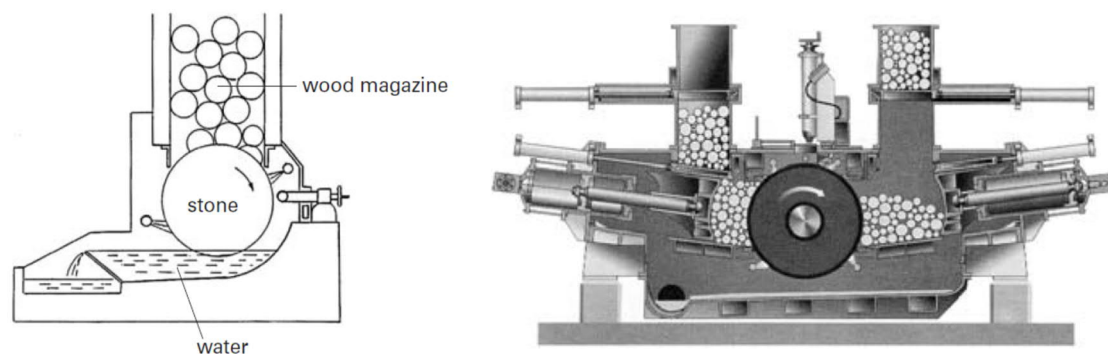


FIGURE 3 Arrangement of grinders [Höglund, 2009].

3.2 Refining

The mechanical pulping process can be distributed to sub-processes, starting from wood chips, conveying them to the refining room for refining and then to the heat recovery system. For instance, in the TMP process from wood chips to a paper furnish, the wood material is exposed to high temperatures and a large amount of mechanical energy. Refiner pulps are produced in different types of disc refiners. In the refiner, wood chips are subsequently worked into a narrow gap between two parallel patterned refiner discs, either one or both of them rotating and chips are first disintegrated to fibres and fibre fragments (Figure 4). Mechanical pulping is based on the discontinuous loading of wood with high-speed energy absorbing to wood the shifting heat [Westermarck, 1999].

Loading can be distributed to high frequency pressing power and shearing force. Due to these forces, the amorphous matter in wood has to be heated to soften the middle lamella. Suitable temperature and moisture assist the softening. Fibres come off relatively complete and a fine fraction is formed. The middle lamella bonds the fibres together, containing much lignin and it is trying to loosen together with the primary wall. Layer S_2 is cellulose rich and hence, an essential source of cellulose fibrils. Figure 4 presents the fracture zones in softwood affected by different mechanical processes: TMP, MDF and RMP. The cell wall layers are P (primary wall), S_1 , S_2 and S_3 (secondary walls) and ML (middle lamella).

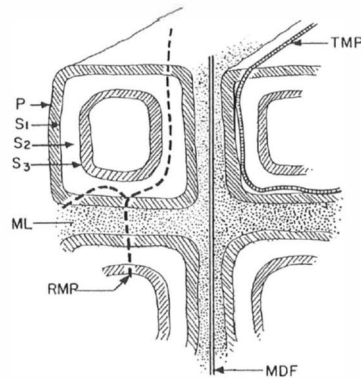


FIGURE 4 Breakdown of the wood matrix as a function of refining temperature: RMP 20-95 °C, TMP 110- 150 °C and MDF 170-190 °C [Franzén, 1986].

Wood softening is affected by morphological arrangement and chemical interconnection between wood components. The lignin is softened at a certain temperature depending on moisture. Softening temperatures of isolated lignin is found to range from 127 °C to 193 °C and the softening point of wet lignin is about 90 °C. Therefore, the temperature of wood chips must be warmed up to 100 °C before entering the refiner [Chow and Pickles, 1971; Tienvieri et al., 1999].

The most used refiners are the single-disc (SD) refiner and the double-disc (DD) refiner (Figure 5). Single-disc refiners have lower production capacity, a maximum of 250 tons/day.

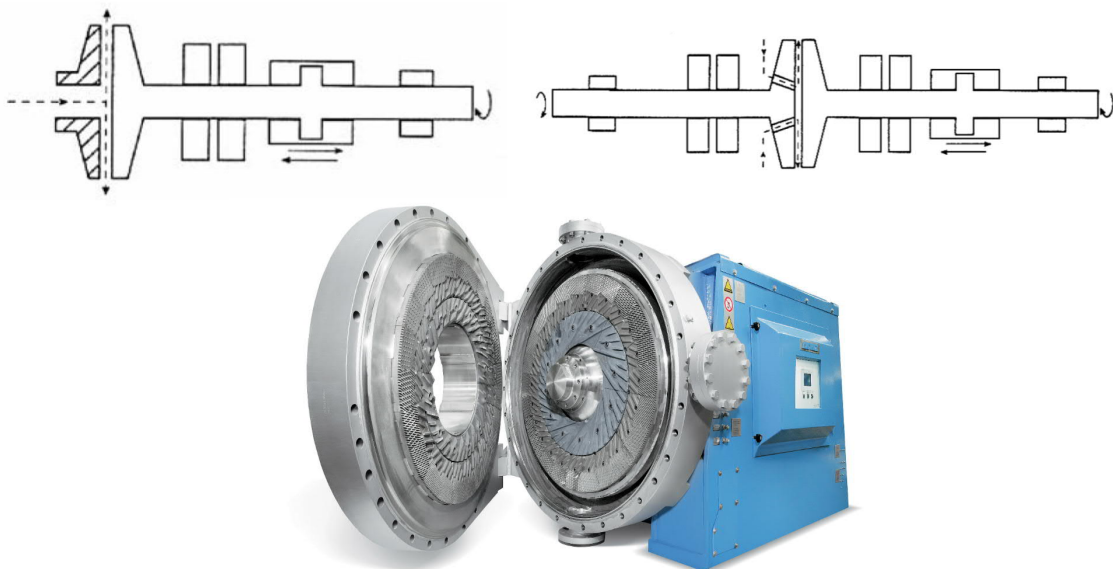


FIGURE 5 Upper side: principle of SD (left side) and DD (right side) refiners and below: actual version of SD refiner [Höglund, 2009; <https://www.andritz.com/products-en/pulp-and-paper/pulp-and-paper/pulp-production/mechanical-pulp/p-rc-apmp-process>, 2019].

In the SD refiners, the chips are fed into the refining zone between the stationary and rotating disc. Because of the centrifugal force, the chips migrate to outer shell, decreasing to individual fibres in the narrow blade gap section. Discontinuous loading is achieved by the bars of refining segments; then, the wood is heated. The distance between the discs is smaller than the chips, lowering in the direction the fibres are going. The double-disc refiner has two rotating discs [Tienvieri et al., 1999; Westermarck, 1999].

The chips are washed to remove heavier components from the chip flow, such as stones and sand. Also, sawdust and bark are removed during washing. The washing of wood chips adds to the moisture content of the chips, making the moisture level more uniform. The washing of chips increases their temperature, due to the washing water, which is usually from 70 °C to 85 °C. Prior to refining, the chips are preheated in order to warm and soften them and equalise the temperature. The retention time in the preheater is from 1-3 min and the temperature is between 110-130 °C. The preheating increases the number of long fibres. In the TMP, a separate impregnation system, such as in the CTMP processes, is not used [Smook, 1992].

Consistency of out coming pulp is from 30% to 50%. After the first stage refining, the pulp is blown with steam to the second stage of steam separator cyclone or pulp classifying. Saturated steam accruing in the process is used to steam the feed water in the power plant as well as in the drying section of the paper machine. Recovery of 70% of the heat can be achieved using this modern heat recovery technique [Westermarck, 1999].

According to Westermarck [1999], TMP has a relatively small enrichment of lignin in the fibre surface material and this is due to defibration in the production process. High amounts of fines are created during the refining processes. The secondary wall has a lower lignin content than the middle lamella. The typical distribution of mechanical pulp fibre length is a low content of long fibres and high content of fines [Lindholm, 1999]. An extended refining time and energy-input increase the number of fines in the pulp [Cheing, 1994]. The fines fraction of mechanical wood pulp sometimes has a noticeably lower degree of whiteness (up to 10% ISO) than the long fibre fraction and is more difficult to bleach [Roick et al., 1991]. The reasons for this are recognised to be the higher lignin content and much higher heavy metal and extractives content in fines fraction.

TMP fines mainly consist of material from the middle lamella region and the primary wall [Sundberg, 2000]. Lignin and hemicellulose molecules, such as arabinans and galactans, are present in high numbers in the fines and middle lamella. Therefore, the number of arabinogalactans is higher in the fines than in the fibres. Pectin is located in the middle lamella and the primary wall [Westermarck and Vennigerholtz, 1995]. Wood resin and polysaccharides are mainly substances released from TMP.

The overall structural changes occurring in lignin are small when wood is converted to a mechanical pulp by grinding or refining, although the content of chromophoric structures changes as the wood material goes through the different refining stages [Pedneault et al., 1997; Svensson et al., 1998]. Lignin makes up

nearly one-third of the pulp, and any attempt to break down its main structure usually leads to new chromophoric groups and a deepening of colour. The phenolic content remains somewhat constant, and no noticeable changes in the relative distribution of different types of lignin sub-structures have been detected. For instance, the structure of the most abundant linkage between phenyl propane units (β -O-4) is almost inactive to mechanical actions [Cheing, 1994]. However, in refining, the β -1 and β -5 structures, which are among the major structural units in lignin, are easily converted into the corresponding stilbene structure according to the reaction shown in Figure 6 [Varhimo, 1999; Li et al., 2000]. The stilbene, in turn, is a strong absorber of visible light and easily oxidised to deeply coloured quinones of various types [Lee and Sumimoto, 1999]. Various studies have observed that the small amounts of aryl- α -carbonyl structures formed in lignin oxidation reactions during refining are also contributors to the discolouration of mechanical pulps [Johansson and Gellerstedt, 2000].

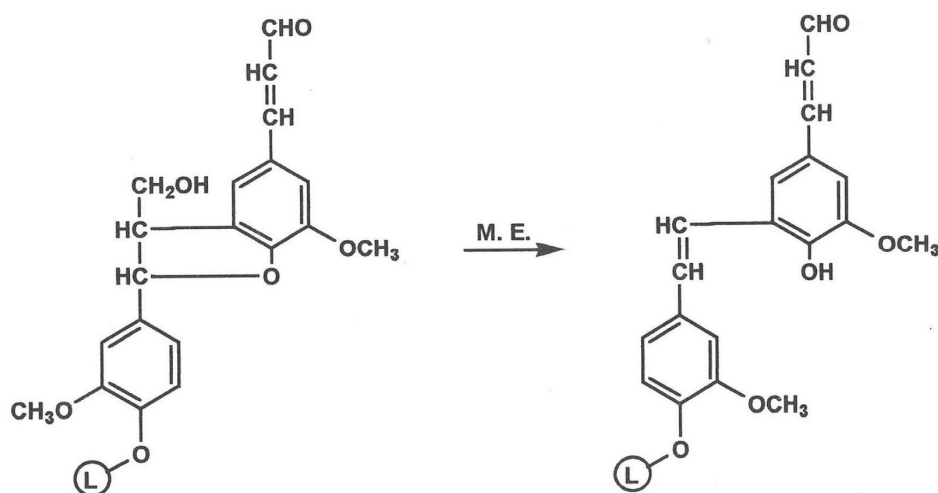


FIGURE 6 Formation of a stilbene from β -5 structures as the result of mechanical treatment of wood [Gellerstedt, 2001].

4 CHEMISTRY OF LIGNIN-PRESERVING BLEACHING

Bleaching reactions are classified mechanistically as electrophilic or nucleophilic reactions. In lignin-retaining bleaching, the typically occurring reactions are nucleophilic, which involve anions and, to a much lesser extent, radicals. In an initial step, the reactions are essentially reductive and involve nucleophiles, which attack the electron-deficient carbon atoms in carbonyl- and conjugated carbonyl-containing structures [Gierer, 1986; Dence, 1996]. A relatively large number of reaction types have been identified as contributing to the overall effect produced when pulps are bleached. Examples of reactions which are determined to be the more significant types and specific to a single bleaching chemical are presented in the following two chapters where dithionite and hydrogen peroxide bleaching are discussed in great detail.

The brightness of high-yield pulps is close to that of the raw wood material. However, besides the wood species, origin and age—storage, bark content, processing conditions, metal ion content and light-scattering ability also have a clear impact upon pulp brightness [Lindholm, 1999]. Table 1 presents some typical brightness levels of unbleached mechanical pulps produced from Norway spruce (*Picea abies*).

Table 1 Typical brightness values of unbleached mechanical pulps [Lindholm, 1999]

Pulp type		Brightness [% ISO]
GW, SGW	Stone groundwood (pulp)	60-65
PGW	Pressure groundwood (pulp)	60-63
TMP	Thermomechanical pulp	57-60
CTMP	Chemithermomechanical pulp	60-67

The objective of bleaching mechanical pulps is to increase pulp brightness without degrading and dissolving lignocellulosic material [Gierer, 1986]. The bleaching is based on elimination of coloured groups in lignin, which is the reason why it is often referred to as lignin-preserving bleaching [Alén, 1999]. The increase in brightness can be achieved by an oxidising (hydrogen peroxide) or a reducing (sodium dithionite) agent, either as a single-stage process or as a two-stage process with peroxide followed by the reductive dithionite stage. In general, we can consider the rule of thumb in bleaching to be that the higher the initial brightness, the higher the final brightness of the pulp if the same quantity of bleaching reagent is added. However, although the peroxide may increase the brightness up to 25% ISO and the combination peroxide-dithionite to 10–26% ISO, in dithionite bleaching, final brightness values over 71% ISO are unattainable no matter what the initial brightness values are [Strunk, 1987]. Nevertheless, high brightness should not be considered as the only primary goal of bleaching. Concerning the pulp end use, it is more economical to bleach only to the required brightness, not to the highest brightness attainable.

4.1 Chromophoric groups in mechanical pulp

Colour problems encountered in pulps arise either from the present wood colour or the chemical changes which take place during the grinding and refining processes [Hon and Glasser, 1979]. In bright softwoods, such as spruce, the predominant contribution of the natural colour comes from the lignin, for which partial chemical structure is presented in Figure 7. Extractives account for a minor part of the colour, whereas cellulose and hemicelluloses are practically uncoloured.

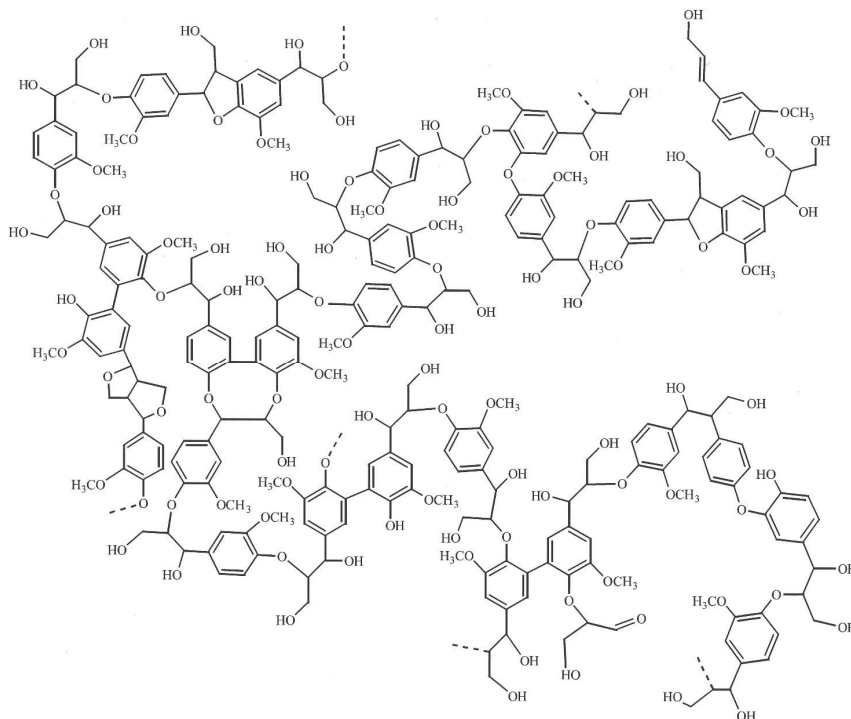


FIGURE 7 Suggested partial structure of softwood lignin [Henriksson, 2009].

The yellowish hue of wood can be attributed to the presence of small amounts of heterogeneously distributed coloured lignin structures or chromophores, which absorb light [Pew and Connors, 1971; Agarwal and Atalla, 2000; Gellerstedt, 2001]. The quantitatively most important of these are α -carbonyl groups, ortho- and para-quinones and coniferyl aldehyde-type structures, of which the last one has been estimated to account for 10–20% of the total light absorption of softwood lignin at an effective wavelength of 457 nm. Although the absorption maxima of these compounds (Figure 8) are located in the near-UV region ($\lambda < 400$ nm), the tails of the peaks extend into the visible absorption region, accounting for their characteristic colours. Moreover, it has been suggested that when incorporated into a cellulose matrix, the tail absorbance of the chromophores is displaced to higher wavelengths and intensified.

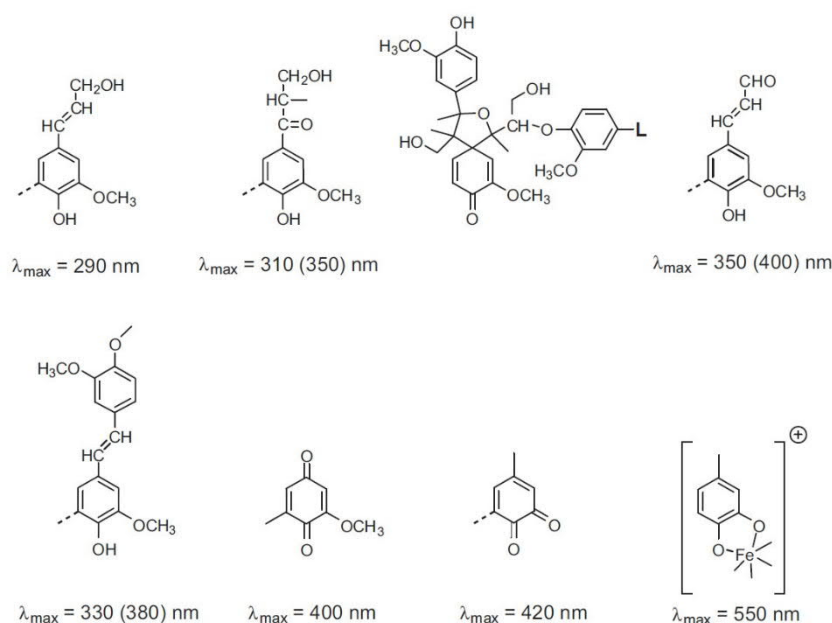


FIGURE 8 Examples of suggested chromophores in wood and their approximate light absorption maxima [Gellerstedt, 2001].

In addition, native lignin also contains a variety of colourless structures that can condense into chromophores in rather mild process conditions, giving rise to a rapid discolouration [Pew and Connors, 1971]. For instance, in the reaction between hydroquinones or catechols and oxygen, which can be accelerated by the presence of heavy metal ions, the corresponding quinones are formed. Despite years of research, knowledge of the nature of chromophoric systems involved and the mechanism of their formation is still quite poor.

Oxidative demethylation, that is, loss of methoxyl groups, has been attributed to the suggested presence of *o*- and *p*-quinonoid units in wood whereas side chain displacement reactions are known to generate them in unbleached mechanical pulps [Hon and Glasser, 1979; Dence, 1996]. Alternatively, hydrolysis of *o*- and *p*-ketals in lignin biosynthesis, as well as light-initiated reactions in wood or pulp, may form *o*- and *p*-quinonoid structures. Unsubstituted *o*- and *p*-quinones are inherently unstable in the presence of moisture and heat. However, their proposed presence in lignin or a lignocellulosic matrix implies that they become stabilised through linkage to adjoining structural units. The contribution of *o*- and *p*-quinones to the absorbance of lignin at 457 nm is considerable, 30–65% by rough estimation.

Another proposed source of colour in lignin is catechols, which form complexes with metal ions, especially with ferrous (Fe^{2+}) or ferric (Fe^{3+}) ions [Dence, 1996]. These catechol complexes show colour because they have absorption maxima in the visible region of the spectrum. The presence of catechols in lignin has been established by various approaches. The most convincing of them is based on methylation of milled wood lignin (MWL), which is followed by permanganate and peroxide oxidation treatments in sequence. The calculations upon the

average molar absorptivity value indicate, for instance, a catechol content of about 1% for spruce MWL.

Other chromophoric systems, such as free radicals, are also expected to contribute to the colour of lignin in wood [Hon and Glasser, 1979; Dence, 1996]. Autoxidation, irradiation by UV and visible light, transition metal-catalysed oxidation, enzymatic and fungal attack and mechanical action are known to generate free radicals. One of the most likely reactions is the formation of phenoxy radicals in the oxidation of phenolic hydroxyl groups. An absorption maximum of approximately 400 nm has been attributed to these intermediates of degradation and discolouration process.

4.2 Structural changes in lignin chromophores

In mechanical pulps, the bleaching reactions between dithionite and the chromophores have not been studied as have the reactions of peroxide bleaching. Some studies approached the fundamentals utilising model compound bleaching [Polčín and Rapson, 1971; de Vries and Kellogg, 1980]. The attempt was to identify chromophore systems susceptible to reduction by dithionite with UV or IR spectroscopy in order to give statements on the response of different chromophore systems to dithionite. The results dictated only that the chromophore structures with a broad absorption maximum at 450–500 nm are affected. Suggestions of their types have been presented, but no clear arguments have been provided [Svensson et al., 1998].

It is generally considered that dithionite reduces relatively simple quinoidic structures to their corresponding leucochromophores, catechol and hydroquinone forms. Dithionite ion is capable of reducing only the uncondensed structures; however, the condensed structures are known to resist the reduction. The reduction of an *o*-benzoquinone unit to the catechol dianion by a sulphur dioxide radical ion is illustrated in the upper section of Figure 9.

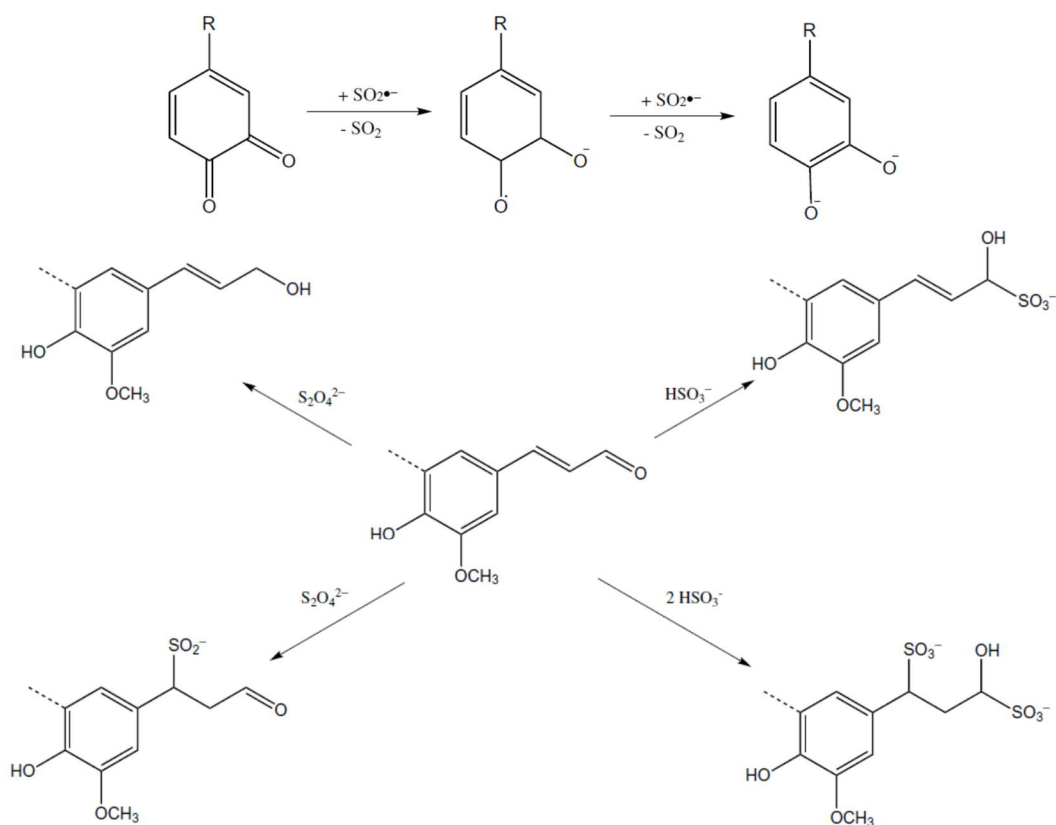


FIGURE 9 Elimination of quinone- and coniferaldehyde-type chromophores by reaction with dithionite and bisulphite ions [Dence, 1996; Makarov, 2016].

Also, coniferaldehyde-type structures are believed to be susceptible to dithionite. Such chromophore groups can be removed in several ways, as seen in the lower section of Figure 9. The dithionite ion can serve either as a reductant for the aldehyde group or an adduct in a nucleophilic conjugate addition reaction. The by-product, bisulphite ion, can react with α , β -unsaturated aldehydes, such as those present in a coniferaldehyde unit forming mono- and disulphonates. The reactions shown in Figure 9 lead to the partial reduction of the chromophore system. Consequently, the broad absorption maximum observed in the visible region of the spectrum before bleaching is shifted to the near-UV spectral region.

Under the prevailing bleaching conditions, α -aryl ketone-type structures are somewhat stable towards the reducing action of dithionite [Dence, 1996]. At higher temperatures, aliphatic and aromatic aldehydes and ketones, such as α -carbonyl groups, are known to undergo conversions to primary and secondary alcohols. Also, coloured ferric (Fe^{3+}) ion complexes are reported to become reduced by dithionite to less coloured ferrous (Fe^{2+}) ion compounds [Lindholm, 1999].

5 CHEMISTRY OF SODIUM DITHIONITE BLEACHING

The objective of lignin-preserving bleaching processes is to selectively eliminate colour-contributing groups while maintaining pulp yield. In addition, bleaching chemicals should themselves be colourless and run at reasonable cost [Barton et al., 1987; Ellis, 1996]. To classify as a reductive bleaching agent, the agent should reduce lignin aldehyde and ketone groups to alcohols and reduce quinones to hydroquinones [Rapson, 1969]. Commercially known reagents are bisulphite, dithionite (hydrosulphite) and borohydride [Hills and Richards, 1989]. In addition, formamidine sulphinic acid (FAS) is used for colour stripping [Minor, 1992; Engstrand and Johansson, 2009]. The brightness increase up to 14% ISO for TMP is supplied predominantly by sodium dithionite. In general, a single-stage treatment is sufficient for newsprint-type pulps, but in order to achieve higher brightness levels of over 80% ISO, a two-stage peroxide-dithionite process is required [Lindholm, 1999]. Due to relatively mild conditions in dithionite bleaching, the papermaking potential of the pulp is not affected and the yield losses are apparently small.

5.1 Composition and stability of sodium dithionite

The year 1870 may be considered as a starting point of the development of the chemistry of sulphur-containing reducing agents. Schutzenberger, on the basis of Schönbein's earlier observations, successfully prepared sodium dithionite (Figure 10) for the first time. In 1906, BASF was the first company to produce sodium dithionite in powder form by a zinc dust process. The name "hydrosulphite" conveys the mistaken notion that the compound contains hydrogen. By the time this mistake was recognised, the brand name "Hydrosulphite Conc. BASF" had become so well-known commercially that the company decided not to change the name [Makarov, 2016].

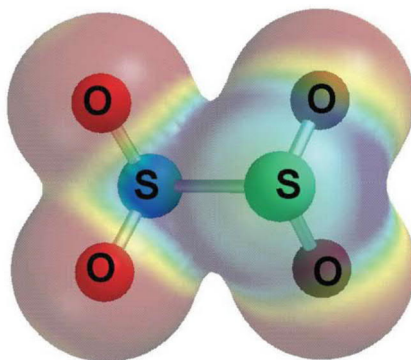


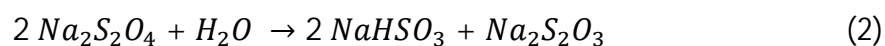
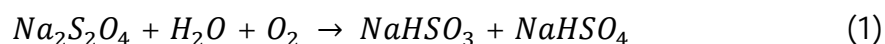
FIGURE 10 Dithionite ion structure [Makarov and Silaghi-Dumitrescu, 2013].

Sodium dithionite is an unstable white crystalline solid that decomposes in water and is rapidly oxidised by oxygen. Under anaerobic conditions and at room temperature, alkaline solutions of dithionite decompose slowly. It can be purchased as a liquid or powder, but it can be also produced on-site from commercial solutions (Borol[®]), also called borohydride generated hydrosulphite (BGH).

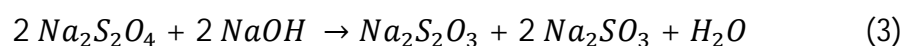
The solutions made commercially by the reduction of sodium bisulphite with sodium borohydride contain sodium borate (NaBO₂) as a by-product. However, it does not participate in bleaching reactions, and thus, there is no difference in behaviour of commercial and conventional dithionite [Ellis, 1996]. In general, all dithionite bleaching solutions contain additives, such as anti-oxidants, pH buffers and chelates. Alkali is added on-site if the pH of the solution is below the optimum range 9–11. The additives have a significant role in maximising the bleaching efficiency of dithionite, although they have no direct role in the elimination of colour.

Dithionite chemicals are available as a liquid or a powder base, and bleaching efficiency can be increased by utilising additional chemicals as stabilising agents. Also, some dithionite grades contain additives to reduce the powder's flammability. An active dithionite concentration can be between 50-90%. The best way to use dithionite powder is to make 2–10% solution and the only critical point is to prevent air permeability in the dissolution system. Powder-based dithionite mixtures can be stored in closed containers over a long period.

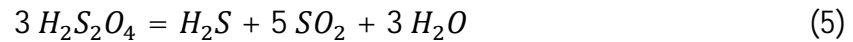
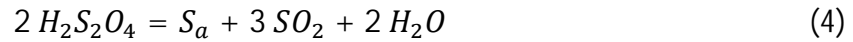
As a liquid, dithionite is quite unstable, especially if air is present or the solution is a weakly acidic medium (Eq. 1). In anaerobic conditions (Eq. 2), secondary reactions can also take place and generate other stable sulphur species, such as sulphate (SO₄²⁻), dithionate (S₂O₆²⁻) and hydrogen sulphide (H₂S) in traces.



If a dithionite aerobic decomposition reaction is regarded to be a very fast, anaerobic decomposition can be delayed a few days [Wayman and Lem, 1970; Dence, 1999]. Anaerobic decomposition reactions depend on storing temperature and the solution's alkalinity. Keeping the liquid at a low temperature and under alkali conditions can maintain stability for a few days. The rate of this Equation (3) is greatly affected by pH.



As a conclusion, fundamental primary reactions; induction period (Eq. 4) in which active non-colloidal sulphur (S_a) is formed, and autocatalysed the fast-phase reaction (Eq. 5) can be written as follows [Čermák and Smutek, 1975]:



In the dithionite bleaching system, the principal active ion species is the dithionite anion, $S_2O_4^{2-}$. Pemberton et al. [1995] have proved by means of electron spin resonance (ESR) spectroscopy that the dithionite ion dissociates into a sulphur dioxide radical ion (Eq. 6). However, the radical ion is very unstable, and it gives rise to sulphur dioxide and a sulphonylate dianion (Eq. 7) and both species are also known for their reducing properties [Cermák and Smutek, 1975].



Other sulphur-containing compounds present in dithionite bleaching solutions are introduced as minor impurities during the synthesis of dithionite or are formed from the dithionite during bleaching (Eqs. 8-10). Of the sulphur-containing by-products, only sulphur dioxide (SO_2) and the bisulphite ion (HSO_3^-) have some direct bleaching effect where they eliminate chromophore systems partially or totally [Polčín and Rapson, 1969]. In addition, it is interesting to note that at low concentration, $HO-SO_2^-$ can easily yield the $SO_2^- \cdot$ radical anion and the $\cdot OH$ radical (Figure 11).

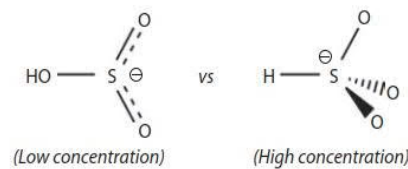
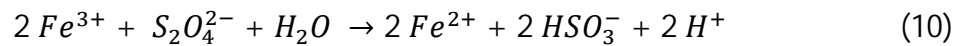
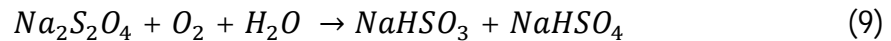
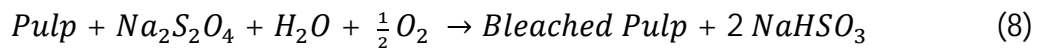
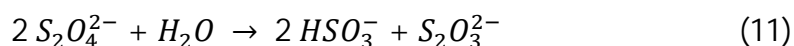


FIGURE 11 Bisulphite anion structure [Golding, 1960].

In order to bleach efficiently, those reactions where dithionite is lost through decomposition should be minimised. In practice, the presence of oxygen should be avoided, and the temperature and the pH should be kept in the optimal range during bleaching. Sodium dithionite powder blends are stable over long periods of time, but aqueous solutions are inherently unstable [Ellis, 1996]. In the presence of air, dithionite decomposes in a relatively short time into sulphite and sulphate according to the reaction (Eq. 9). A slower decomposition is encountered under anaerobic conditions resulting in the formation of bisulphite and thiosulphate according to the reaction (Eq. 11). However, the stability of solutions

can be improved by maintaining the solutions at low temperatures (c.a. 7 °C) and an alkaline pH (10.0–12.5).



The data currently available in the literature on the lifetime of dithionite and its decomposition products are highly disputed (Table 2). One of the factors influencing determined decomposition rates of dithionite and, thus, partially explaining scattering of the data, is the pH at which experiments have been performed. It has been consistently shown since the initial work in the early 1900s that de-composition of dithionite greatly accelerates as the pH level decreases.

Table 2 Summary of previous dithionite studies and experimental conditions and results

Reference	Experimental conditions	Conclusion
Telfeyan et al. [2019]	Unbuffered solution, pH ~7 and ~9, prevented outgassing of H ₂ S	Pseudo 1 st order half-life of 10.7 days for pH ~7 and 33.6 days for pH ~9
Kovács and Rábai [2002]	Concentrations and temperature varied systematically over a wide range pH and redox potential	In this article, rate constants are in Table 1
Kovács and Rábai [2001]	0.001–0.05 M and in the temperature interval 20–60 °C	In this article, rate constants are in Table 1
de Carvalho and Schwedt [2001a and 2001b]	[S ₂ O ₄ ²⁻] = 0.0065 M, background solutions of formaldehyde, NaOH, HMTA in glycerol and water, (NH ₄) ₂ HPO ₄ /NH ₄ OH and Triton X-100	Major reaction products: S ₂ O ₃ ²⁻ and SO ₃ ²⁻ Minor reaction products: S ²⁻ and elemental S
Münchow and Steudel [1994]	T = 20 °C; [S ₂ O ₄ ²⁻] = 0.0214 M; pH: 5.7, 13	Reaction products: S ₂ O ₃ ²⁻ , SO ₃ ²⁻ and S ₂ O ₄ ²⁻ in alkaline solution persists (experiments not exceeding 2 h)
Amonette et al. [1994]	T = 30 °C; Ar (95%), H ₂ (4%); [S ₂ O ₄ ²⁻] = 0.002, 0.013 and 0.06M; CaCO ₃ buffer	0.06 M: t _{1/2} = 135 h; k _{app} = 8.5·10 ⁻⁵ min ⁻¹ 0.002 M: t _{1/2} = 243 h; k _{app} = 4.8·10 ⁻⁵ min ⁻¹
Holman and Bennett [1994]	T = 42–88.5 °C; N ₂ purged, Excess bisulphite pH: mildly acidic	d[S ₂ O ₄ ²⁻]/dt = -k ₁ [S ₂ O ₄ ²⁻][HSO ₃ ⁻]-k ₂ [S ₂ O ₄ ²⁻]0.5[HSO ₃ ⁻][S ₃ O ₆ ²⁻] k ₁ =(3.1 ± 0.3·10 ² M ⁻¹ s ⁻¹ ·T-exp(-(54.3 ± 5)/RT) k ₂ =(1.67 ± 0.2·10 ⁷ M ^{-3/2} s ⁻¹ T-exp(-(78.4 ± 7)/RT)
Kilroy [1980a,b]	T = 82 °C; Ar atmosphere; [S ₂ O ₄ ²⁻] = 0.02–0.08 M; buffer: NaOH	k = 0.014–0.018 (mol/L) ^{0.5} min ⁻¹

Table 2 Summary of previous dithionite studies and experimental conditions and results (continued)

Reference	Experimental conditions	Conclusion
Čermák and Smutek [1975]	T = 20 °C; pH ~ 4; [S ₂ O ₄ ²⁻] ≤ 0.0025 M	Major reaction products: H ₂ S, elemental S and SO ₂ Parallel and consecutive reactions: S ₂ O ₃ ²⁻ , S _n ²⁻ and S _n O ₆ ²⁻
Lem and Wayman [1970]	T = 23 °C; Ar atmosphere; [S ₂ O ₄ ²⁻] = 1, 2, 5, 10·10 ⁻³ M; pH range: 3.5, 4, 4.5, 5 (buffers: CH ₃ COO ⁻ and Na ₂ HPO ₄ /C ₆ H ₈ O ₇)	-dC/dt = k ₁ [H ⁺]C + k ₂ [H ⁺] C(C ₀ -C) k ₁ : 1.67·10 ⁻¹ L mol ⁻¹ s ⁻¹ k ₂ = 5.83·10 ³ L ² mole ⁻² s ⁻¹
Burlamacchi et al. [1969]	T = 60–90 °C [S ₂ O ₄ ²⁻] = 0.067, 0.125, 0.25 M; pH = 6 (phosphate buffer)	-d[S ₂ O ₄ ²⁻]/dt = k'[S ₂ O ₄ ²⁻][HSO ₃ ⁻] k' = 0.57–7.8·10 ³ L mol ⁻¹ s ⁻¹
Spencer [1967]	T = 15–35 °C [S ₂ O ₄ ²⁻] = 0.015–0.2 M in solution of HSO ₃ ⁻ , SO ₃ ²⁻ and NaCl (pH 5.2)	First-order decay Decomposition products: S ₃ O ₆ ²⁻ and S ₂ O ₃ ²⁻
Rinker et al. [1965]	T = 60–80 °C; [S ₂ O ₄ ²⁻] = 0.0055–0.0115 M; pH = 4–7 (KH ₂ PO ₄ and NaOH)	R _{induction} = k _c [S ₂ O ₄ ²⁻]T ^{3/2} ·[H ⁺] ^{1/2} k _c = 1.3·10 ⁸ ·e ^{-12000/RTL} mol ⁻¹ sec ⁻¹
Lister and Garvie [1959]	T = 88 °C; N ₂ atmosphere; [S ₂ O ₄ ²⁻] = 0.034–0.142 M; buffer: 0.05–0.2 M NaOH	k = 4.5·10 ⁻⁴ min ⁻¹

5.2 Manufacture of sodium dithionite

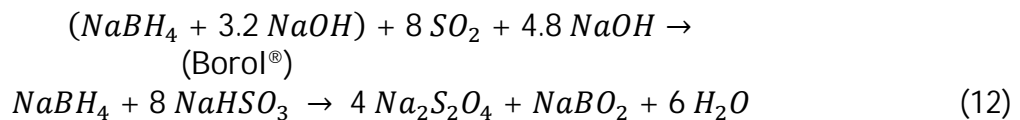
Several manufacturing processes for sodium dithionite have been developed. Preparation methods are based on the reduction of sulphur dioxide, or defined sodium bisulphite (SO₂ + H₂O). The following procedures are commercially available: (1) zinc dust—sodium carbonate process, (2) electrolytic or cathode reduction process, (3) sodium formate process, (4) sodium borohydride process and (5) sodium amalgam process [Nayar, 1972].

Borohydride (Borol[®]) Generated Hydrosulphite (BGH) has been in use for decades to generate fresh hydrosulphite on mill sites to bleach mechanical pulps. It is a proven conventional technology for bleaching mechanical pulps, and for recycled fibres colour stripping Direct Borohydride Injection (DBI) has been developed [Meyers et al., 1999]. The BGH process requires the mixing of Borol[®] solution, sodium bisulphite (SBS), and sulphuric acid chemicals at a fixed molar ratio and pH to generate sodium hydrosulphite at maximum efficiency.

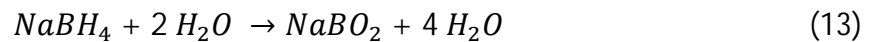
Even though BGH and Premix (DBI) processes are similar, as they both require Borol[®] solution and SBS in the premixing process, the Borol[®] solution and sodium bisulphite molar ratios are flexible and may vary to meet the bleach performance criteria. The chemicals are mixed prior to the application points to generate bleach liquor at a higher pH than the BGH process, and the generated liquor

is not stored for a long time. Thus, the process generates a mixture of reductive chemicals which, under certain bleaching conditions, provide enhanced bleaching performance than applying hydrosulphite alone [Wasshausen et al., 2006].

The Borol[®] solution consists of 12% sodium borohydride (NaBH₄) and 40% sodium hydroxide (NaOH). A Borol[®] bleach generating unit allows a mechanical pulp mill to generate its own bleaching liquor on-site at a reduced cost relative to merchant dithionite. The generation of dithionite is based on the fast chemical reaction between sodium borohydride or its equivalent, sulphur dioxide and sodium hydroxide.



In reality, secondary hydrolysis decreases yield 10-15%.



The optimum pH for Borol[®]-generated hydrosulphite is 6–6.5 and if the pH is above 7, sodium bisulphite subsides into unreactive sodium sulphite.

Figure 12 presents two alternative hydrosulphite on-site manufacturing flow-line diagrams. The right side is sodium bisulphite; sulphur dioxide/water and Borol[®] streams are combined and blended in a static mixer. The preparation of bleaching liquor is fast and the solution is forced through a degassing unit where generated hydrogen gas is separated and redirected to the open atmosphere. A ready-for-use bleaching solution is pumped into the storage tank or mixed directly with the pulp.

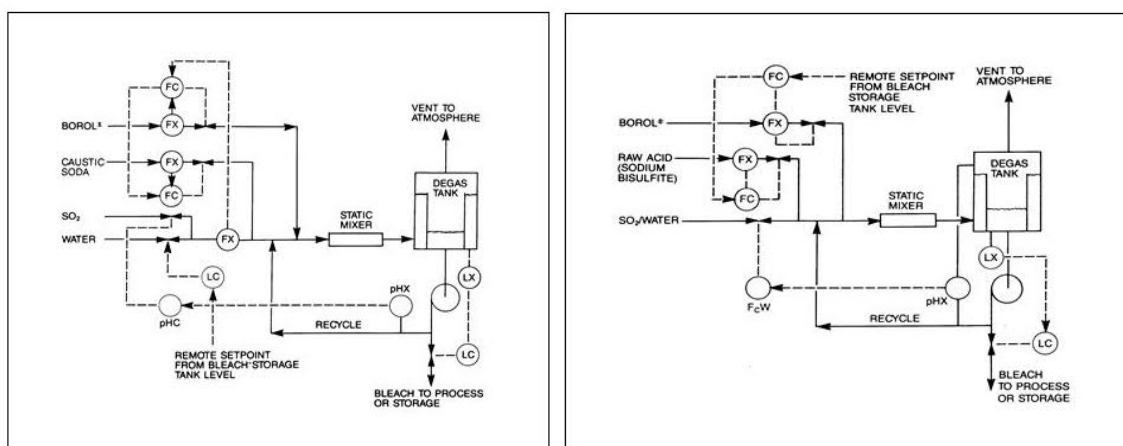


FIGURE 12 Typical flow diagrams of sodium dithionite production [Lindholm, 1999].

5.3 Primary bleaching variables

In order to ensure the maximum increases in brightness, the process variables should be optimised, and the reactor should be kept devoid of contaminants, such as entrained air, heavy metal ions and loss of bleaching chemicals prevented by adequate mixing. Although each variable produces a measurable result, finding the optimum bleaching conditions is difficult because the process variables are all interdependent. The conditions usually applied in dithionite bleaching are presented in Table 3.

Table 3 Typical conditions for dithionite bleaching

Chemical charge, [% on pulp]	0.5–1.0
Reaction pH	5.5–6.5
Consistency, [%]	3–5 (8–12)
Temperature, [°C]	50–70
Retention time, [min]	30–60
Chelating agents	Added, if the metal concentration in the pulp is high

5.3.1 Dosage

Dithionite dose is the most important of all variables. Doses of 0.5–1.0% of active $\text{Na}_2\text{S}_2\text{O}_4$ on pulp are usually applied, but some variation between mills, wood species and the equipment used appears [Dence, 1999; Lindholm, 1999]. As seen in Figure 13, there is a ceiling in the brightness gain that can be achieved by increasing the dithionite dose. The excess volume of dithionite has a minimal effect on brightness, and once the plateau is reached, the excess dithionite decomposes to thiosulphate and bisulphite according to the reaction in Eq. (11).

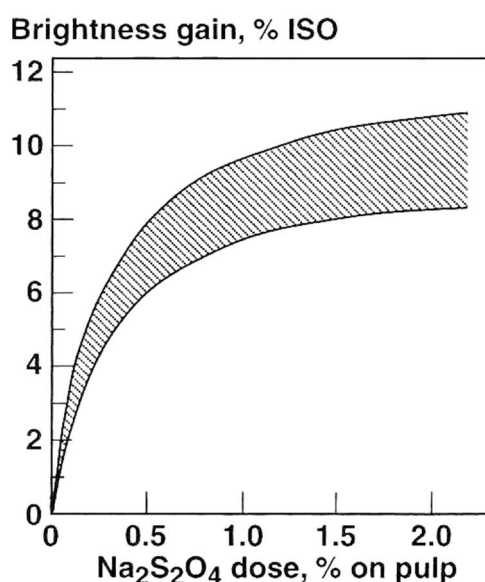


FIGURE 13 Brightness increase in dithionite bleaching [Lindholm, 1999].

5.3.2 pH

The relationship between pH and the stability of dithionite solutions is well recognised: at pH levels below 4.0, the dithionite starts to decompose whereas at high pH levels, the solutions are rather stable [Dence, 1999; Lindholm, 1999]. However, because the high pH levels darken the pulp and the low pH levels may lead to H₂S formation, evolving into an unpleasant odour, the optimum bleaching conditions for the pH are in the range of 5.5–6.5 [Sullivan, 1982].

During the bleaching stage, the pH is reduced by 0.3–1.0 units as a result of pulp bleaching and decomposition reactions. Buffers are generally included in the commercial dithionite-based solutions to maintain the reaction pH in the optimum range. Controlling the pH decreases the brightness loss, which takes place as the pH is decreased.

5.3.3 Consistency

Within the 3–5% range, pulp consistency has a minimum effect on brightness response. At such a low consistency, the entrainment of air into the pulp, which has a detrimental effect both on dithionite chemicals as well as the reduced chromophores, can be avoided. However, new equipment operating in medium consistency, that is, in the consistency range of 8–12%, has been developed. This equipment is superior to the conventional ones with respect to brightness gain and the size of the bleaching reactor; the resulting brightness, 1–2% ISO units higher than that obtained in low-consistency bleaching, is attained in medium-consistency pumps, which are much smaller than the conventional bleaching towers [Dence, 1999; Lindholm, 1999].

5.3.4 Temperature

The optimum temperature in dithionite bleaching depends on several factors. Typically, dithionite bleaching operates in the temperature range of 45–60 °C. In most cases, a temperature of 60 °C is optimum both from a bleaching response and from an energy cost point of view. Generally, the higher the temperature, the higher the bleaching rate and final brightness [Barton et al., 1987]. However, at higher temperatures brightness reversion is accelerated and at temperatures close to 100 °C, dithionite also encounters physical limits and decomposes.

5.4 Secondary variables

The retention time is not a critical variable in dithionite bleaching [Dence, 1999; Lindholm, 1999]. Most bleaching typically occurs within the first 10–20 min following the dithionite addition. However, sufficient additional retention times are typically provided in order to fully utilise the reductive capacity of the bleaching agent. Most mills are designed for a retention time of 30–60 min, but an increase

in temperature, mixing, or pulp consistency may allow the use of lower retention time.

Small amounts of different metals are present in raw wood material. However, the more important sources of contaminating metals in pulp are different process steps, particularly regarding the chemicals added. Iron, copper, aluminium, chromium and manganese are especially known to restrict brightness gain by catalysing the decomposition of dithionite according to the reaction (6) [Barton et al., 1987; Smook, 1992]. They also reduce the brightness stability by re-oxidising the reduced chromophore groups.

Chelating or sequestering agents, such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA) or sodium tripolyphosphate (STPP), are added in order to control the detrimental effect of metals on brightness (mainly iron, copper, aluminium, chromium and manganese). Polčin and Rapson [1969] have reported that a significant decrease in colour as well as improved stability towards aging of pulp can be achieved by the removal of heavy metals with EDTA. In general bleaching processes, EDTA is used in a pH range below 7.0 whereas DTPA is more suitable for alkaline systems. The effect of different sequestering agents on brightness response is illustrated in Figure 14. However, it is noteworthy that 0.1–1.0% of chelant per ton of pulp produces adequate effect; the excessive numbers of chelating agents are known to have an adverse effect on brightness.

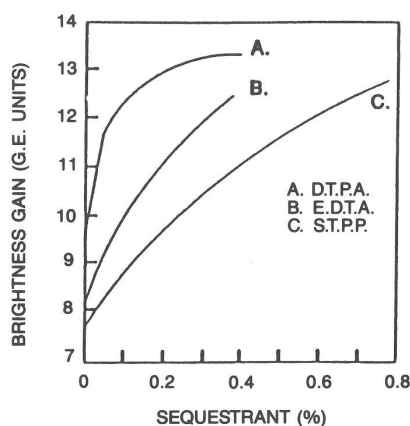


FIGURE 14 Effect of different sequestering agents on brightness [Barton et al., 1987].

5.5 Bleach plant designs

The choice of the dithionite bleach addition point depends on the level of brightness gain required. The results presented in Table 4 are averages for each type of design. The differences in brightness gain are mostly due to exposure of the pulp to air and retention time control: the more air present in bleaching and the more difficulty in controlling the retention period length, the lower the brightness response.

Table 4 Brightness gain in different addition points of the bleaching chemical

Brightness gain [% ISO]	Addition point
4–6	Refiner (single-stage)
8–10	Tower (single-stage)
2–6	Stock chest (single-stage)
9–14	Refiner and tower (double-stage)

Normally, mechanical pulps are bleached either in a tower or in a chest. Due to the lower response of TMP than, for example, groundwood to bleaching, refiner bleaching was introduced in order to increase the bleaching effect. Many pulp mills can inject $\text{Na}_2\text{S}_2\text{O}_4$ at different locations in the process to control the final brightness of the paper (Figure 15). The main injection point can be located in a medium consistency (MC) pump where a relatively large amount of $\text{Na}_2\text{S}_2\text{O}_4$ is used, usually before an up-flow tower. The subsequent addition to the refining plates in refiners constitutes a high turbulence zone and is optimal for the addition of bleaching chemicals. Daneault et al. [1994] have also observed that in optimal conditions, the brightness gain for post-refining bleaching can achieve approximately the same values as for standard laboratory bleach experiments.

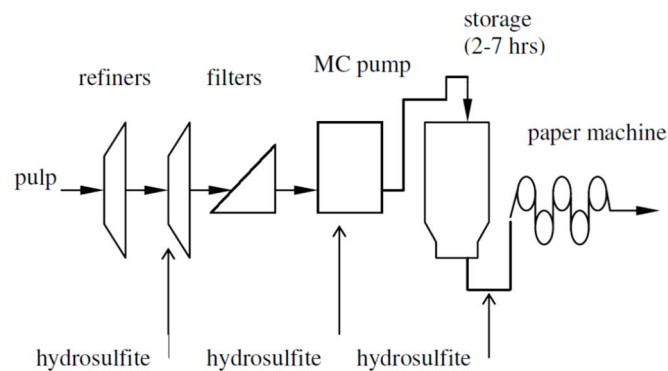


FIGURE 15 Simplified diagram of a TMP process with three hydrosulfite injection points [Major, 2005].

In the pulping process, according to Figure 16 some evolving darkening reactions can take place and influence pulp brightness level [Lindholm, 1999].

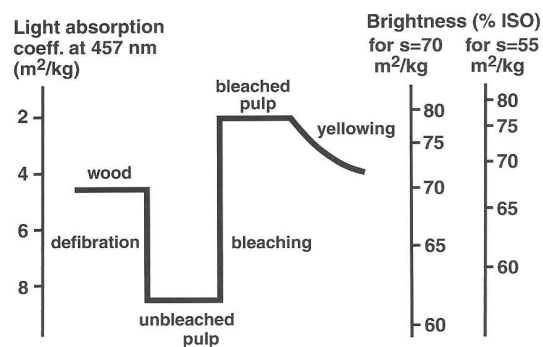


FIGURE 16 Development of light absorption during mechanical pulp manufacturing.

6 EXPERIMENTAL

6.1 Laboratory-scale bleaching experiments

6.1.1 Typical pulp compositions

One of the typical Finnish paper mill untreated TMP raw material was characterised, and findings of composition and chemical analysis could be presented (Tables 5 and 6). Pulp and their fractions (fibres and fines) were characterised for fibre composition (Bauer McNett fractionator, BMN) and fiber length (Kajaani FS-200). As expected, the chemical properties of the fines diverged most from the others [Kleen et al., 2003]. Lignin, extractives and metals were concentrated in the fines. Some differences in the carbohydrate composition of the pulp and the fractions were detected. The fines were rich in galactose (galactans) and galacturonic acid (pectins), but poor in mannose (glucomannans).

Table 5 TMP fibre characteristics

	Original pulp	Fibres	Fines
Fibre length, [mm]	1.54	2.04	0.75
Mesh ¹ >1.19 mm, [%]	27.3	49.4	0.1
Mesh ¹ 0.91 mm, [%]	9.9	12.5	0.5
Mesh ¹ 0.53 mm, [%]	18.7	21.6	6.1
Mesh ¹ 0.13 mm, [%]	18.1	12.4	26.7
Mesh ¹ <0.13 mm, [%]	26.0	4.1	66.6

¹Sieve mesh indicates the particles retained by the sieve

Table 6 Chemical analysis of the TMP (original pulp) and its fractions

Component	TMP	Fibres	Fines
Lignin, [% of dw ¹]	25.5	21.0	30.0
Gravimetric Soluble	25.4	20.9	29.9
	0.1	0.1	0.1
Carbohydrates ² , [% of dw ¹]	71.5	74.9	62.2
Rhamnose	0.13	0.1	0.27
Arabinose	1.1	0.94	1.6
Galactose	2.1	1.4	3.0
Glucose	48.4	51.3	39.9
Xylose	5.7	5.9	6.0
Mannose	12.6	14.1	9.6
Methylglucuronic acid	0.54	0.61	0.6
Galacturonic acid	0.89	0.63	1.4
Glucuronic acid	<0.1	<0.1	<0.1

¹Dry wood

²Monosaccharide units in carbohydrates

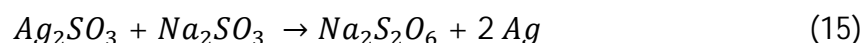
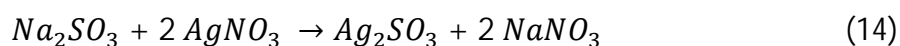
Table 6 Chemical analysis of the TMP (original pulp) and its fractions (continued)

Component	TMP	Fibres	Fines
Extractives, [% of dw ¹]	1.3	0.23	1.3
Extractives, [mg/g]	6.3	1.0	5.5
Triglycerides	1.7	<1	1.1
Fatty acids	1.1	0.4	1.4
Resin acids	1.1	0.4	0.1
Sitosterol	0.2	0.1	0.3
Steryl esters	1.2	0.1	1.9
Lignans	1.1	0.1	0.7
Total, [% of dw ¹]	98.3	96.1	93.5
Metals, [mg/g]	3.97	1.57	2.68
Na	1.9	0.083	0.16
K	0.26	0.045	0.059
Ca	0.81	0.84	1.3
Mg	0.12	0.18	0.21
Fe	0.003	nd ³	0.01
Cu	0.80	0.40	0.90
Zn	0.013	0.004	0.006
Mn	0.068	0.017	0.037

¹Dry wood³Not detected

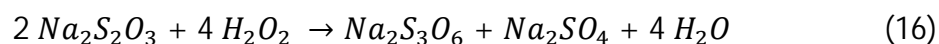
6.1.2 Chemicals and standards

For ion chromatographic determination of sulphur compounds, standards were made by commercial products except for dithionate, trithionate and tetrathionate. Reactants in the inorganic synthesis of sodium dithionate dihydrate ($\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$) were sodium sulphite and silver nitrate, in which case the end products were sodium dithionate and metallic silver [Schlessinger, 1962]:



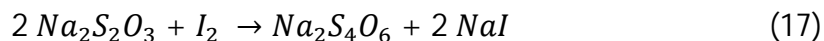
The yield from the theoretical maximum was approximately 70% and the end product purity was increased recrystallisation by a water/ethanol mixture. Loss in mass was about 10% from every recrystallisation.

Potassium trithionate was synthesised using sodium thiosulphate 5-hydrate and hydrogen peroxide as reactant:



The hydrated end product, sodium trithionate, was switched to an anhydrous potassium analogue by mixing it with potassium acetate.

Sodium tetrathionate dihydrate was synthesised mixing sodium sulphate pentahydrate in a mortar with iodine:



Built-up pasta was washed impurity-free with ethanol, and during every recrystallisation, about 25% of salt was lost. These standard reagents were kept under partial vacuum.

A new laboratory-scale bleaching device was specially developed for the experiments (Figure 17). The most important advantage of this device was the ability to take filtrate samples during the bleaching experiments; an on-line pH measurement was also possible. An appropriate quantity of sodium dithionite liquor was injected by a syringe through an injection port equipped with a septum. The liquor migrated very quickly through the pipe into the pulp. The rest of the liquor was rinsed into the pulp by a continuous nitrogen flow. Nitrogen was also used in removing air from the pulp. A gas-flow meter and a pressure-regulating valve controlled the flow of nitrogen. The reactor was heated by a water bath that maintained the appropriate temperature very precisely. There was also a possibility to use a heat jacket in pre-heating. Temperature and pH were measured by a combined temperature/pH probe with a controlling unit.

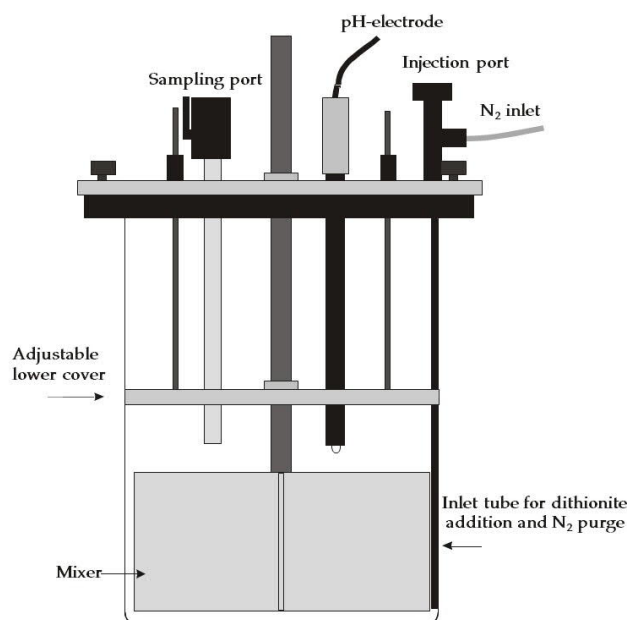


FIGURE 17 The dithionite bleaching reactor.

6.1.3 Bleaching procedures

Almost all the bleaching experiments were carried out in the same way in the bleaching device introduced previously. An appropriate amount of pulp was weighed into the reactor (target 40 g of dry pulp) and then diluted normally by ultra-high quality (UHQ) water to a consistency of 5%. Usually, EDTA was added and air was removed from the pulp with nitrogen gas. The warm-up process took

about 30 min, and after that, the initial pH value of pulp was adjusted by a definite volume of 0.1 M NaOH or 0.1 M H₂SO₄. The volume of the pH adjustment chemical and EDTA liquor was taken into account in consistency calculations.

When the bleaching temperature and the initial pH were adjusted, the dithionite liquor was added and time monitoring was started. An appropriate supply of dithionite in each case was determined by ion chromatography (IC) and the exact addition was determined by weighing. During the injection of dithionite, the pulp was mixed for 20 s, and after that, the pulp was mixed every 5 min for 5 s. Nitrogen bubbling continued during bleaching and the total bleaching time was 30 min.

After 30 min, the reactor was opened and the pulp was poured out. The pulp was filtrated through wire bags (with 50 µm and 100 µm pore sizes) and then washed by ion-exchanged water (c.a. 3 L/40 g dry pulp). The filtrate of pulp was placed into a plastic bottle and then frozen. After the washing stage, the pulp was centrifuged to 20–35% consistency and then the pulp was homogenised. The dry content of the pulp was analysed by a Moisture Analyser. When the dry content of the pulp was known, two hand sheets (100 g/m²) were made for brightness and colour measurements. Occasionally, a brightness pad was made for the measurements of optical properties. In the condition cabinet sheets and pads were dried overnight (14–16 h) at a constant temperature (23 °C) and humidity (50%) before measurements.

6.1.3.1 Preparation of sodium dithionite liquors

BGH was made in a laboratory-scale set-up. The preparation of BGH liquor was made according to the procedure of Morton Inc. [Wang and Sibiet, 1998]. The procedure used was slightly modified and further developed from this chemical supplier procedure. The difference between these methods was the use of sulphur dioxide gas (SO₂ water) in the pH control instead of sulphuric acid (H₂SO₄) used in the Morton procedure. SO₂ water is usually used in mill-scale production.

The procedure was as follows:

- N₂ gas was used to prepare the bleaching solution anaerobic.
- 130 mL of UHQ water was measured into the reactor and it was cooled down to about 10 °C.
- 4.7 g of sodium disulphite was inserted into the reactor.
- Sulphur dioxide gas (SO₂) was used to adjust pH value to about 2.
- Borol[®]-solution was carefully dispensed until pH was elevated to 6.
- The rest of the Borol[®] solution was added by means of SO₂ gas, that is, pH must remain in a range 6-7. Altogether, the amount of Borol[®] solution added was 3.06 mL. The SO₂ gas line tube was unplugged from the reactor and the pH was adjusted to 8.5 with 1 M NaOH.

Sodium dithionite liquor from dithionite powders was prepared as follows:

- 130 mL UHQ water was placed in an airtight vessel.
- Air was removed from the water by nitrogen gas.
- An appropriate quantity of powder (8–11 g) was dissolved into the water.
- The solution was mixed by a magnetic stirrer during dissolving and storing.
- The dithionite liquor was stored in a water bath (15–25 °C) under nitrogen gas.
- The concentration of sodium dithionite was between 50–70 g/L.

6.1.3.2 Dithionite liquor and filtrate samples

An exact amount of dithionite liquor was sampled by a digitally fixed volume pipette and then liquor was introduced into a formaldehyde solution [Steudel and Münchow, 1992; Polenov et al., 2002]. The filtrate samples were taken during bleaching experiments through the sampling port of the bleaching reactor. The filtrate sample was extracted from the pulp through a glass-made pipe; the lower end of the pipe was covered with a wire cloth in order to prevent the fibre from blocking up the pipe. The sample was collected with a suction test tube, from which the sample was quickly poured out into a beaker. From this beaker, an exact quantity of filtrates was pipetted into a formaldehyde solution as quickly as possible.

6.1.3.3 Experimental design

The mill PGW bleaching trials aimed to clarify the effects of some general factors, such as temperature, pH, dithionite dosage and EDTA addition, on dithionite bleaching. One critical factor affecting bleaching performance was the dithionite grade. The objective was to discover which dithionite grade of the three commercial dithionite grades (AA, BB and CC) was the best in the case of PGW. AA was sodium borohydride-based, BB and CC were powder-based dithionite grades.

Degradation products of dithionite in bleaching filtrates were also studied in these trials. The purpose was to follow the reaction pathways of dithionite under different bleaching conditions and to determine the main proportions of sulphur compounds in filtrates during bleaching.

The effects of different process factors on dithionite bleaching response were investigated using the Taguchi method. For the elucidation of results, an L18 matrix was designed for these bleaching experiments. Unused columns are not present (Table 7).

PGW was ground from black spruce and balsam fir. The initial ISO brightness at a consistency of 5% was 63.2% ISO and the pH value of the pulp was 5.9.

After receiving, the pulp was frozen in plastic bags (4 L) in order to prevent contamination. Before bleaching experiments, the pulp was allowed to defrost at room temperature.

Table 7 The experimental design for PGW

Trial	Pulp washing	Dithionite dosage [% on pulp]	pH	Temperature [°C]	Dithionite grade	EDTA [% on pulp]
1	ON	0.4	5.0	50	AA	0
2	ON	0.4	6.0	70	BB	0.2
3	ON	0.4	7.0	90	CC	0.4
4	ON	0.8	5.0	50	BB	0.4
5	ON	0.8	6.0	70	CC	0
6	ON	0.8	7.0	90	AA	0.2
7	ON	1.2	5.0	70	CC	0.2
8	ON	1.2	6.0	90	AA	0.4
9	ON	1.2	7.0	50	BB	0
10	OFF	0.4	5.0	90	BB	0.2
11	OFF	0.4	6.0	50	CC	0.4
12	OFF	0.4	7.0	70	AA	0
13	OFF	0.8	5.0	70	AA	0.4
14	OFF	0.8	6.0	90	BB	0
15	OFF	0.8	7.0	50	CC	0.2
16	OFF	1.2	5.0	90	CC	0
17	OFF	1.2	6.0	50	AA	0.2
18	OFF	1.2	7.0	70	BB	0.4

Pulp washing was one of the used factors in these trials. Before bleaching, about 4 kg of pulp, having a consistency of about 7.5%, was diluted by 20 L of ion-exchanged water and mixed for 2 h. Then the pulp was thickened to a consistency range of 30–32% in order to lessen the number of contaminants that could interfere with dithionite. If washing was not used (OFF in the matrix), the pulp was directly diluted to a consistency of 5% by UHQ water before bleaching.

The levels of other factors could be seen from the experimental matrix. All dithionite dosages were calculated according to the amount of active sodium dithionite. The dithionite and EDTA dosages were expressed as percentages of air-dry pulp. The pH values in these experiments were equal to the initial pH values before dithionite addition. Two empty columns did not have any effect on these trials. After the actual PGW experiments were done, six control experiments were carried out. This comparison was made from the black spruce pulp.

6.2 Mill-scale bleaching trials

The objective of this trial was to evaluate the feasibility of dithionite for refiner bleaching and prevent corrosion problems [Nakatsu et al., 2007; Choudhary et al.,

2015] caused by dithionite and its decomposition products. Traditional tower bleaching with dithionite is limited to about 10% ISO units brightness gain and in this level of performance, the use of dithionite is more economical than hydrogen peroxide. Two-stage bleaching performed in a refiner and a tower with dithionite may increase brightness gain more than 12% ISO units.

Chemical reactions were the most efficient in the refiner for several reasons. First, the pulp consistency was higher compared to tower bleaching, indicating a good chemical-to-wood ratio. This could also mean more chemical-to-wood reactions and fewer chemical decomposition reactions. Although the retention time inside the refiner was very short, the temperature was very high, and therefore, it drove the bleaching reactions forward. With the normal retention times in the tower bleaching, a high temperature would lead to unwanted darkening reactions. Refiner mixing was very intensive, giving more opportunities for chemical and wood interactions.

6.3 Analytical methods

6.3.1 Ion chromatography

Dithionite has been determined formerly by iodimetry [Wollak, 1930; Danehy and Zubritzsky, 1974], polarography [Wayman and Lem, 1970], Raman spectroscopy [Meyer et al., 1980] and spectrophotometry [Veguta et al., 2017]. All these above-mentioned analytical methods fail to give a representation of dithionite decomposition products. Capillary electrophoresis attempt to address that deficit [Kokkonen et al., 2004; de Carvalho and Schwedt, 2005].

Both the bleach liquor and bleaching filtrate samples were analysed using an IC system equipped with UV-Vis and electrochemical detectors to determine various sulphur-containing anions. Sodium dithionite samples must be processed in anaerobic conditions, and an analytical approach requires removal of oxygen; otherwise, it could be a primary source of error. Each sample was first introduced to a 2% (by volume) formaldehyde solution and then filtrated through a membrane prior to IC analysis to prevent the air-oxidation of anions in sampling actions. The base of the IC method on the mobile phase ion chromatography (MPIC) was essentially the same as described previously in an article by Steudel and Münchow [1992], but the application was further developed. The method allowed simultaneous quantitative analysis of the most abundant anions (Figure 18): dithionite ($S_2O_4^{2-}$), sulphide (S^{2-}), sulphite (SO_3^{2-}), sulphate (SO_4^{2-}), thiosulphate ($S_2O_3^{2-}$), dithionate ($S_2O_6^{2-}$) and polythionates ($S_nO_6^{2-}$).

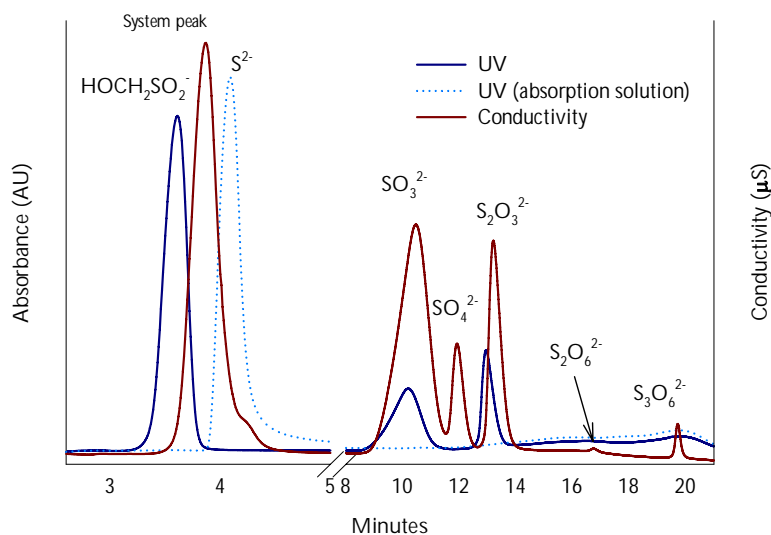


FIGURE 18 Detection of sulphur anions.

6.3.2 EDXRF

Determination of sulphur in biomass material has been performed by numerous methods that usually require total demolish of the sample [Axelson and Simonson, 1982; Robinson et al., 2009]. In this study, the sulphur content of unbleached and bleached pulp samples was determined by an energy dispersive X-ray fluorescence spectrometer (EDXRF). The radiation source in this analyser was a mini X-ray tube and detector was a proportional counter. Only the covalently-bonded sulphur was determined by this method because the pulp sample was heavily washed by UHQ water before analysis. A pellet consisting of 1.4 g of the milled pulp was measured under a thin polyester film (Mylar, thickness 2.5 μm) using a collection time of 300 s. The calibration of the EDXRF spectrometer was accomplished by an addition method using an unbleached pulp sample as a fundamental matrix. Each sample was analysed twice (both sides of pellet) and the mean value was used in the subsequent calculations. The method is represented in detail in Publication IV.

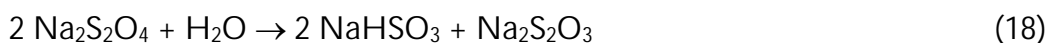
7 RESULTS AND DISCUSSION

7.1 Decomposition pathways

In this study, the thermochemical decomposition of borohydride-produced sodium dithionite was investigated under industrial conditions to simulate storing conditions. The laboratory-scale experiments were carried out under a nitrogen atmosphere in the temperature range of 10-60 °C utilising two initial dithionite concentrations (0.18-0.22 mol/L and 0.28-0.32 mol/L) typically used in a mill environment. For these experiments, an IC method for analysing the most abundant anions forming from the decomposition of dithionite was applied: sulphite SO_3^{2-} , thiosulphate $\text{S}_2\text{O}_3^{2-}$, sulphide S^{2-} , sulphate SO_4^{2-} and polythionates $\text{S}_n\text{O}_6^{2-}$. In these concentration ranges differences in decomposition rates were difficult to observe. As an example, in some cases, the most abundant volatile product (H_2S) was also monitored from a receiver flask during treatments and the material balance of sulphur indicated that other products, such as free sulphur, may be present (Figure 19). The formation of elemental sulphur as one of the by-products was not measured quantitatively and only oscillation of calculated total sulphur content was observed. Oscillation of these monitored anions were quite low, approximately < 10% of measured concentration range.

These preservation experiments indicated that most of the liquors contain, besides a dithionite ion, an undesirable build-up of sulphur anions (e.g., SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$ and SO_3^{2-}) in relatively high concentrations. The presence of these degradation products generally increases in higher temperatures or the presence of air. The thermochemical decomposition of dithionite followed several main reaction pathways and is dependent on the corresponding solution conditions (Eqs. 18- 20).

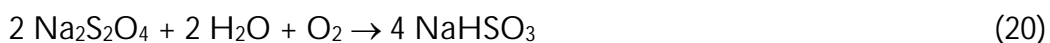
Anaerobic:



Aerobic, excess of oxygen:



Aerobic, oxygen is reaction restrictive:



Degradation of dithionite was monitored during different temperatures, including simultaneous detection of various sulphur-containing anions (Figures 19-23). Analysis of the end products of the thermal decomposition of dithionite showed that they were mainly bisulphite and thiosulphate in a mole ratio of approximately one-half, which was in accord with the stoichiometry of Equation (18). Detailed decomposition curves of dithionite were also arranged to see if predictions of different reaction mechanisms are fulfilled [Cermák and Smutek,

1975]. In each situation there is an induction period in which the concentration of the dithionite ion decreases slowly, followed by an abrupt decrease (autocatalytic phase) in dithionite concentration (Figure 23).

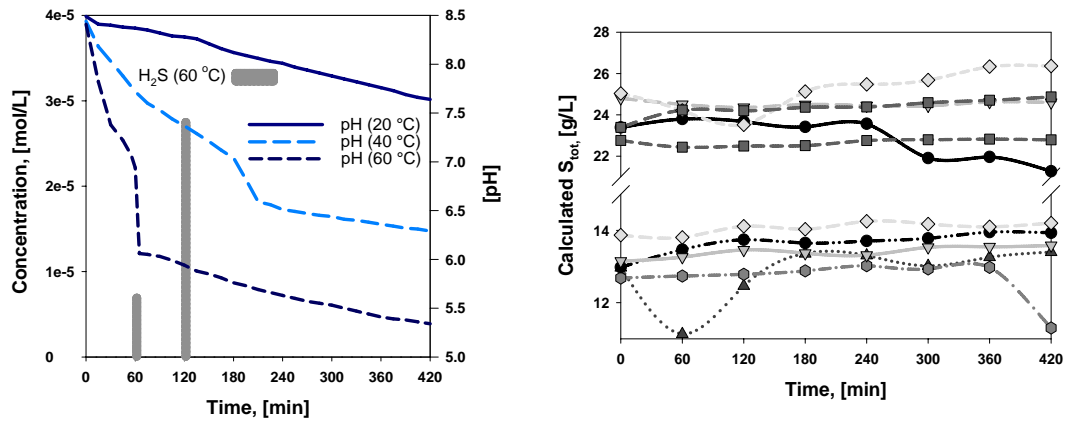


FIGURE 19 Examples of dithionite decomposition pH curves (on left) and calculated total sulphur content of degradation experiments (on right).

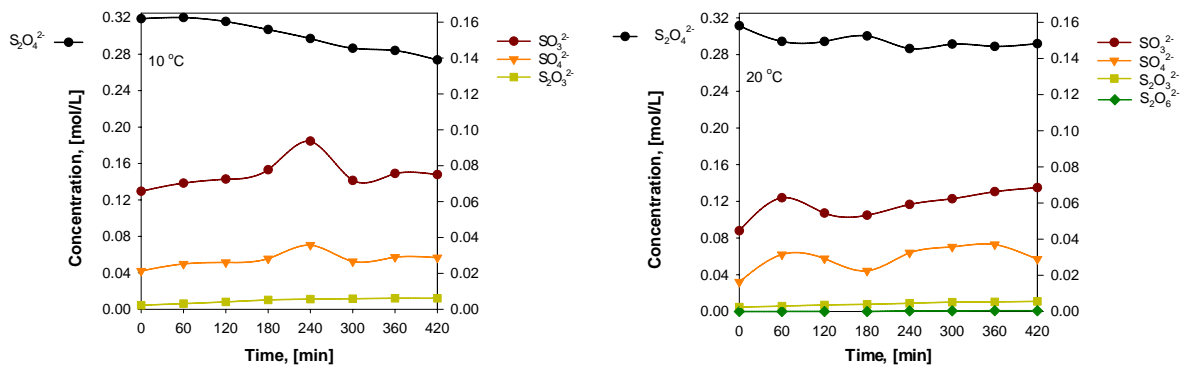


FIGURE 20 Decomposition curve of dithionite and degradation products at 10 °C and 20 °C.

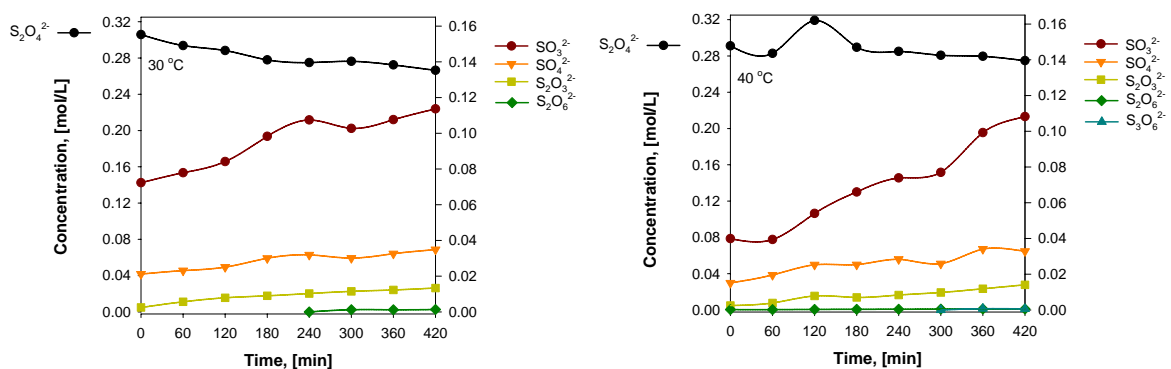


FIGURE 21 Decomposition curve of dithionite and degradation products at 30 °C and 40 °C.

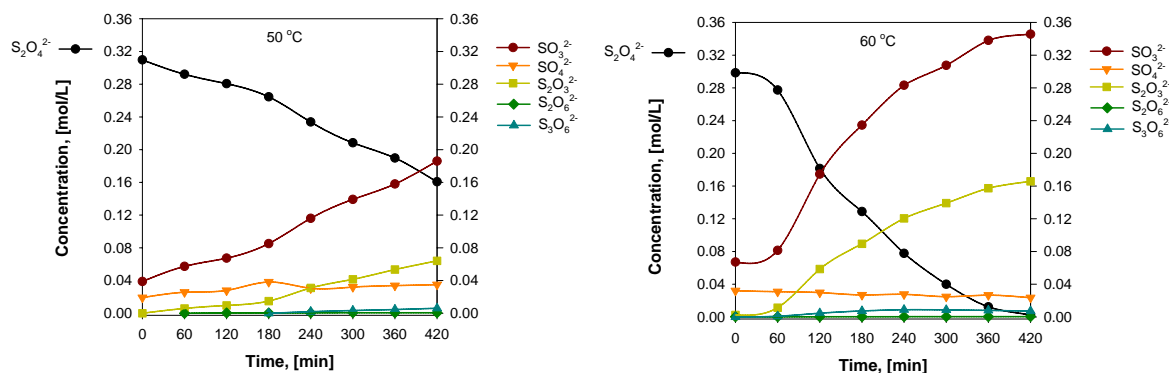


FIGURE 22 Decomposition curve of dithionite and degradation products at 50 °C and 60 °C.

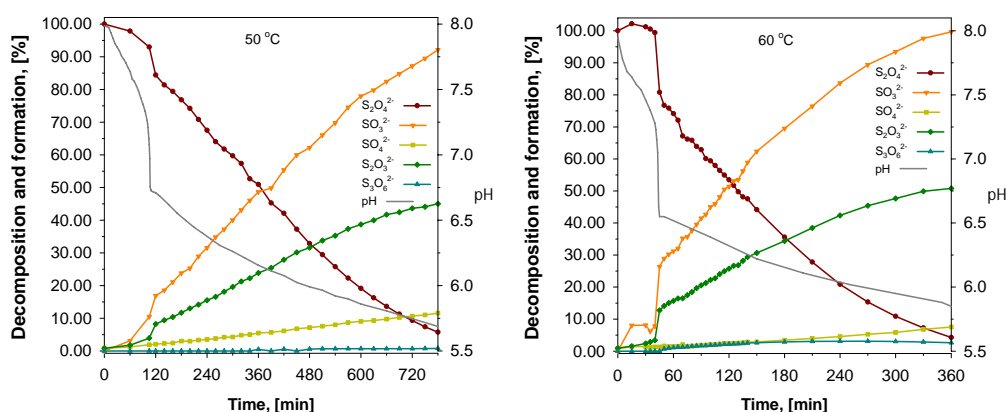


FIGURE 23 Detailed anaerobic decomposition curve of dithionite and degradation products at different temperatures.

Sodium dithionite is widely used in bleaching of mechanical pulps and recycled fibres. Dithionite bleaching is a useful tool for pulp brightening, for example, in the production of newspaper, where the brightness target is reasonably low. For processes of higher paper grades, dithionite can be used in sequential bleaching consisting of several dithionite stages or separate peroxide and dithionite stages. The way dithionite is used in the process is determined by the brightness of the initial pulp and the brightness target of the paper.

The chemistry of dithionite bleaching is considered problematic and complex. For example, depending on the efficiency of the process, various sulphur compounds, such as sulphite, sulphate, thiosulphate and polythionates, are simultaneously present at different concentrations in the bleaching filtrate. The same constituents with dithionite are also present in bleach liquor and some of these can be found in pulps (Figure 24).

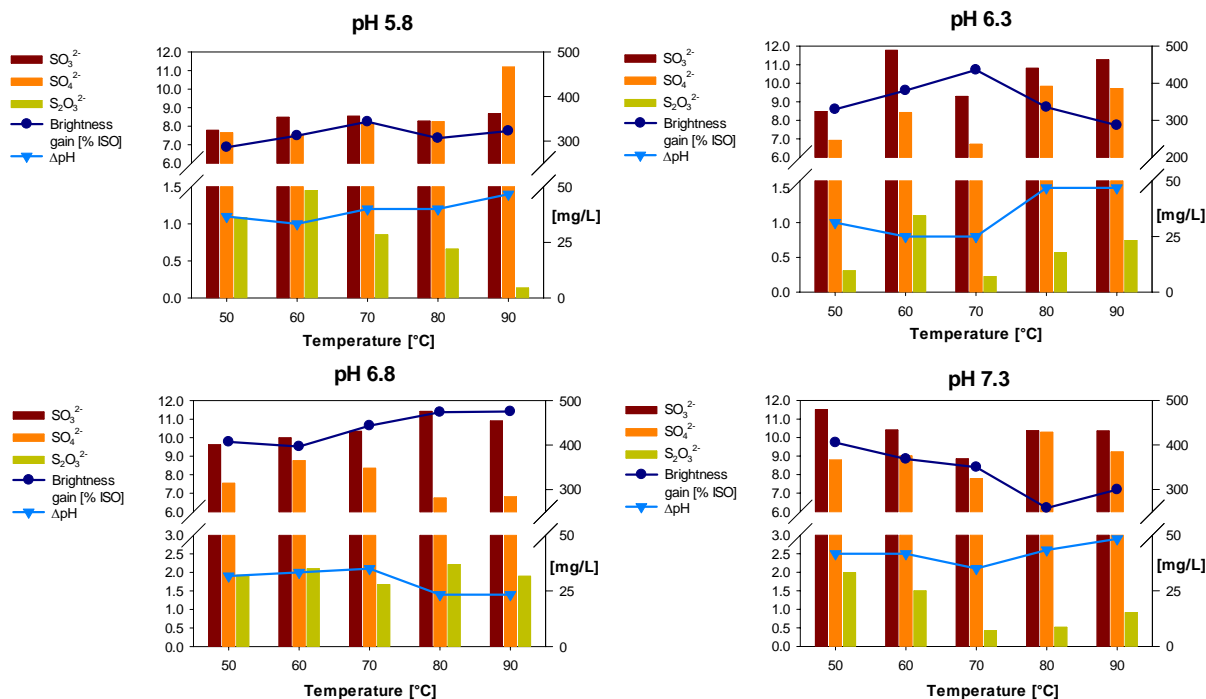


FIGURE 24 Screening the effect of bleaching pH to TMP brightness and the presence of different anions after bleaching.

To conclude the reaction pathways of dithionite decomposition in bleaching, sulphur compounds after bleaching were also analysed. In laboratory-scale bleaching experiments, it was possible to determine the concentrations of various sulphur species, starting from dithionite and terminating with bleaching filtrates.

The mean concentrations between sulphur species after bleaching and the added dithionite on laboratory-scale experiments are presented in Figure 25. The most significant finding dealing with the mechanism was probably the increase in the sulphur content of pulp and it was found to correlate to a high degree with pulp brightness (Figure 26). Based on this new information, the evolved mechanism for dithionite bleaching is later illustrated (Figure 29).

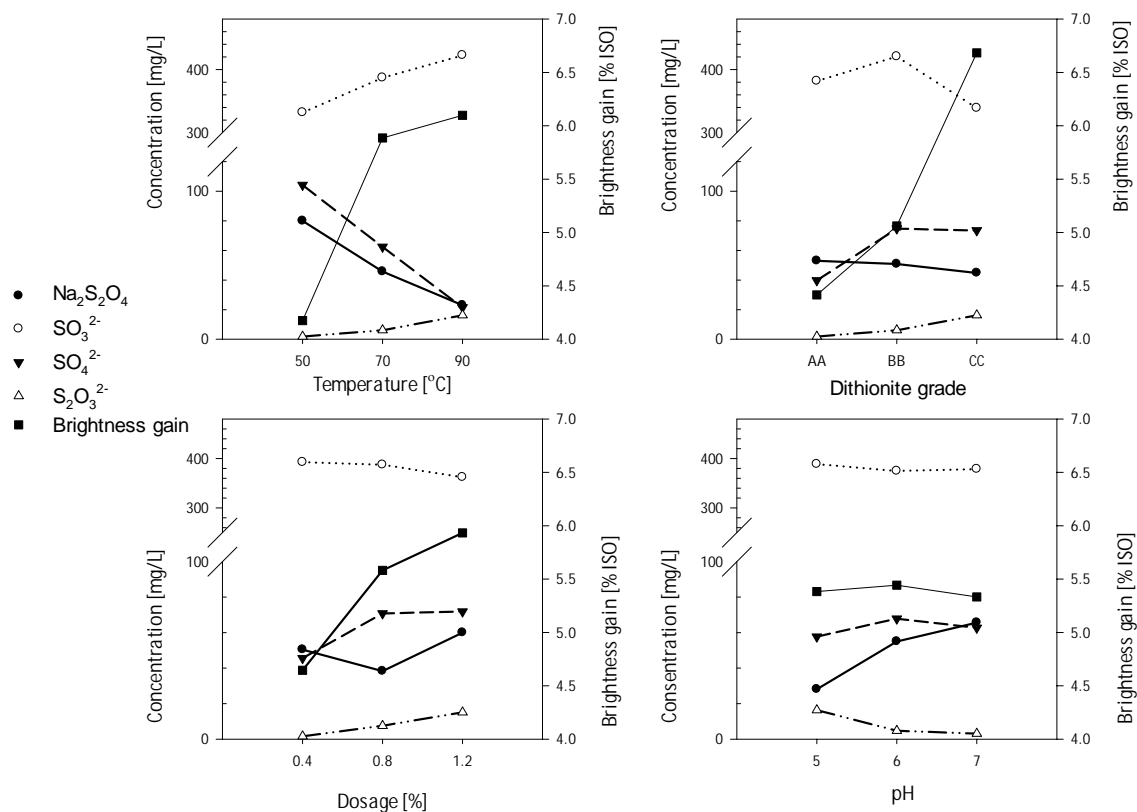


FIGURE 25 Correlation curves of temperature, dithionite grade, dosage and pH to residual sulphur anions and PGW brightness [Publication I].

The most significant factor regarding the decomposition of dithionite was temperature. The quantity of residual dithionite decreased when temperature increased, and at 90 °C, the amount of residual dithionite after 30 min was negligible. The sulphite concentration in filtrates was at higher temperatures to a greater extent, indicating improved bleaching efficiency, which was proven also by brightness gain. The volume of sulphate decreased in relation to temperature. This could also be explained simply by greater bleaching efficiency at higher temperatures. The level of thiosulphate was slightly raised when temperature increased. This was explained by the fact that an increase in temperature expedited the direct thermal decomposition of dithionite to thiosulphate.

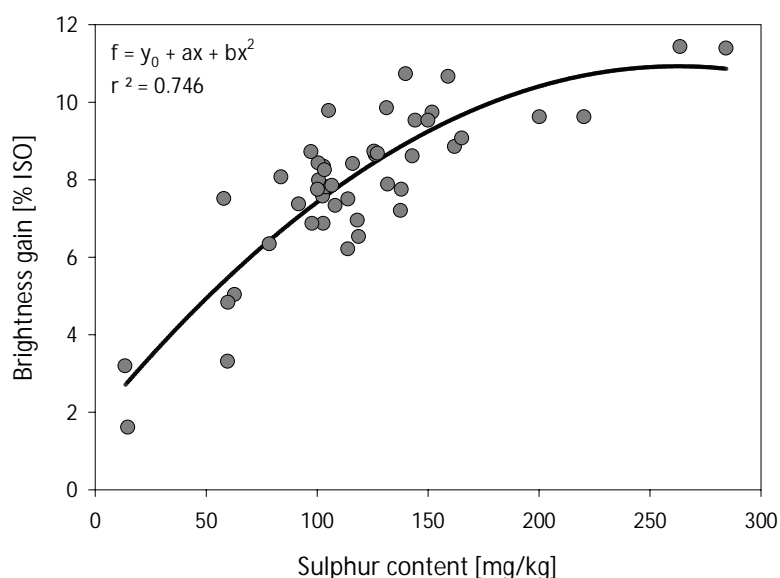


FIGURE 26 Brightness gain vs. sulphur content in PGW pulp. Collected data contain all preliminary bleaching experiments [Publication I].

Another important factor in decomposition reactions was bleaching start-up pH. The initial pH had a clear effect on the amount of residual dithionite and thiosulphate. There was more residual dithionite remaining after 30 min when a higher pH was maintained. On the contrary, the concentration of thiosulphate was significantly lower at pH 7. It was concluded that there was evidence that bleaching in neutral pH did not have a detrimental effect on dithionite.

According to the Taguchi method, it was discovered that temperature was the most important factor on dithionite bleaching. An increase in temperature improved bleaching efficiency, which could be clearly seen from the improved brightness response and concentrations of sulphur species. However, the temperature of the mill-scale process cannot be raised excessively because as energy consumption increases, so do expenses, which means that benefit of increased brightness is lost. Selecting of bleaching point to a place in the process, in which temperature is naturally higher and mixing is efficient, would be a more rational approach.

Dithionite dosage is an essential factor concerning dithionite bleaching. Usually, the more dithionite is utilised, the higher the brightness gain achieved. The optimum dosage level should be carefully determined because in most cases, it is the only way to cut down the expenses of dithionite bleaching. There is no general rule regarding the optimum dosage for dithionite bleaching because each process and pulp is different and, therefore, the optimum dosage is different. Nevertheless, normally, a dosage over 1.0% for a single bleaching stage is considered to be overdosing.

In some cases, dithionite grade turned out to be a significant factor in bleaching. The precise reason for the different behaviour of grades in relation to brightness response is still unknown. However, dithionite grade should be carefully optimised for each process. The role of pH can also be important in some

situations in dithionite bleaching. If the pH of pulp is clearly below a value of 5, the efficiency of bleaching gets worse, which can be seen, for example, in the higher concentration of thiosulphate in filtrate. Generally, pH is not a major factor of dithionite bleaching if it is in the range of 5–6.5.

7.2 Laboratory-scale bleaching

The aim of PGW bleaching trials was to clarify the effects of some general factors on dithionite bleaching, such as temperature, pH, dithionite dosage and EDTA addition. One very important factor affecting bleaching performance was dithionite grade. The objective was to find out which dithionite grade of the three commercial dithionite grades (AA, BB and CC) was the best in the case of the PGW mill.

The degradation products of dithionite in bleaching filtrates were also studied in these trials. The purpose was to follow the reaction pathways of dithionite at different bleaching conditions and to determine the main proportions of sulphur compounds in filtrate during bleaching.

7.2.1 Pulp brightness

The brightness gain values achieved in these trials are listed in Table 8. It was possible to separately calculate the effect of each factor on brightness gain by the Taguchi method. The effect of each factor is shown in Figure 27. The brightness values in this figure were the mean values of experiments done at the same level, for example, the brightness value at 50 °C was the mean value of six experiments carried out at 50 °C. The higher the variations in brightness gain, the more critical each factor is in relation to brightness. The results of the control experiments are in Table 9.

Table 8 The experimental design for the dithionite bleaching trials of the PGW mill

Trial	Pulp washing	Dithionite dosage [% on pulp]	pH	Temperature [°C]	Dithionite grade	EDTA addition [% on pulp]	Brightness gain [% ISO]
1	ON	0.4	5.0	50	AA	0	2.80
2	ON	0.4	6.0	70	BB	0.2	5.46
3	ON	0.4	7.0	90	CC	0.4	6.37
4	ON	0.8	5.0	50	BB	0.4	4.75
5	ON	0.8	6.0	70	CC	0	7.69
6	ON	0.8	7.0	90	AA	0.2	5.62
7	ON	1.2	5.0	70	CC	0.2	7.74
8	ON	1.2	6.0	90	AA	0.4	7.16
9	ON	1.2	7.0	50	BB	0	4.56
10	OFF	0.4	5.0	90	BB	0.2	4.69
11	OFF	0.4	6.0	50	CC	0.4	4.83
12	OFF	0.4	7.0	70	AA	0	3.83
13	OFF	0.8	5.0	70	AA	0.4	4.66
14	OFF	0.8	6.0	90	BB	0	5.09
15	OFF	0.8	7.0	50	CC	0.2	5.68
16	OFF	1.2	5.0	90	CC	0	7.78
17	OFF	1.2	6.0	50	AA	0.2	2.42
18	OFF	1.2	7.0	70	BB	0.4	5.94

Table 9 Results of control experiments

Experiment	Dosage [% on pulp]	Brightness gain CC [% ISO]	Brightness gain AA [% ISO]
initial	0	0	0
1	0.6	6.262	5.841
2	0.9	7.683	7.155
3	1.2	8.471	7.855

In this case, dithionite grade and temperature were the most important factors. About 37% of brightness gain could be explained by dithionite grade and about 31% by temperature. Dithionite dosage also had a significant effect on brightness, and washing the pulp improved brightness response to some extent. The initial pH and the EDTA addition did not have a significant impact on brightness response.

Washing the pulp reduced the number of metals and extractives in the pulp slurry. This should explain the enhanced brightness gain in experiments utilising washing because less dithionite was directly decomposed and fewer metals were available for darkening reactions. On the other hand, in washing, fines were lost to some extent, which was disadvantageous for brightness response. In washing, about a 1% ISO drop in brightness occurred, although brightness gain was always calculated from the same initial brightness value.

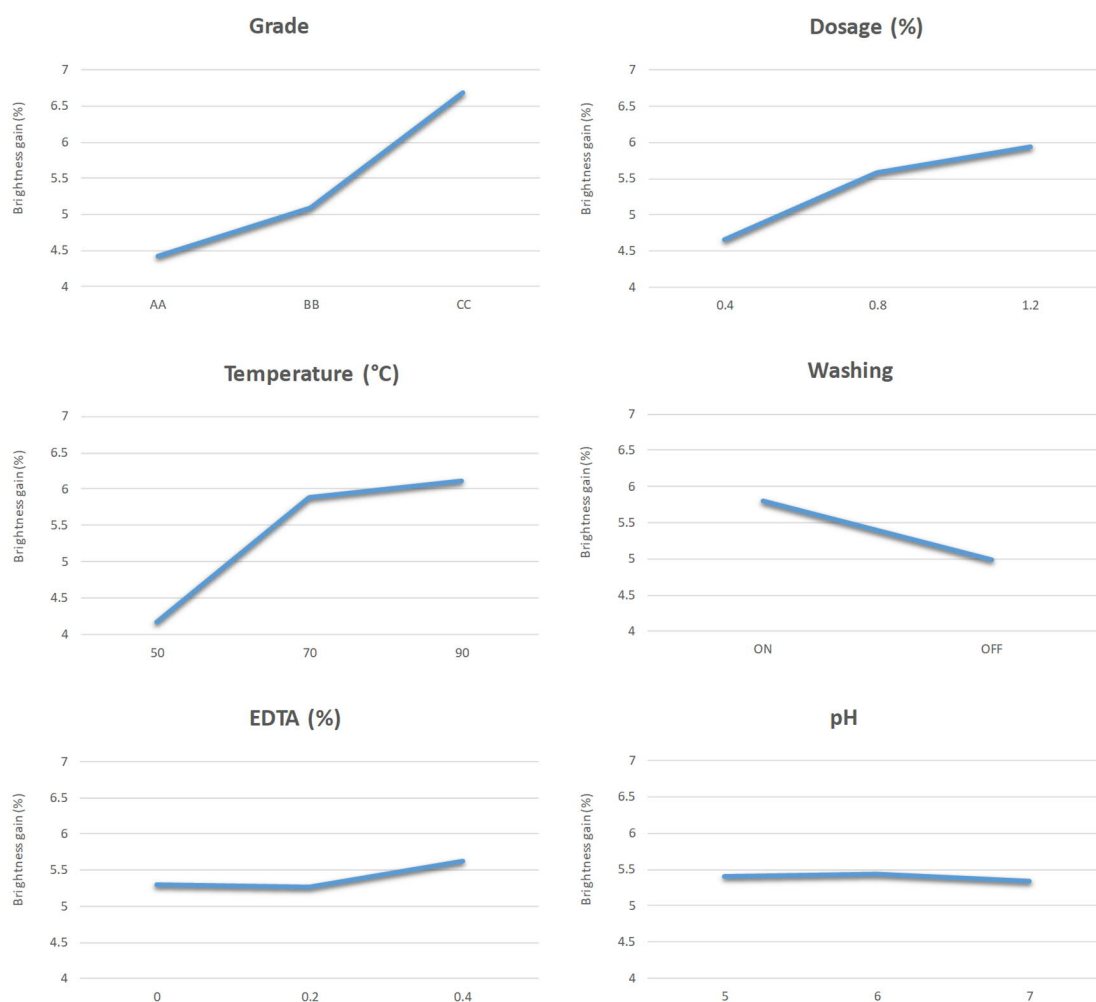


FIGURE 27 Brightness response of each factor at different levels in the PGW experiments.

Dithionite grade had a significant impact on brightness gain. The brightness response of the CC powder seemed to be superior compared to the other two grades. In this case, the mean CC brightness gain was over 2% ISO more than the AA response. BB was also slightly higher than AA regarding brightness. At higher temperatures, the brightness response was significantly upgraded. Thus, it could be said that bleaching temperature should be at least 70 °C for PGW, but there was only a modest benefit of 90 °C compared to 70 °C.

Dithionite dosage had an expected effect on brightness—the bigger the dosage, the better the brightness. The initial pH did not affect the brightness response, which could be explained by several factors. In these experiments, three different dithionite grades were studied and each had a different effect on pH. Therefore, the initial pH value changed right after the dithionite addition and the extent of this pH change was always different. In the control experiments, CC gave a slightly improved brightness gain than AA. These experiments confirmed that CC was a competent choice for the PGW process.

7.2.2 Sulphur analyses

During each experiment, the reaction products of dithionite were analysed three times from filtrates. The samples were taken after 10, 20 and 30 min. The average results of these analyses are presented in Figure 28. Each point in the figure is an average of all 18 experiments. The results are reported as percentage molar proportions between sulphur species and added sodium dithionite. For example, if all sulphur of added sodium dithionite could be found from the filtrate, the total sulphur content should be 100%. Only the reaction products of sodium dithionite and total sum of these products (total sulphur) are shown. Other sulphur species (sulphite, sulphate, thiosulphate and trithionate) present in the initial bleach liquor do not affect these results because the concentrations of these species were subtracted from the filtrate results.

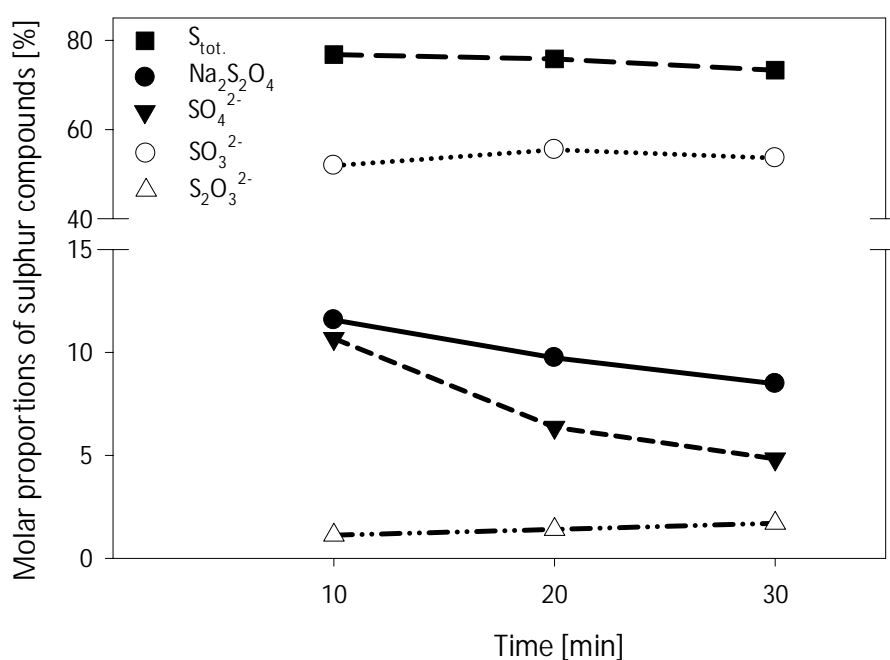


FIGURE 28 Average results of sulphur species at different points in time.

The sulphite (bisulphite in bleaching pH) level in filtrates was quite stable from 10 min to 30 min. Thus, bleaching reactions of dithionite were almost over after 10 min, although there was still residual dithionite in filtrates after 30 min. The volume of residual sodium dithionite in filtrates was decreased as a function of time, which was an expected result. The quantity of thiosulphate increased slightly during bleaching.

The quantity of dithionite-based sulphate decreased as time elapsed in experiments. Because sulphate is the highest oxidation state of the sulphur species, it could not be reduced back to a lower level (e.g., sulphite). On average, only 75% of the sulphur species from sodium dithionite were found from the filtrates. The other 25% were not seen in the filtrate analysis and were migrating with pulp.

The lost supply of sulphur could be explained by two separate phenomena. Sulphate ions probably formed ionic bonds with the fibre surfaces and, in addition, sulphite and dithionite could react with fibres so that the quantity of covalently bonded sulphur in pulp increased. A more significant amount of covalently bonded sulphur in pulp has also been observed in our other studies, which supports the idea that, indeed, sulphonation reactions happen in dithionite bleaching.

The data of sulphur analyses were also analysed by the Taguchi method in order to clarify which process factors affected the chemistry of dithionite bleaching. In these calculations, molar proportions between sulphur species and added sodium dithionite were used as in Figure 28. In this report, it is impossible to deal with every results, which is why only the primary results are reviewed here. These results were based on the filtrate analyses after 30 min. The most significant factor regarding the chemistry of dithionite bleaching was temperature, which had an obvious impact on each decomposition and reaction product of dithionite. The volume of residual dithionite decreased when temperature increased, and at 90 °C, the amount of residual dithionite after 30 min was ordinarily negligible. The sulphite level in the filtrate was greater at higher temperatures, indicating improved bleaching efficiency. The augmented bleaching efficiency at higher temperatures was proved by enhanced brightness gains. The quantity of sulphate decreased in relation to temperature. This could be explained by improved bleaching efficiency at higher temperatures. The level of thiosulphate was slightly raised when the temperature increased. This was explained by the fact that the rise in temperature accelerated the direct thermal decomposition of dithionite to thiosulphate.

Another key factor in decomposition reactions of dithionite was the initial pH, which had clear impact on the volume of residual dithionite and thiosulphate. There was more residual dithionite left in filtrates after 30 min when the pH was higher. On the contrary, the quantity of thiosulphate was significantly higher at pH 5 than at higher pH levels.

The dithionite grade also had some effect on concentrations of sulphur species in filtrates. For example, in the BB experiments, there was slightly more sulphite in filtrates than in the experiments of the two other grades. On the other hand, the CC powder yielded more thiosulphate into filtrates than the two other grades.

In addition, the effect of dithionite dosage on concentrations of sulphur species was observed, although molar proportions were used in calculations, which should eliminate the dosage effect in the sulphate and thiosulphate levels. Proportionally, the larger the dosages, the greater the presence of sulphate and thiosulphate in filtrates. This clearly showed the poor bleaching efficiency of large dithionite dosages.

7.2.3 Conclusions

The results based on the Taguchi L18 experimental design indicated that temperature, dithionite grade and dosage were the most important factors in efficient

dithionite bleaching of PGW. The temperature should be at least 70 °C in order to get the full benefit of dithionite bleaching. Also, the analyses of sulphur species confirmed that the higher the temperature, the better the bleaching efficiency (more sulphite and less sulphate in filtrates).

Also, the larger the dithionite dosage, the higher the brightness achieved, although the 1.2% dosage was an overdose because, on average, the difference in brightness gain between the 0.8% and 1.2% dosages was below 0.5% ISO. In addition, more substantial sulphate and thiosulphate levels in filtrates after bleaching indicated that the use of a high dosage (1.2%) was considered as overdosing.

Surprisingly, dithionite grade proved to be a very significant factor in dithionite bleaching of the PGW mill. The CC dithionite powder was found to be superior for PGW in terms of brightness gain. This powder gave quite a good bleaching response at almost every condition, for example, low dosages (0.4%) of CC gave excellent brightness response (gain 5-6% ISO). On the contrary, AA gave favourable results only at the optimum conditions. Also, CC gave heightened results over AA in the control experiments, which were done under constant conditions.

The definite reason for different bleaching responses of dithionite grades is still not known. One explanation could be the stabilisers that powder dithionites contain but AA does not. Therefore, the reason may be the high quantity of extractives in pulp, which reduces the efficiency of AA. The difference in brightness response of grades could not be explained by analyses of sulphur species. There were no significant differences in the decomposition and reaction products of dithionite between the three grades.

The initial pH level was revealed to be a poor factor in this kind of experiment where dithionite grades were compared. Each grade used in these experiments, after adding, had different effects on the pH of pulp. Because of this, the impact of the initial pH on brightness response diminished. Thus, this effect should be determined separately. However, one important impact of pH was noticed. At the initial pH 5, the amount of thiosulphate was clearly larger than at pH 6 or 7. At the mill-scale, the pulp pH in dithionite bleaching should always be over 5 because too high a thiosulphate level can cause corrosion [Garner, 1985; Laitinen, 1999].

The observed sulphur balance (Figure 29) in the laboratory-scale bleaching experiments can be summarised as follows. In anaerobic conditions and after 30 min bleaching, over 50% of dithionite is decomposed to sulphite; without exception, residual dithionite (10-15%) is found. The accumulation of thiosulphate depends on the dithionite characteristic and unfavourable bleaching conditions. The total sulphur content of pulp (3-10%) correlates to a high degree with pulp brightness.

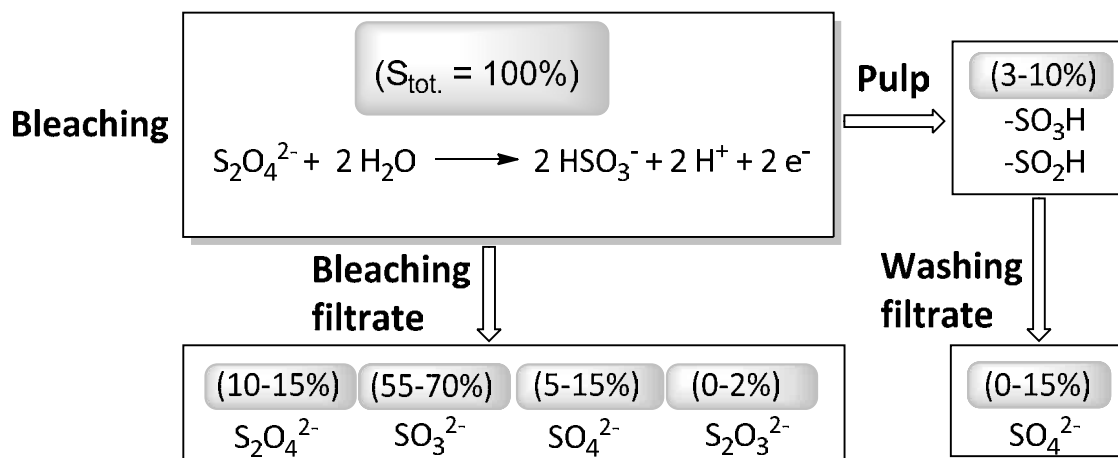


FIGURE 29 Reaction pathways of dithionite bleaching and the mean molar proportions (%) between sulphur species and added dithionite after 30 min in laboratory-scale bleaching.

7.3 Mill-scale bleaching

7.3.1 Performance of production unit

Sulphur analysis from the production unit showed that the composition of dithionite solution remained homogeneous and seasonal variation in the storage tank was almost non-existent. At the beginning of the monitoring period, solution stability was not optimal as seen from formed decomposition products. The reason for stability improvement was that the chemical supplier checked the chemical feed adjustment of the dithionite production unit.

The variation in thiosulphate concentration appeared to be quite large, but the monitoring period also included values before the modification of the dithionite production unit. Measured results during the year 2003 indicated that there was no need to make further adjustments to the production unit (Figure 30).

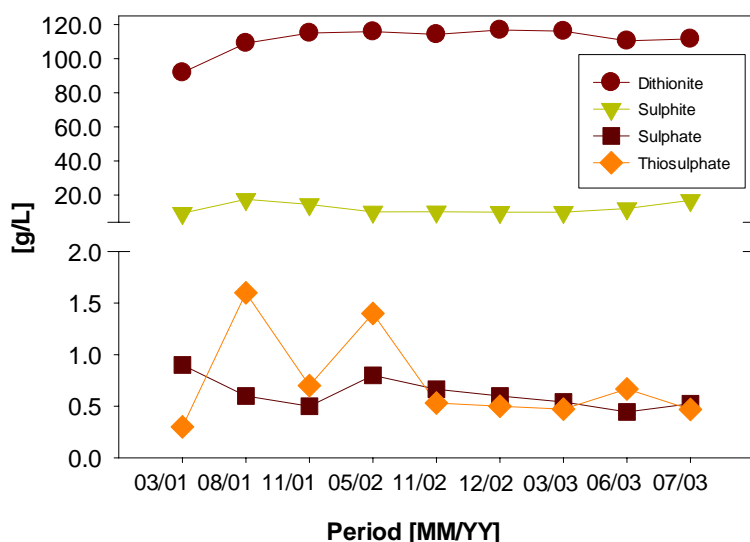


FIGURE 30 Composition of the dithionite solution in the storage tank.

7.3.2 Refiner dilution waters after bleaching

The sulphur compound levels found from separate refiner dilution waters were dissimilar because production lines used dithionite in unequal quantities (Tables 10 and 11). The production of higher paper grades could result in an up to tenfold higher thiosulphate concentration in the process waters compared to the production of lower grades. Also, diluting waters, mainly thiosulphate, was diluted slowly in the process waters when the paper mill switched paper grade.

Table 10 Sulphur concentrations in 1st refiner dilution waters

Paper grade, (degree of bleaching)	SO ₃ ²⁻ [g/L]	SO ₄ ²⁻ [g/L]	S ₂ O ₃ ²⁻ [mg/L]	S _{tot} [g/L]
72, (1/1)	0.186	1.16	113	0.526
68, (1/2)	0.118	1.04	66	0.433
65-68, (1/2)	0.114	0.89	34	0.362
63, (1/2)	0.081	0.82	15	0.315

Table 11 Sulphur concentrations in 2nd refiner dilution waters

Paper grade, (degree of bleaching)	SO ₃ ²⁻ [g/L]	SO ₄ ²⁻ [g/L]	S ₂ O ₃ ²⁻ [mg/L]	S _{tot} [g/L]
72, (1/1)	0.029	0.341	18	0.136
68, (1/2)	0.035	0.300	7	0.119
65-68, (1/2)	0.026	0.294	4	0.111

Compared to production lines, the volume of total sulphur was only one-third; likewise, the thiosulphate concentration was lower. This was because dithionite was used only when needed to bleach additional brightness.

7.3.3 Pressure and consistency

The aim of these trials was to utilise different refining parameters, consistency and pressure, to find out their impact on brightness and sulphur ions formed during bleaching. Pressure and consistency trials were run twice. The second trial was the confirmation run from the results obtained from the first trial. In addition, the sampling at that time was done from both refining stages and the amount of total sulphur from bleached pulp was analysed. The brightness values achieved during the first-stage trials are listed in Table 12. Different combinations of parameters in first-stage did not have any effect on brightness. High casing pressure at first-stage refining seems to be detrimental to dithionite and thiosulphate formation took place. Correlations between various sulphur ions and process variables are illustrated in Figures 31 and 32.

Table 12 Pressure and consistency trials at first stage refining. Sulphur results are based on consistency

Sample (consistency/ feeding pressure/ casing pressure) [%/kPa/kPa]	SO ₃ ²⁻ [g/kg]	SO ₄ ²⁻ [g/kg]	S ₂ O ₃ ²⁻ [mg/kg]	Total S [g/kg]	Δ [% ISO]
(43/167/424), initial	2.9	3.7	20.1	2.4	-
(50/302/455)	3.3	3.2	40.4	2.4	0.1
(49/304/623)	3.2	3.2	45.3	2.4	0.6
(50/415/729)	3.8	2.5	72.9	2.4	0.2
(45/139/353)	2.4	4.2	27.8	2.4	1.0
(52/173/429)	2.8	3.6	35.8	2.4	0.1
(35/171/437)	3.0	4.3	36.2	2.6	3.3

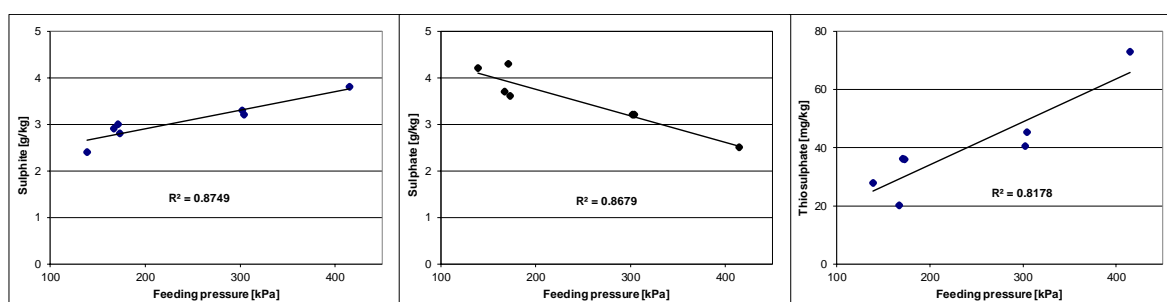


FIGURE 31 Correlation between various sulphur ions and first-stage feeding pressure.

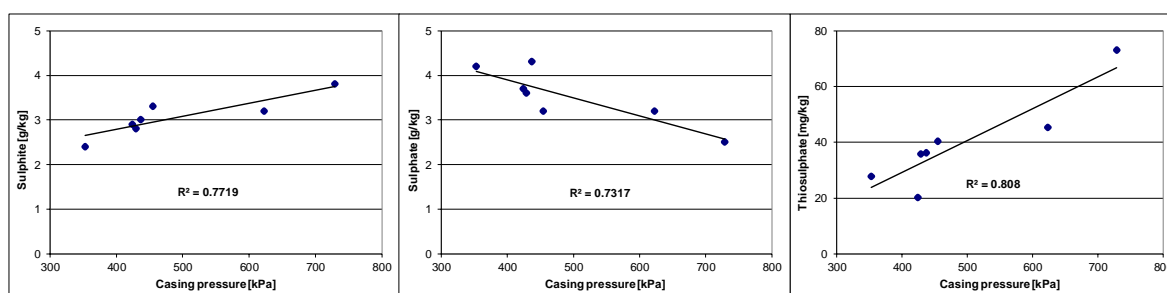


FIGURE 32 Correlation between various sulphur ions and first-stage casing pressure.

Parameters used in both stages did not have any notable effect on brightness response (Table 13). High refining consistency elevated thiosulphate concentration in bleaching effluents, especially at second-stage refining. At low consistency, the volume of thiosulphate decreased although thiosulphate levels were very high. Because the paper mill used a considerable amount of dithionite in the refining stages, it is difficult to arrive at an exact conclusion about the performance of bleaching reactions. Normally, in conventional bleaching conditions, sulphite concentration in filtrates after bleaching is higher than sulphate, indicating successful bleaching reactions. In this case, however, it was not seen easily. The only observation was the high-consistency trial that increased the thiosulphate level, indicating that some of the dithionite was unnecessarily wasted through decomposition reactions caused by the minimal quantity of dilution water.

Table 13 Pressure and consistency trials at first- and second-stage refining. Results are based on pulp consistency

Sample (Consistency/feeding pressure/ casing pressure) [%/kPa/kPa]	SO ₃ ²⁻ [g/kg]	SO ₄ ²⁻ [g/kg]	S ₂ O ₃ ²⁻ [mg/kg]	Total S [g/kg]	Pulp S _{tot} [mg/kg]	Δ [% ISO]
1 st (47/150/454), initial	3.77	3.96	51.37	2.50	725	-
2 nd (44/328/471), initial	6.06	6.44	48.65	4.25	940	-
1 st (34/245/458)	3.41	4.30	49.59	2.47	765	0.4
2 nd (39/322/432)	4.83	6.17	41.62	3.66	1035	0.4
1 st (40/344/452)	3.60	4.66	45.75	2.66	810	-0.2
2 nd (37/318/442)	5.15	5.87	54.81	3.69	1005	0.5
1 st (64/150/467)	3.88	3.16	47.99	2.27	855	0.2
2 nd (77/331/391)	5.52	4.03	88.89	3.24	1210	-0.1
1 st (40/150/442)	3.32	5.24	23.42	2.73	905	1.2
2 nd (36/320/436)	4.86	6.48	31.92	3.76	1065	1.0
1 st (61/332/754)	4.28	3.07	64.94	2.42	930	1.2
2 nd (47/325/436)	4.72	5.70	49.51	3.46	1185	0.4
1 st (39/298/588)	4.17	4.95	33.23	2.98	870	1.2
2 nd (38/325/456)	6.01	5.76	50.44	4.00	1075	0.9
1 st (38/283/450)	4.04	5.06	41.39	2.97	700	0.8
2 nd (37/319/487)	6.35	5.56	78.51	4.08	900	1.3
1 st (45/150/446)	3.65	4.64	38.34	2.67	640	1.0
2 nd (39/316/447)	5.90	6.14	56.39	4.08	880	0.9

From the diagram in Figure 33, it can be seen that the amount of covalently bonded sulphur (sulphonation of lignin) in pulp increases as pulp flows from the first to the second refining stage and at the same time brightness is improved. According to this, the substitution reaction can consume about 22% of infeed sulphur; the rest of it flows with the dilution waters.

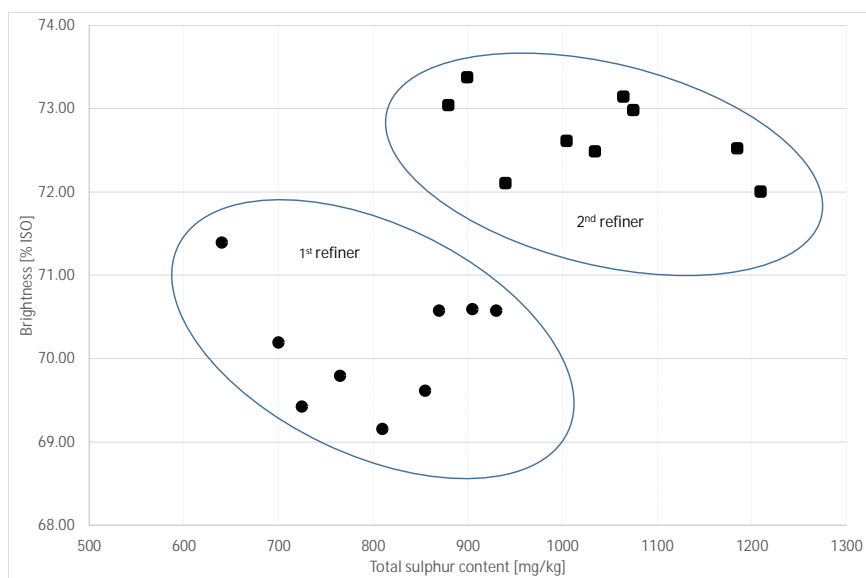


FIGURE 33 Total sulphur content of pulp after different refining stages.

7.3.4 Dithionite feed point

The feeding points of dithionite to the refiner disc gap were tested and no correlation between thiosulphate formation and different feeding points were observed. The dosage level of dithionite to the feeding screw may have weak correlation to sulphite, sulphate and thiosulphate formations (Table 14).

Table 14 Dithionite feeding point tests. Results are based on pulp consistency

Feeding point, (degree of bleaching)	SO ₃ ²⁻ [g/kg]	SO ₄ ²⁻ [g/kg]	S ₂ O ₃ ²⁻ [mg/kg]	Total S [g/kg]	Freeness [mL]	Δ [% ISO]
1 st screw	3.3	2.6	30	2.23	488	7.1
2 nd screw	3.7	3.1	22	2.52	177	10.7
1 st screw, (high)	2.4	3.5	14	2.14	460	8.5
2 nd screw, (high)	3.8	4.8	21	3.13	172	10.3
1 st disc gap, inner radius	2.2	2.4	19	1.69	499	5.8
2 nd disc gap, inner radius	3.4	3.4	21	2.52	170	9.5
1 st disc gap, outer radius	1.5	2.9	10	1.57	490	6.6
2 nd disc gap, outer radius	3.2	3.9	15	2.59	157	10.0
1 st disc gap, outer radius, (high)	1.8	4.2	12	2.14	507	7.9
2 nd disc gap, outer radius, (high)	4.1	4.7	19	3.20	190	10.6

7.3.5 Dosage and pH

The aim of these trials was to compare the dithionite bleaching dosage to different pH levels of bleach liquor (Table 15). It was assumed that increasing the liquor pH has the potential to stabilise dithionite and possibly increase brightness. There was no impact in brightness values achieved in these trials. One possible reason for variations in results could be the pump feeding caustic to the liquor. The quantity of thiosulphate ions found in bleaching filtrates also indicates poor bleaching efficiency.

Table 15 Dosage and pH trial. Results are based on pulp consistency

Sample, (degree of bleaching)	SO ₃ ²⁻ [g/kg]	SO ₄ ²⁻ [g/kg]	S ₂ O ₃ ²⁻ [mg/kg]	Total S [g/kg]	Δ [% ISO]
(0), No bleaching	0.0	0.4	0	0.13	-
(1/2), pH 10.0	2.5	2.1	18	1.70	6.8
(1/2), pH 10.5	2.0	2.6	30	1.67	5.6
(1/2), pH 11.0	2.4	2.7	98	1.93	6.0
(1/1), pH 10.0	3.5	5.3	24	3.18	8.3
(1/1), pH 10.5	3.1	4.4	23	2.72	7.6
(1/1), pH 11.0	3.1	5.0	49	2.97	7.4

7.3.6 Process state correlations

The primary goal was to make a sulphur recovery model using various refining consistencies and different refining pressures (Figure 34). The following considerations could be made from these experiments. Over 99% of all supplied sulphur could be found from refiner outputs. Refiner blowback steam consisted of only 0.1-0.2% of all supplied sulphur to the process. About 75% of the infeed sulphur in pulp could be washed from the fibres, possibly going elsewhere in the process (e.g., dilution water tanks). The sulphur content in the first-stage forward steam was approximately ten times higher than the content in the second-stage forward steam. Dithionite could cause three times more sulphur content to refiners than sulphur migrating in the dilution water. In the first stage, dithionite dosage correlated to brightness; otherwise, high pressure or high consistency did not seem to affect brightness. Sulphite, sulphate and thiosulphate analysed from pulp correlated with refining consistency and refined freeness. Feeding the dithionite to an outer radius disc gap gave approximately 0.5% ISO improved brightness than feeding the dithionite to the feeding screw or inner radius of the disc gap.

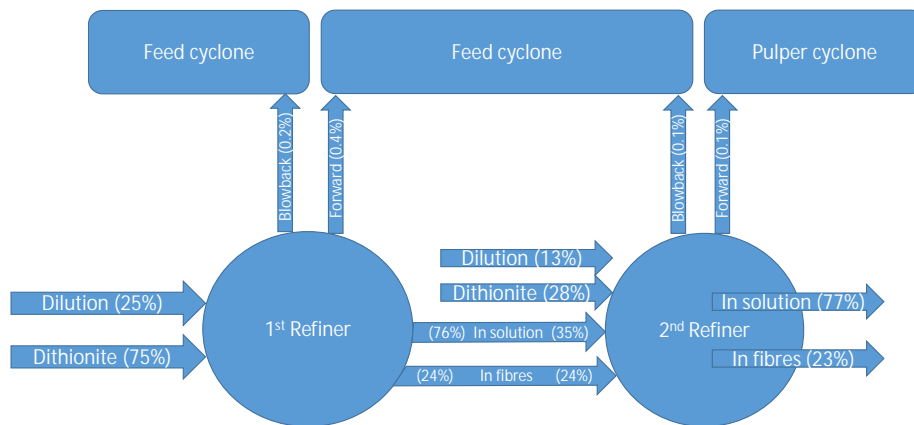


FIGURE 34 Recovery model for the sulphur flows in TMP process.

7.3.7 Conclusions

The primary target of these experiments was to operate different refining consistencies and different refining pressures. Reliable results from these trials were restricted by the scale of the experiments; accordingly, for every test run, only one pulp sample was analysed. A direct correlation between sulphur content in pulp and steam versus process variables was not found. For example, a test with high refining pressure (casing pressure over 750 kPa) did not seem to improve brightness. Correlations between various sulphur ions and process variables were found.

The following results were found from the tests. In the first stage, dithionite dose correlates to sulphur (in the aqueous phase) and brightness. High pressure or high consistency did not seem to have an effect on brightness. Sulphur absorption to pulp did not correlate with process variables, pulp consistencies, or freeness. Sulphur absorption in steam did not correlate with refiner parameters. Analysed sulphite, sulphate and thiosulphate from pulp filtrates correlated with refining consistency and refined freeness. A possible reason for these found correlations could be that higher refining consistencies increase disc gap temperature.

Sulphur recovery model results revealed that almost all input sulphur to the process flows with the fibres. Contributions of the sulphur output (3.4 kg/h from the first stage, 4.6 kg/h from the second stage) from the refiner were approximately 99.5% with fibres in blowlines and 0.5% with steam to heat recovery. Sulphur with the fibre lost to heat recovery was not evaluated. Substantially 75% of sulphur in blowlines might be washed out from fibres in lower consistencies during the process. Furthermore, 25% of the input sulphur into the refiner is caused from sulphur mixed with dilution waters.

Results from the tests show that dithionite absorption into the process and fibres in the first-stage refining was worse than when dithionite was feed to the second-stage refiner. The sulphur content in the first-stage steams was 10 times

higher than in second-stage steams. The reason for that could be that dithionite absorption is deficient in the chips in the first-stage refining, and absorbability was better for once-refined fibres. Another possible reason could be the lower blowback steam flow of the second-stage refiner. Results from the trials when dithionite was fed to the disc gap in the first-stage support that hypothesis. Based on these results, an improved feeding point for dithionite could be the refiner disc gap or the second-stage feeding cyclone (after steam separation) when pulp is refined once and the infiltration area of the pulp is the largest.

Correlations from analysed pulp brightness and sulphur content of the pulp or steam to process measurements were not found. For example, high refining pressure or high consistency refining were not observed to decrease the bleached pulp brightness. The low number of samples (one sample per test point) could weaken the correlations. The best correlation to brightness was found from sulphur dose: a 3% higher dose increases brightness by approximately 1% ISO.

The optimum pH range for dosing dithionite to refiner bleaching was more alkaline than conventional tower bleaching with practicable pH 10-12. Excessive use of a bleaching agent in this monitoring period was minimised and economical (chemical) savings were predominant. Also, fluctuation in process pH could be lower if the bleaching agent dosing range was kept narrow and dithionite decomposition reactions controlled.

Studying paper machine runnability and maintaining control of the whole water process take much effort and time. As a matter of fact, only thiosulphate corrosion has been studied intensively. In problem situations, where active dithionite concentration drops, for example, during a long storage period, dosage must be increased to get the same finish brightness to the paper. This brings significant decomposition problems.

CONCLUDING REMARKS

During mechanical defibration, different chromophoric structures are formed into pulp. These structures contribute to pulp colour and are particularly associated in lignin and extractives, but pulp carbohydrates can also contain chromophoric components. In order to improve the bleachability of pulp and, stabilise product brightness, profound data on reactions between bleaching chemicals and pulp constituents under various conditions are necessary.

Some general features of variable impacts in dithionite bleaching are well known (e.g., temperature, pH, time, consistency and chemical dosage). In each case, the effect of these variables should be evaluated separately. One very significant factor affecting bleaching performance is the dithionite grade or the original state of dithionite. It is not always apparent which is the best way to produce a dithionite solution considering the brightness gain in the mill environment.

The results based on the experimental design showed that the temperature, dithionite grade and dosage are the most critical factors in dithionite bleaching. The bleaching temperature should be at least 70 °C in order to get the full benefit of dithionite bleaching. As expected, the greatest brightness was achieved when dithionite dosages were quite high; after that optimum level, an increase in chemical dosage gave only minor brightness gain.

Powder-based dithionites worked better in some circumstances and Borol®-based dithionite produces favourable brightness gain only when optimum conditions were used. Based on the results achieved in these studies, adjustments in processes could be made by using the most critical process variables only.

Traditional tower bleaching with dithionite is limited to about 10% ISO brightness gain, depending on the wood species used for pulping. At this level of performance, the use of dithionite is more economical than hydrogen peroxide. As the markets demand higher paper grades, new operational combinations to utilise bleach chemicals are introduced, for example, two-stage bleaching with dithionite performed in refiner and the tower may increase brightness gain more than 12% ISO.

Chemical reactions are the most efficient in the refiner for several reasons. First, the pulp consistency is higher compared to tower bleaching, indicating an excellent chemical-to-wood ratio. This also means more chemical-to-wood reactions and fewer chemical decomposition reactions. Although retention time inside a refiner is very short, the temperature is very high and, therefore, drives the bleaching reactions forward. With the retention times commonly used in tower bleaching, high temperature would lead to unwanted darkening reactions. In a refiner, mixing is very intensive, giving more opportunities for chemical and wood interactions.

Further studies should be focused on understanding the role of chemistry on two-stage (peroxide-dithionite) sequential bleaching at various bleaching combinations.

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ORIGINAL PAPERS

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CHEMISTRY OF DITHIONITE BLEACHING. PART 1. EFFECT OF BLEACHING VARIABLES

by

Jukka Pekka Isoaho, Jori Soininen and Raimo Alén, 2019

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Chemistry of dithionite bleaching. Part 1. Effect of bleaching variables

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SUMMARY

The role of common variables, such as dithionite charge (0.4%, 0.8% and 1.2%) based on air-dried pulp, pH (5, 6 and 7) and temperature (50°C, 60°C and 70°C) in the laboratory-scale sodium dithionite (hydrosulphite, Na₂S₂O₄) bleaching of pressure groundwood spruce pulp was screened. The experiments were designed by the Taguchi method. The main approach was to analyse concentration changes in all the sulphur-containing and dithionite-derived anions by ion chromatography during bleaching (brightness gain 6-7% ISO) for determining in each case the active sodium dithionite actually present. The typical mass balance of sulphur over bleach filter (10-15% in S₂O₄²⁻, 55-70% in SO₃²⁻, 5-15% in SO₄²⁻ and 0-2% in S₂O₃²⁻) and pulp (3-10%, estimated bound to fibres as -SO₃H and -SO₂H groups) was determined. In addition, the earlier postulated reaction mechanism could be confirmed by these detailed experiments.

Keywords: Bleaching, dithionite, ion chromatography, process variables, sulphur balance

INTRODUCTION

The target of lignin-retaining bleaching of high-yield mechanical pulps is to increase pulp brightness without subtracting pulp yield by destroying selectively chromophoric structures of lignin (1). Commonly used bleaching agents are sodium bisulphite (NaHSO_3), sodium dithionite also known as sodium hydrosulphite ($\text{Na}_2\text{S}_2\text{O}_4$), sodium borohydride (NaBH_4) and hydrogen peroxide (H_2O_2) for high brightness grades (2). The brightening with $\text{Na}_2\text{S}_2\text{O}_4$ is achieved by reduction and require good mixing and anaerobic conditions. The main reductive reactions are nucleophilic and comprise anions and radicals. The essential initial actions include the attack of nucleophilic agents, for example, sulphur dioxide radicals (SO_2^\bullet) or bisulphite (HSO_3^-) anions, to the electron-deficient carbon atoms in carbonyl- and conjugated carbonyl-containing structures (1,3). Additionally, a great number of secondary reactions have been identified as contributing to the overall bleaching influence (4).

The theoretical aspects of the sulphur chemistry dealing with dithionite decomposition are very complicated and in aqueous solutions, they can be divided into aerobic or anaerobic reactions (5-7). Hence, to meet the satisfactory clarity of bleaching reactions, an accurate determination and identification of water-soluble sulphur anions is required. A widely accepted mechanism for the degradation of sodium dithionite under bleaching conditions was presented by Auhorn and Melzer (8), although that study introduced primary decomposition products only. This proposed mechanism was also confirmed to be accurate in our earlier studies (9). However, minor sulphur-containing impurities are also always present during the manufacturing of dithionite and must be taken into account when the total sulphur balance is calculated. In order to develop control and optimisation strategies for a dithionite bleaching process, including several possible addition points of the bleaching agents with varying chemical compositions, a improved knowledge of outgoing brightness at a given addition point is needed (10).

Depending on the efficiency of the bleaching process, various sulphur anions, such as sulphite (SO_3^{2-}), sulphate (SO_4^{2-}), thiosulphate ($\text{S}_2\text{O}_3^{2-}$) and polythionates ($\text{S}_n\text{O}_6^{2-}$) are present at different concentration levels in the bleaching filtrate. In typical mill storage conditions, an aqueous solution of sodium dithionite also undergoes decomposition reactions, forming the same products as those in bleaching and some of the ions combine chemically with pulp fibres. In the mill environment, typical causes for these decomposition reactions are thermal impact and delay time in the storage tank. Generally accepted practice for the successful utilisation of bleaching agents should be based on filtrate analysis and an indication of sulphite anions. On the other hand, the excessive presence of sulphate anions indicate aerobic conditions and an inadequate bleaching system. Thiosulphate anions are considered as secondary decomposition products of dithionite decomposition and their presence may suggest inadequate thermal conditions or an overdose of bleaching chemicals.

Data on dithionite bleaching kinetics are also needed for developing control and optimisation of the overall process. It is interesting to note that there is only limited information available on the kinetics of pulp bleaching applications. Most mill-scale experiments are performed under very specific conditions and cannot be utilised for clarifying the kinetic aspect of operational conditions.

Detailed decomposition kinetics of dithionite in aqueous solutions have been published for decades, but these approaches have not been extended to monitor the consumption of dithionite during its bleaching reactions with pulp. In this study, concentration changes in all the sulphur-containing and dithionite-derived anions were investigated during bleaching of pressure groundwood (PGW) spruce pulps under varying conditions. The Taguchi method was used for experimental design because this method reduced the total number of experiments and in some cases, the bleaching results could be

explained in more detail (11). In this method, orthogonal matrices were used for experimental design, allowing changes in several factors at the same time. Effects of different factors on the bleaching process could be separately handled because the method assumed factors to be independent. Furthermore, the percentage proportion of the total effect (contribution) for each factor could be calculated and the significant factors of dithionite bleaching could be rather easily detected.

EXPERIMENTAL

Reagents and bleaching chemicals

All reagents used were analytical grade (\geq purum p.a.) and the purity of the commercial dithionite powder blends was analysed (**Table 1**). The sodium borohydride water-based solution was a mixture containing sodium borohydride and sodium hydroxide ($\text{NaBH}_4 + 3.2 \text{ NaOH}$). During bleaching experiments, the reactor and sampling procedure were protected by nitrogen gas. Sulphur dioxide gas (SO_2 , product grade 3.8) used in the generation of bleaching liquor was obtained from Oy AGA Ab, Riihimäki, Finland. The deionised water used for these experiments was purified with a Milli-Q Plus system (UHQ-water, Millipore, Bedford, MA, USA).

Table 1. The content of active sodium dithionite in the bleaching chemical used

Grade	Manufacturer information [%]	Analysed [%]
AA*	85-95	ND**
BB	67-75	~63
CC	66	~60

*Borohydride generated hydrosulphite.

**Not determined.

Bleaching set-up

To prevent major disadvantages (i.e., improper mixing and presence of atmospheric oxygen) in traditional reductive bleaching experiments with a sealed plastic bag, in this study, a new set-up for bleaching was designed (**Fig. 1**). The most important characteristic of this apparatus was to take filtrate samples during bleaching and measure pH on-line. The reactor and its covers were made from stainless steel and polyvinyl chloride (PVC), respectively. The lower cover was adjustable, allowing the control of the excluded volume, to give evenly distributed pulp and ensure good mixing. The volume used in bleaching was usually between 900-1000 mL and the maximum amount of dry pulp was 40 g at a consistency of 5%.

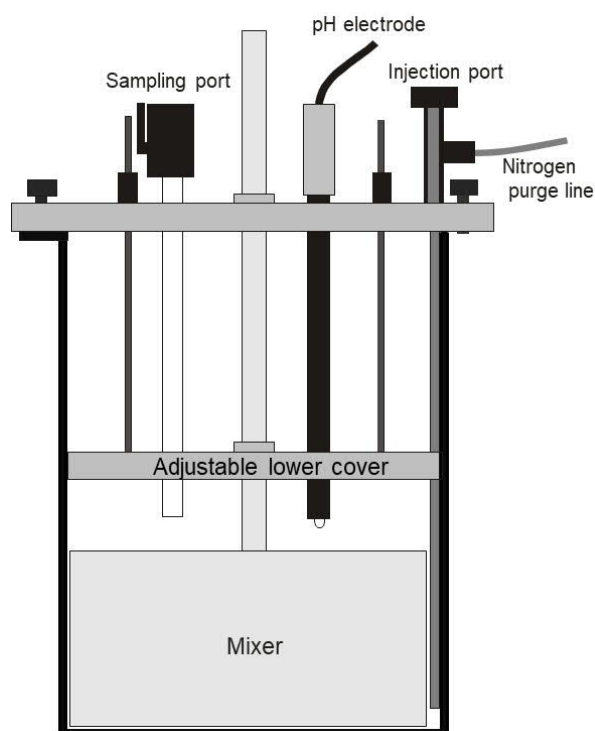


Fig. 1 Schematic diagram of the bleaching reactor.

At first, an appropriate amount of sodium dithionite liquor was injected by a syringe through an injection port. The liquor was purged with nitrogen gas into the pulp and a continuous flow of nitrogen was allowed to prevent bleaching liquor oxidation. Nitrogen was also used in removing air from the pulp. A gas flow meter and a pressure-regulating valve were used for controlling the flow of nitrogen. The reactor was preheated by a heat jacket. When needed to obtain expected temperature and maintain temperature stability during bleaching, a water bath was used. Temperature and pH were measured by a combined temperature/pH electrode with a controlling unit.

Preparation of sodium dithionite liquors

Sodium borohydride generated hydrosulphite (BGH) was made on a laboratory scale based on the procedure of Morton Performance Chemicals (12). The procedure used in these experiments was slightly modified and BGH generation corresponded to the mill scale on-site production and concentration.

The preparation of sodium dithionite bleaching liquor using an alkaline borohydride solution was as follows: The required volume of UHQ-water was measured into the reactor and cooled off to below 10°C, simultaneously making the solution oxygen-free with nitrogen gas. The calculated amount of sodium metabisulphite (NaS_2O_5 , Riedel-deHaën) was mixed with the oxygen-free solution and the sulphur dioxide (SO_2) gas line was opened. An alkaline borohydride-solution was added carefully until the pH was elevated to about 6.0. The pH remained between 6.0-6.5 and continued control over the sulphur dioxide gas line as well as BGH addition was maintained. The sulphur dioxide gas line was unplugged from the reactor and the dithionite solution was adjusted to pH 8.5 with 1 M NaOH. The generated solution was stored cool and under a nitrogen atmosphere.

Dilutions of dithionite powder blends were prepared as follows: UHQ-water was placed in an airtight vessel and the air was removed by nitrogen gas. An appropriate amount of powder was dissolved into

the water and the solution was agitated during dissolving and storing (15–25°C) under a nitrogen atmosphere. The target concentration of sodium dithionite was between 50–70 g/L.

Pulp and bleaching procedure

PGW pulp from black spruce (*Picea mariana*) and balsam fir (*Abies balsamea*) was used. The initial brightness and suspension of the pH at bleaching consistency was 63.2 (% ISO) and 5.9, respectively. After receiving, the mill-made pulp was frozen and stored in order to prevent contamination prior to bleaching. All the bleaching experiments were carried out correspondingly and an appropriate amount of pulp was weighed into the reactor (target value 40 g of air-dried pulp) and then diluted normally by UHQ-water to a consistency of 5%. The pulp was made oxygen-free during the preheating stage (30 min) and when it was completed, bleaching adjustment reagents, i.e., ethylenediaminetetraacetic acid (EDTA), NaOH or H₂SO₄, was added. Due to the pH adjustment and EDTA addition, the volume correction was taken into account in consistency calculations.

The bleaching chemical addition was based on the exact active concentration of dithionite and was calculated after ion chromatographic analysis. During the injection of dithionite, the pulp was mixed continuously for 20 s and at bleaching experiment intervals of 5 min. Nitrogen purging was uninterrupted and the bleaching time was 30 min. The dithionite and EDTA dosages were expressed as percentages of air-dry pulp.

At the end of each experiment, the reactor was opened and the pulp was filtrated through synthetic wire bags (50 µm and 100 µm pore sizes). The filtrate was recovered and pulp was washed by UHQ-water (~3 litre/40 g dry pulp). After washing, the pulp was centrifuged to a consistency of 20–35% and fibres were homogenised. The dry content of pulp was analysed by an IR-200 Moisture Analyzer (Denver Instruments, Arvada, CO, USA). Since the dry content of pulp was established, laboratory handsheets (100 g/m²) were made for brightness and colour measurements. Sheets were dried overnight (14–16 hr) at a constant temperature (23°C) and humidity (50%) before measurements.

ANALYTICAL METHODS FOR SULPHUR COMPOUNDS

Ion chromatography

To determine various sulphur-containing anions, the bleaching liquor and filtrate samples were analysed correspondingly using a Dionex 4500i ion chromatographic system (Sunnyvale, CA, USA) equipped with a quaternary gradient pump module, an anion self-regenerating suppressor (ASRS I) as well as sequentially connected VDM-2 (UV-Vis) and PED-2 electrochemical (in the conductivity mode) detectors. To prevent the air oxidation of samples, each solution was treated with an alkaline (pH 10.5) antioxidant (formaldehyde 36.5%, Riedel-deHaën) solution (2% v/v) and then filtrated through a 0.45-µm membrane prior to ion chromatographic analysis.

Formaldehyde was the most prominent antioxidant for dithionite stabilisation and the solution was stable for days after preparation; this was also found by de Carvalho and Schwedt (13). The chromatographic method was based on mobile phase ion chromatography (MPIC) and was introduced by Steudel and Münchow (14). The method was further developed using a conductivity detector to determine sulphate and improve the overall sensitivity of specific anions. Therefore, the quantitative analysis of the following most abundant anions was possible: dithionite (S₂O₄²⁻), sulphide (S²⁻),

sulphite (SO_3^{2-}), sulphate (SO_4^{2-}), thiosulphate ($\text{S}_2\text{O}_3^{2-}$), dithionate ($\text{S}_2\text{O}_6^{2-}$) and polythionates ($\text{S}_n\text{O}_6^{2-}$).

Energy dispersive X-ray fluorescence

The sulphur content of unbleached and bleached pulp samples was analysed by a Metorex X-MET 920 (Metorex Co.) energy dispersive X-ray fluorescence spectrometer (EDXRF) using a mini X-ray tube as a radiation source and a titanium filter as well as a proportional counter as a detector. Only covalently bonded sulphur was determined by this method because the pulp sample was heavily washed by UHQ-water before analysis. A pellet consisting of 1.4 g of the milled pulp was measured under mylar film (thickness 2.5 μm) using a collection time of 300 s. The calibration of the spectrometer was accomplished by an additional method using an unbleached pulp sample as a matrix. Each sample was analysed twice (both sides of the pellet) and the mean value was used in the subsequent calculations. The calibration is based on previous laboratory work (15).

EXPERIMENTAL DESIGN

The Taguchi experimental design, based on the orthogonal L18 (2^13^7) matrix, was carried out considering variables as seen in **Table 2**. For designing factorial experiments, the DOE v. 1.3F, Total Quality Software (1994) computer program was used. The levels of all variables were chosen with respect to feasible mill conditions. Parameters, such as bleach liquor addition, are previously well known in the literature (16-18). The fundamental aim of bleaching trials was to comprehensively elucidate the general factors (temperature, pH, dithionite and EDTA addition) affecting the dithionite bleaching performance and supplementing this with knowledge of the best dithionite grade. The objective was to find out which dithionite grade (AA, BB and CC) has the most desirable bleaching performance and character with PGW pulp. The composition of different bleaching liquors is represented in **Table 3**.

Table 2. Design (2^13^7) of the dithionite bleaching experiments with PGW pulp

Level	Pulp washing	Dithionite charge*	pH	Temperature (°C)	Blank**	Dithionite grade	EDTA charge*	Blank**
1	ON	0.4	5.0	50	1	AA	0	1
2	OFF	0.8	6.0	70	2	BB	0.2	2
3		1.2	7.0	90	3	CC	0.4	3

*(%) Percentage on air-dried pulp.

**Unoccupied column.

Bleaching filtrates and the degradation products of dithionite were also studied. The purpose was to follow the reaction pathways of dithionite under different bleaching conditions and to determine the main proportions of sulphur compounds in filtrates during bleaching. The effects of different process factors on brightness response (**Table 4**) were investigated by means of laboratory-scale bleaching experiments using the Taguchi method for the experimental design and the interpretation of results. Columns left unoccupied (blank) do not have any effects on these trials and results.

Table 3. The composition of bleach liquor (g/L) in the L18 matrix

Experiment	Na ₂ S ₂ O ₄	SO ₃ ²⁻	SO ₄ ²⁻	S ₂ O ₃ ²⁻	S ₂ O ₆ ²⁻	S ₃ O ₆ ²⁻
1	56.5	9.4	2.8	0.2	+	+
2	49.2	10.7	3.6	0.2	0.4	+
3	51.8	7.1	2.9	+	+	+
4	54.0	8.5	3.1	0.3	0.1	2.1
5	51.2	7.3	3.1	+	+	1.5
6	56.8	8.1	2.7	0.1	+	+
7	52.8	6.3	3.0	+	+	1.6
8	55.6	9.5	2.2	0.2	+	+
9	53.5	12.6	4.0	0.3	0.3	+
10	57.7	9.6	3.4	0.4	+	3.6
11	43.7	6.0	1.9	+	+	+
12	52.7	9.0	2.7	0.2	+	+
13	56.5	11.0	2.5	0.2	+	+
14	56.7	8.2	2.7	0.3	+	1.1
15	43.6	6.6	2.9	+	+	+
16	51.4	5.5	2.1	+	+	+
17	55.1	8.8	2.5	0.2	+	+
18	55.6	8.2	3.6	0.3	0.1	8.4

*+ indicates concentrations below 0.1%.

Table 4. Response table for brightness response (% ISO). The experiments made with laboratory-scale sodium dithionite

	Wash	Dosage	pH	Temperature	Blank	Grade	EDTA	Blank
Level 1	5.794	4.663	5.403	4.173	5.337	4.415	5.292	5.660
Level 2	4.991	5.582	5.442	5.887	5.777	5.082	5.268	5.485
Level 3		5.933	5.333	6.118	5.065	6.682	5.618	5.033
Difference	0.803	1.270	0.108	1.945	0.712	2.267	0.350	0.627
Rank	4	3	8	2	5	1	7	6
Significant level	ON	1.2	6.0	90	2	CC	0.4	1
Response	5.794	5.933	5.442	6.118	5.777	6.682	5.618	5.660

RESULTS AND DISCUSSION

Brightness gain

By means of the Taguchi method, the effect of each parameter could be readily evaluated on brightness gain. The brightness values in **Figures 2-5** were the mean values of the experiments performed at the same level; for example, the brightness value at 50°C in **Figure 2** was the mean value of six experiments carried out at this temperature in the L-18 matrix. The wider the variation in brightness gain, the greater the impact on brightness.

It was determined that temperature (**Fig. 2**) and dithionite grade (**Fig. 3**) were the most important factors. About 37% of brightness gain could be explained by dithionite grade and about 31% by temperature. Dithionite dosage (**Fig. 4**) also had a significant effect on brightness, and washing of pulp improved brightness response to some extent. In contrast, the initial pH (**Fig.**) and the addition of EDTA did not have a notable impact on brightness response.

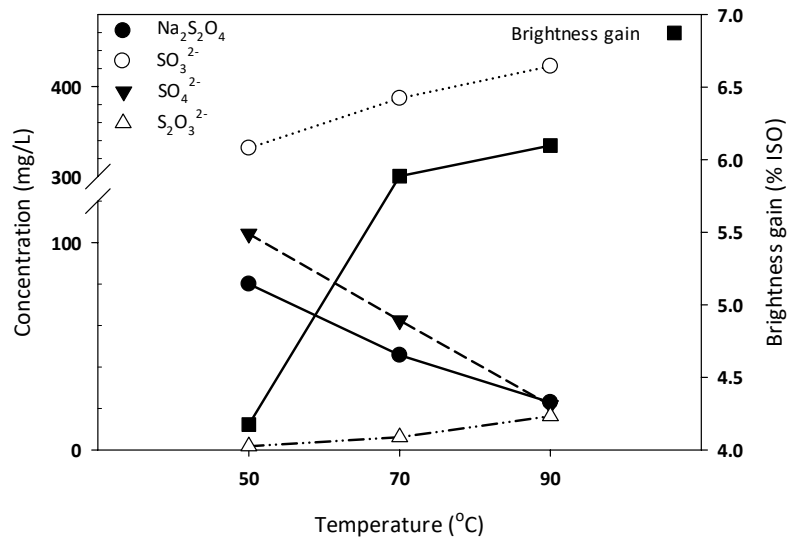


Fig. 2 The concentration of sulphur-containing ions and brightness gain at different temperatures.

The second significant factor regarding the decomposition of dithionite was temperature (**Fig. 2**). It could be concluded that bleaching temperature should be at least 70°C and the only limited advantage was obtained at 90°C. The amount of residual dithionite decreased when temperature increased and at 90°C the amount of residual dithionite after 30 min was negligible. At higher temperatures, the sulphite anions in filtrates were concentrated, indicating better bleaching efficiency, as also indicated from brightness gain. The number of sulphate anions decreased in relation to temperature. This could also be explained simply by an improved bleaching efficiency at higher temperatures. The level of thiosulphate anions was slightly raised when the temperature increased. This was explained by the fact that an increase in temperature speeded up the straightforward thermal decomposition of dithionite into thiosulphate.

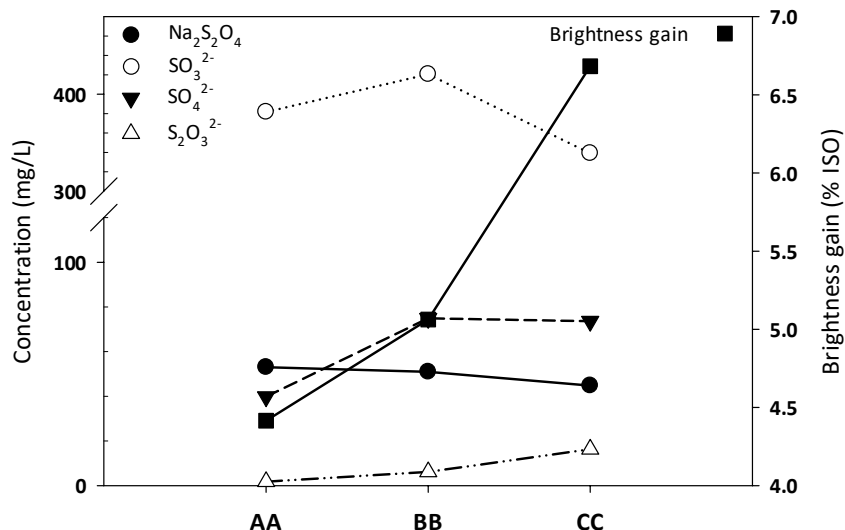


Fig. 3 The concentration of sulphur-containing ions and brightness gain with different dithionite grades AA, BB and CC.

The dithionite grade had a remarkable impact on brightness gain. The brightness response of the dithionite powder blend CC seemed to be superior compared to the other two grades. In this case, the mean brightness gain was 66% greater than the response of AA, and BB was only marginally better than AA. Dithionite grades also had some effects on concentrations of sulphur species in filtrates. For example, in the experiments with the powder blend BB, there was slightly more sulphite anions in filtrates than in the experiments with the two other grades. On the other hand, the powder CC yielded more thiosulphate anions into filtrates than the other two grades. An effective bleaching performance of the blend CC could not be explained by the analysis of sulphur-containing anions.

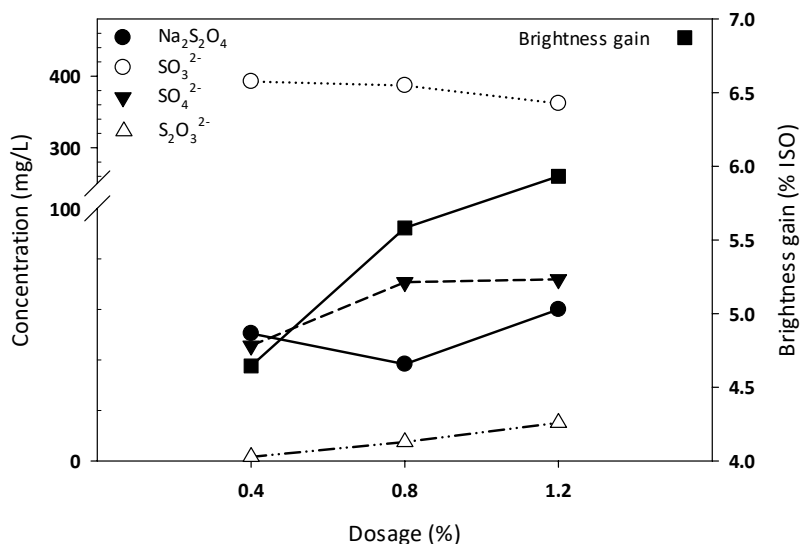


Fig. 4 The concentration of sulphur-containing ions and brightness gain at different dosages.

As expected, dithionite dosage had a clear effect on brightness; the bigger the dosage, the greater the brightness. Additionally, the effect of dithionite dosage on the formation of sulphur species could be easily detected. The effect was shown mainly at sulphate and thiosulphate levels. There were

proportionally more sulphate and thiosulphate anions present in filtrates when larger dosages were used, which clearly showed the poor bleaching efficiency of large dithionite dosages.

The minor effect of the initial pH (**Fig. 5**) on brightness response could be explained by several factors. In these experiments, three different dithionite grades were used and two of them were stabilised powder blends with an individual buffering effect on bleaching pH. In the decomposition reactions of dithionite, the initial bleaching pH had a clear effect on the amount of residual dithionite and thiosulphate anions. There was more residual dithionite present after 30 min when a higher pH was maintained. On the contrary, the concentration of thiosulphate anions was significantly lower at pH 7. It was concluded that bleaching under a neutral pH does not have a detrimental effect on dithionite.

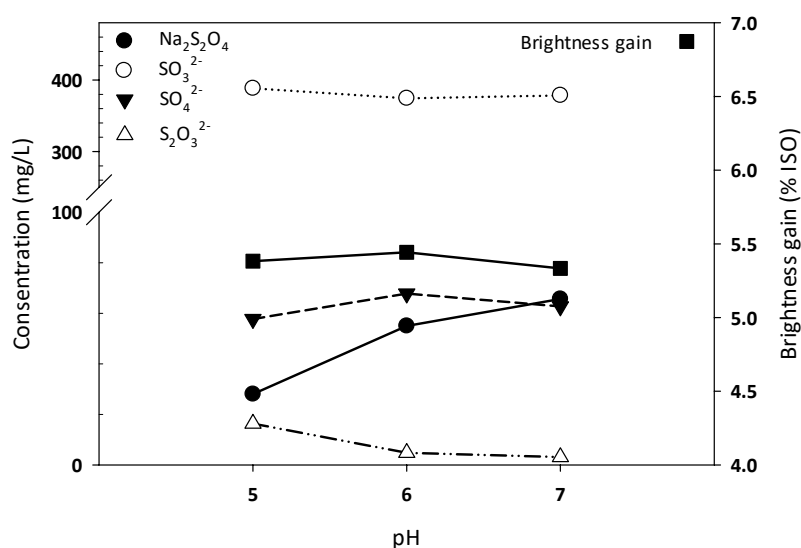


Fig. 5 The concentration of sulphur-containing ions and brightness gain at different initial pH values.

A minor ranked factor washing at the level 1 (ON) position could be explained by reducing the amount of metals and extractives in the pulp slurry. Brightness improvement was due to decreased consumption of dithionite for direct decomposition reactions and fewer metals were available for colouring reactions. Also, pulp fines were lost to some extent in washing and brightness response was lower. Regarding washing, a brightness gain of almost 1% ISO was obtained, although values were proportional to the same initial brightness value.

Bleaching filtrate analyses

The data on the detailed analyses of sulphur filtrates were evaluated by the Taguchi method to clarify the possible effect of decomposition products on bleaching performance. During each bleaching experiment, the decomposition products of dithionite were monitored after 10, 20 and 30 min (**Fig 6**).

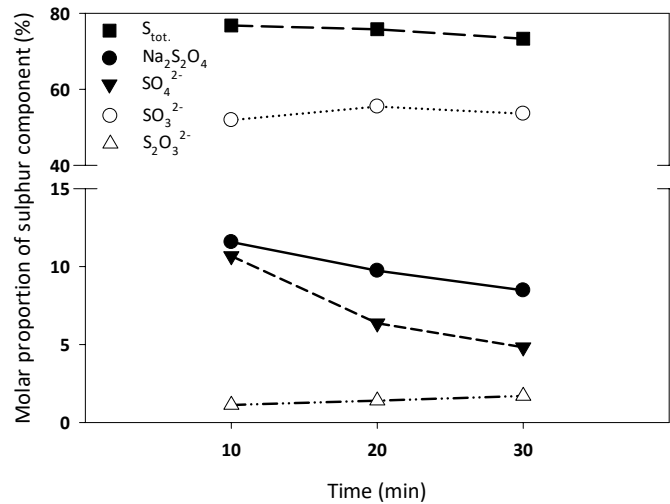


Fig. 6 Development of sulphur balance in bleaching effluents at various reaction times. Factors are taken from Table 2.

In average, only 75% of sulphur species from sodium dithionite were found in the filtrates. The remaining 25% stayed with the pulp. The sulphur balance loss could be explained by two separate phenomena. The sulphate anions were probably forming ionic bonds with a pulp fibre surface and sulphite and dithionite anions were reacting with pulp, which formed covalently bonded sulphur compounds. Correlations between the amount of covalently bonded sulphur and brightness gain have been earlier observed in our preliminary tests and supported the hypothesis that sulphonation reactions occur in dithionite bleaching as well (Fig. 7).

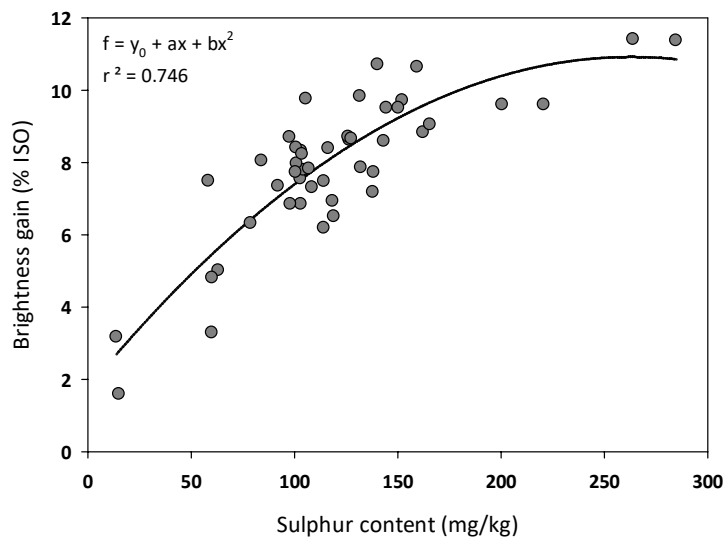


Fig. 7 Brightness gain vs. sulphur content in PGW pulp. Collected data contain all preliminary bleaching experiments.

CONCLUSIONS

The results based on the experimental design suggest that temperature, dithionite grade and dosage are the most important factors for obtaining an efficient dithionite bleaching of PGW. The

temperature should be at least 70°C to get the full benefit. Additionally, the analyses of sulphur species clarified that the higher the temperature, the more sulphite is found in filtrates. A higher dithionite dosage achieves a higher brightness, but thiosulphate levels in filtrates also increased.

Surprisingly, dithionite grade proved to be a very significant factor. One of the powder dithionites was found to be superior in terms of brightness gain. This powder gave good bleaching responses under almost every bleaching condition and particularly, with a low dosage.

The definite reason for different bleaching responses of dithionite grades is still not known. One explanation could be that commercial powder dithionite blends contain additives, such as anti-oxidants, pH buffers and chelating agents. The difference in brightness response of dithionite grades could not be explained by analyses of sulphur species since there were no significant differences in the decomposition and reaction products of dithionite.

The initial bleaching pH was observed as an unsuccessful factor when excessive unequal dithionite grades were compared. At the lowest initial pH, the concentration of thiosulphate anions was clearly higher; therefore, on the mill-scale, the pH of the pulp should be kept above 5.

Observed sulphur balance (Fig. 8) in the laboratory scale bleaching experiments can be presented as follows. In anaerobic conditions, over 50% of dithionite is decomposed to sulphite and without exception, residual dithionite is found. Accumulation of thiosulphate depends on the dithionite characteristic and unfavourable bleaching conditions. In addition, the total sulphur content of pulp correlates to a high degree with pulp brightness.

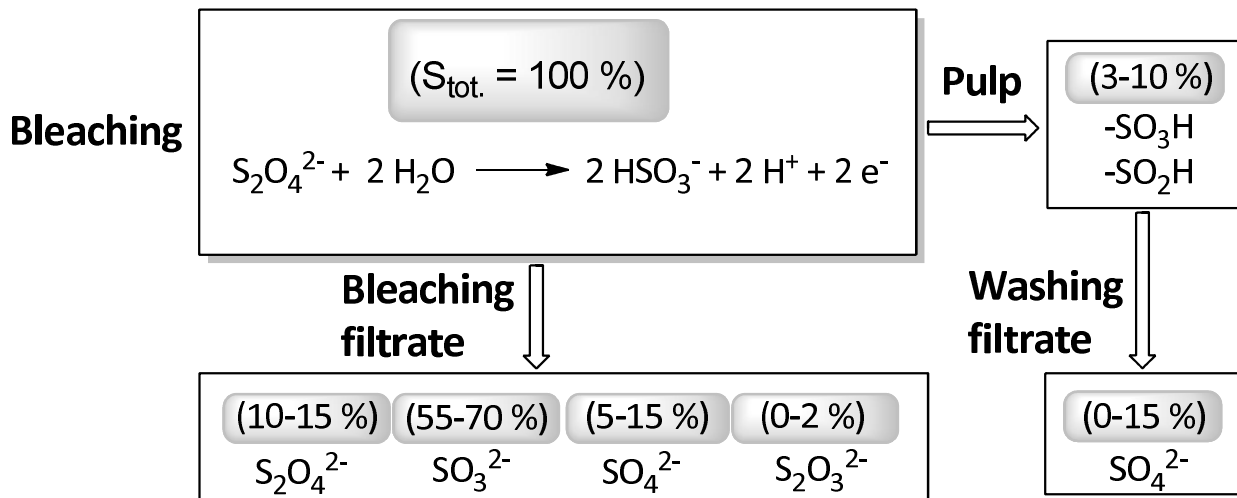


Figure 8. Mass balance of sulphur over the laboratory-scale dithionite bleaching.

Acknowledgement

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II

CHEMISTRY OF DITHIONITE BLEACHING. PART 2. COMPARABLE STUDY WITH DIFFERENT THERMOMECHANICAL PULPS

by

Jukka Pekka Isoaho, Jori Soininen and Raimo Alén, 2019

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Chemistry of dithionite bleaching. Part 2. Comparable study with different thermomechanical pulps

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SUMMARY

The role of common variables, such as dithionite grade, dosage (0.4%, 0.8% and 1.2%, based on air-dried pulp), pH (5, 6 and 7) and temperature (50°C, 60°C and 70°C) in the laboratory-scale sodium dithionite (hydrosulphite, Na₂S₂O₄) bleaching of two different thermomechanical spruce pulps were screened with the experiments designed by the Taguchi method. The effect of pulp origin versus brightness gain was studied using three dithionite grades. The Taguchi method was also used to obtain the correlation between total sulphur content and pulp brightness. In all cases, the most important factors were dithionite dosage and temperature with varying contributions.

Keywords: Bleaching dithionite, ion chromatography, process variables, spruce, sulphur balance, thermomechanical pulp, TMP, recycled fibre, RCF

INTRODUCTION

Optimisation of dithionite use in full-scale bleaching has obtained very little attention in previous studies (1-5). Major processes are controlled manually and have the potential to create unnecessary variations in paper brightness and amounts of residual dithionite from on-site manufacturing and bleaching. Sopenlehto and Moilanen (6) have observed that the manual control based on two types of instruments (sensors for brightness and dithionite residual) can reduce brightness variability and consumption of bleaching chemical.

In our earlier experiments (7,8), the main process parameters that influenced the performance of dithionite bleaching were investigated. This study was aimed to continue the dithionite grade comparison for different kinds of thermomechanical spruce pulps. In the first laboratory-scale experimental design, three same dithionite grades (abbreviations; AA, BB and CC) were used and the pulp sample was taken after the first stage of refining (8). This pulp was very suitable for the detailed study of dithionite bleaching because it contained only a limited amount of process water from the paper mill (PM1). Other factors (dosage, temperature and initial pH) could also be clarified in these laboratory-scale bleaching experiments.

The second objective of this paper was to replicate the earlier bleaching experiments (8) made on a laboratory scale in another paper mill (PM2). The mill used different spruce species as a virgin raw material and also some deinked pulp. Sulphur species in dithionite liquors and bleaching filtrates were studied to evaluate possible corrosion problems of the paper mill.

In this case, the bleaching was also studied using the Taguchi method (9) to clarify further the factors affecting brightness gain. In these laboratory-scale trials, one sodium borohydride-based (DD) and two powder-based dithionite (EE and FF) grades were used.

EXPERIMENTAL

Bleaching experiments were carried out according to the same procedure as applied previously (8). An appropriate amount of pulp was weighed into the reactor and diluted by water to a consistency of 5%. Additionally, EDTA as a complexing agent was added and pulp suspension was made anaerobic with nitrogen gas. The heating time to bleaching temperature took about half an hour and after this period, the initial pH value of pulp was adjusted to a definite volume with 0.1 M NaOH or 0.1 M H₂SO₄. The liquor volumes due to pH adjustment and EDTA addition were taken into account in consistency calculations.

When the bleaching temperature and the initial pH were adjusted, the dithionite liquor was added and the time monitoring was started. In each case, an appropriate amount of dithionite was determined by ion chromatography and the exact addition was determined by weighing. During the injection of dithionite, the pulp was regularly mixed after each time interval of 5 min. Protective nitrogen flushing was continued and the total bleaching time was 30 min.

Reagents and bleaching chemicals

All reagents used were analytical grade (\geq purum p.a.) and the purity of commercial dithionite powder blends (i.e., active content of dithionite) was analysed. The sodium borohydride water-based solution was a mixture containing sodium borohydride and sodium hydroxide (mol ratio 1NaBH₄ + 3.2NaOH). During bleaching experiments, the reactor and sampling were protected

by nitrogen gas. The sulphur dioxide gas (SO₂, product grade 3.8) used in the generation of bleaching liquor was obtained from Oy AGA Ab, Riihimäki, Finland. The deionised water used for all these experiments was purified with a Milli-Q Plus system (UHQ-water, Millipore, Bedford, MA, USA).

Bleaching set-up

An appropriate amount of sodium dithionite liquor was injected by a syringe through an injection port equipped with a septum stopper. The liquor was purged with nitrogen gas into the pulp and a continuous flow of nitrogen was allowed to prevent bleaching liquor oxidation. Nitrogen was also used in removing air from the pulp. A gas flow meter and a pressure-regulating valve controlled the flow of nitrogen. The reactor was preheated by a water bath when needed to obtain the expected temperature and to maintain temperature stability during bleaching. Temperature and pH were measured by a combined temperature/pH electrode.

Preparation of sodium dithionite liquors

Preparation of sodium dithionite bleaching liquor by using an alkaline borohydride solution was made as described earlier (8). Sodium borohydride-generated hydrosulphite (BGH) was built on a laboratory scale based on the procedure of Morton Performance Chemicals (10). The method used in these experiments was slightly modified to correspond to the mill-scale on-site production and concentration.

Dilutions of dithionite powder blends were prepared as follows. UHQ-water was placed in an airtight vessel and the air was removed by nitrogen gas. An appropriate amount of powder was dissolved into the water and the solution was agitated during dissolving and storing (15–25°C) under a nitrogen atmosphere. The target concentration of sodium dithionite was between 50–70 g/L.

Pulp and bleaching procedure

Spruce pulp (PM1) was originated after the 1st -stage refining and was taken from the blow pipe of the refiner. The pulp was dried under nitrogen gas to a consistency of over 90% and then stored at room temperature. The initial brightness of TMP was 57.4% and had a freeness of about 700 mL. The pulp was diluted to a consistency of 5% by UHQ-water and the pH was about 5.

The second pulp sample (PM2) was manufactured from the other spruce species and the pulp for these trials was taken from the medium consistency pump after the disc filter. At the time of sampling, the consistency was about 9.7%. The initial brightness of pulp was 54.9% and the pH value was about 5 after dilution to a consistency of 5%. After receiving, the pulp was frozen in plastic bags to prevent contamination.

The addition of a bleaching chemical was based on the active concentration of dithionite and was calculated according to the ion chromatographic analysis. During the injection of dithionite, the pulp was mixed continuously for 20 s and nitrogen purging was continued to the end of bleaching (30 min). The dithionite and EDTA dosages were expressed as percentages

of air-dry pulp. At the end of bleaching, pulp treatment was the same as shown in our previous study (8).

Analytical methods for sulphur compounds

The determination of various sulphur-containing anions and the total sulphur content of pulp was performed correspondingly using the same methods as described earlier (8). The quantitative analysis of the following most abundant anions by ion-chromatography was possible: dithionite ($S_2O_4^{2-}$), sulphide (S^{2-}), sulphite (SO_3^{2-}), sulphate (SO_4^{2-}), thiosulphate ($S_2O_3^{2-}$), dithionate ($S_2O_6^{2-}$) and polythionates ($S_nO_6^{2-}$). An energy-dispersive X-ray fluorescence (EDXRF) spectrometer was used to determine the total sulphur content of pulp. Both sides of the sample pellet were measured and the mean value of results was used in the subsequent calculations.

EXPERIMENTAL DESIGN

The effect of process factors on the dithionite bleaching response was investigated by means of laboratory-scale bleaching experiments using the Taguchi method for the experimental design and interpretation of results (9). Firstly, an L9 matrix was designed for these trials. The levels of factors used in these experiments are presented in **Table 1**.

Table 1. The experimental design for the dithionite bleaching trials (PM1)

Trial#	Initial pH	Temperature [°C]	Dosage [%]	Grade
1	5.0	50	0.4	AA
2	5.0	70	0.8	CC
3	5.0	90	1.2	BB
4	5.8	50	0.8	BB
5	5.8	70	1.2	AA
6	5.8	90	0.4	CC
7	6.6	50	1.2	CC
8	6.6	70	0.4	BB
9	6.6	90	0.8	AA

The experiments were carried out according to the procedure described earlier (8). The dithionite dosages were calculated based on the amount of active sodium dithionite and the dosages were expressed as percentages of air-dried pulp. The initial pH values in the experimental design were equal to those values of pulp before the dithionite addition.

The following Taguchi L9 matrix was designed for the PM2 experiments. The levels of each factor used in these trials are presented in **Table 2**. The dithionite dosages were calculated according to the amount of active sodium dithionite as well as powder-based dithionites. Dosages were expressed as percentages of air-dried pulp.

Table 2. The experimental design in the dithionite bleaching trials (PM2)

Trial#	Grade	Dosage [%]	Temperature [°C]	Initial pH
1	DD	0.2	50	5.0
2	DD	0.6	70	5.8
3	DD	1.0	90	6.6
4	EE	0.2	70	6.6
5	EE	0.6	90	5.0
6	EE	1.0	50	5.8
7	FF	0.2	90	5.8
8	FF	0.6	50	6.6
9	FF	1.0	70	5.0

Bleaching results were also studied by means of the total sulphur content of pulp. The purpose was to follow the reaction pathways of dithionite under different bleaching conditions and determine the main proportions of the total sulphur chemically bonded to this uptake pulp. The effects of different process factors on total sulphur were investigated by means of laboratory bleaching experiments using the Taguchi method in the experimental design and in the interpretation of results.

RESULTS AND DISCUSSION

Brightness gain

When applying the Taguchi method, it was possible to evaluate readily the effect of each parameter on brightness gain. The brightness values were the mean values of experiments done at the same factor level. For example, the brightness value at 50°C in **Figure 1** was the mean value of three experiments carried out at this temperature in the L9 matrix.

In the case of PM1 (**Fig. 1**), dithionite dosage and grade proved to be the most significant factors: over 90% of brightness gain could be explained by these two factors. The contribution of dosage was about 62% and that of dithionite grade was about 31%. A minor linear effect was also caused by bleaching temperature. As found in our previous studies (8), the initial pH had no effect on brightness gain.

Dithionite dosage had an expected impact on brightness response. The more dithionite utilised, the more brightness gain was observed. The slope of brightness response declined slightly after a dosage of 0.8%. The average brightness response of AA was about 2% ISO brightness, which was better than that of CC and about 2.4% ISO brightness better than BB.

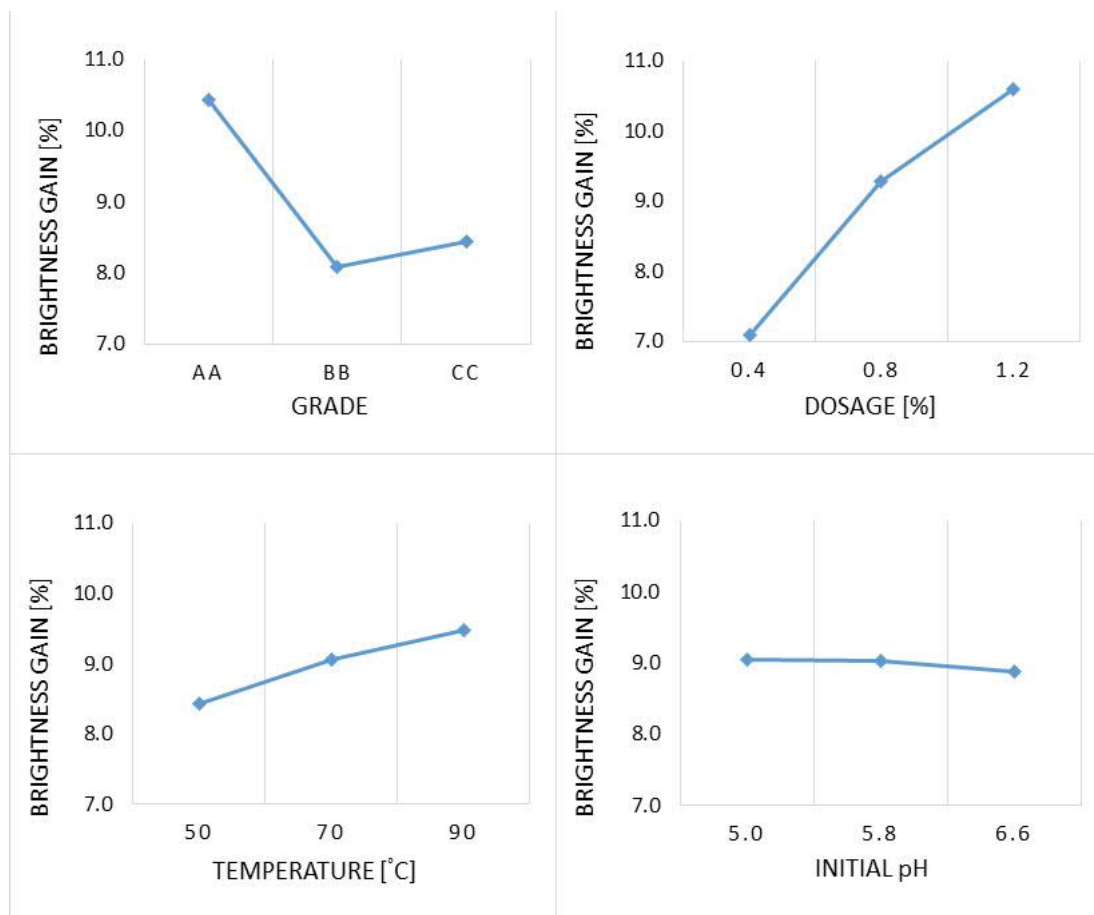


Fig. 1 Bleaching of thermomechanical pulp from PM1; the contribution of dosage is 62% and grade 31%.

The bleaching efficiency of PM1 pulp could be improved by the increase in temperature; the higher the temperature, the higher the brightness, although the difference between the average brightness responses at 50°C and 90°C was only 1% ISO. Hence, it was obvious that the pulp can be bleached efficiently even at 50°C. A weak improvement in brightness gain as a function of temperature could be explained by increasing some darkening reactions at higher temperatures.

As expected, dithionite grade was a significant factor of dithionite bleaching (**Fig. 1**). In this case, AA gave better brightness gain than other dithionite grades. This phenomenon could not be directly proved by analyses of sulphur species, although minimal amounts of thiosulphate anions in filtrates in the experiments with AA seemed to indicate good bleaching efficiency. Because conflicting results of grade responses were observed for pressure groundwood and thermomechanical pulps, it was concluded that dithionite grade should be carefully selected in each case (8).

For PM2 the impact of each factor is presented in Figure 2. In this case, dosage and temperature were the most important factors with contributions of almost 77% and 22%, respectively. Hence, the total brightness gain could be mainly explained by these two factors.

The brightness gain values were improved remarkably (about 4%) when dithionite dosage was increased from 0.2% to 0.6% (**Fig. 2**). The highest dosage gave only a small brightness

improvement when compared to the mean brightness gain with a dosage of 0.6%. Additionally, brightness gain was improved almost linearly as a function of temperature and the difference in mean brightness values between 50°C and 90°C was almost 3% ISO.

In this case, the effect of dithionite grade on brightness response was negligible. In practise, the responses of chemicals were similar when the same amount of active dithionite was utilised. In contrast, the initial pH did not have any effect on the brightness response.

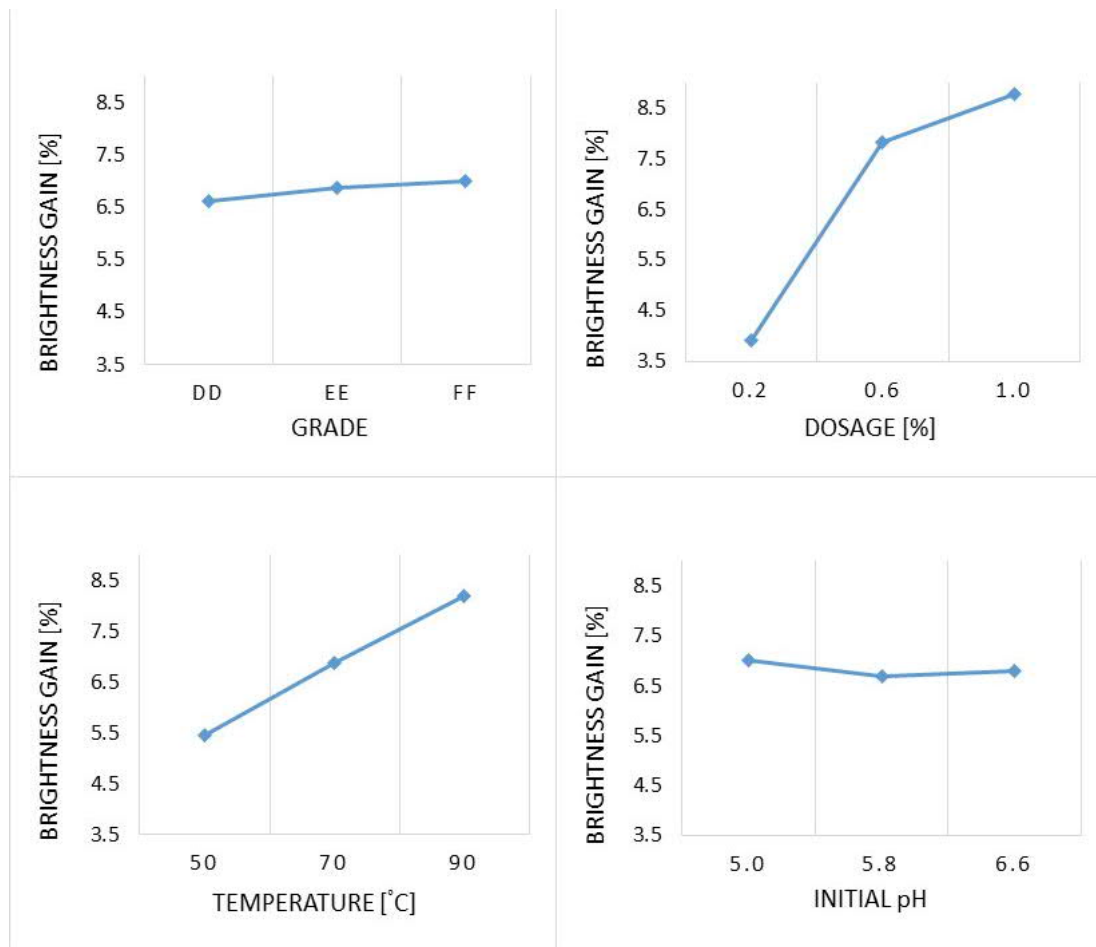


Fig. 2 Bleaching of thermomechanical pulp from PM2; the contribution of dosage is 77% and temperature 22%.

According to the above-presented PM2 results, temperature and dithionite dosage were the important factors. The optimum response to bleaching was clearly gained with an addition of 0.6%. However, It is not economical to use dosages over 0.6% if it is not necessary for obtaining the higher target brightness. The bleaching efficiency could also be improved by increasing temperature.

Another significant finding of these experiments was the fact that dithionite grade did not affect brightness response and all these grades behaved almost equally. Hence, it could be concluded that in the case of PM2, it is not reasonable to change dithionite grade.

Pulp sulphur analyses

According to the sulphur analyses of bleaching filtrates, some portion of the sulphur disappeared during bleaching. One reasonable explanation for this phenomenon was chemical bonds that were formed between the sulphur species and pulp. These laboratory-scale studies aimed to clarify only the quantity of covalently bonded sulphur. Previous studies indicated that some portion of sulphur linked to pulp (8,11).

The amount of covalently bonded sulphur can increase via a few pathways in dithionite bleaching (3). Both dithionite and bisulphite can react with lignin in a way that covalent bonds are formed between the carbon of a coniferaldehyde group in lignin and a sulphur group. Dithionite and bisulphite cause attachment of sulphur to lignin as $-SO_2$ and $-SO_3$ groups, respectively.

The data of total sulphur analysis were evaluated by the Taguchi method to clarify if the studied factors could explain bound sulphur. In some cases, it might be of benefit to adsorb sulphur to fibres. The average results of the factors are presented in **Figures 3** and **4**.

On average, the total amount of sulphur in filtrate compared to that in the added sodium dithionite was over 90%. The rest, <10%, migrated with pulp. Correlations between the amount of covalently bounded sulphur and brightness gain have been observed earlier in our preliminary tests, which supported the hypothesis that sulphonation reactions exist in dithionite bleaching. It could be concluded that the bonding of sulphur species with pulp is more plausible in the case of pressure groundwood pulp than for thermomechanical pulp.

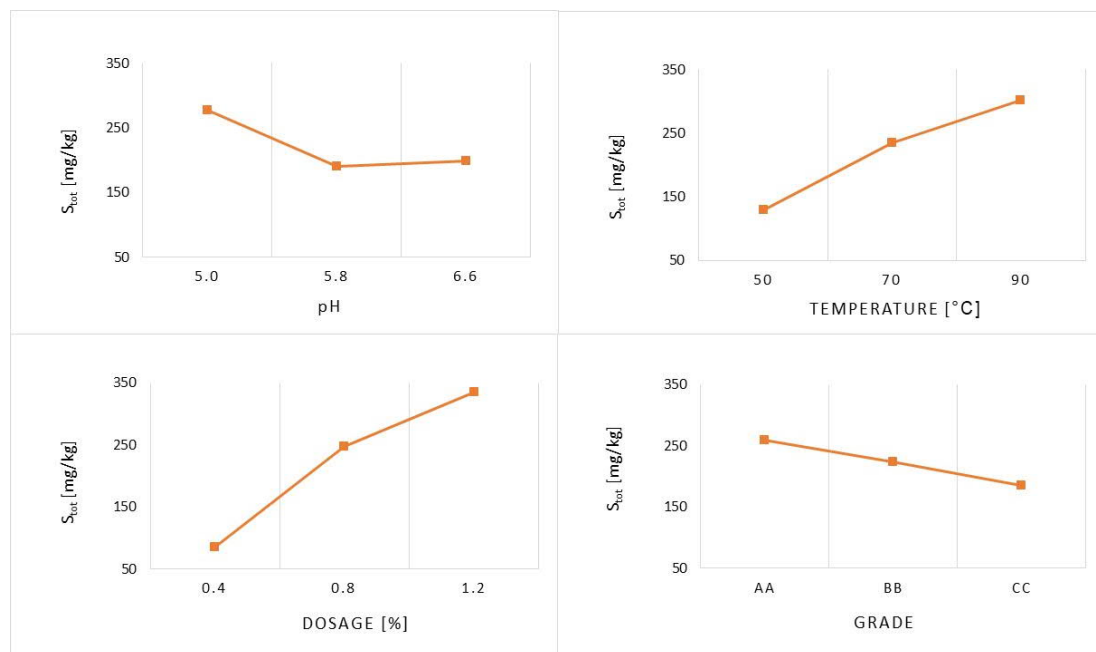


Fig. 3 Sulphur analysis in bleaching of thermomechanical pulp from PM1; contributions are dosage 59% and temperature 28%.

The most substantial factor regarding the sulphur adsorption was dithionite dosage (**Fig. 3**); this factor could explain almost 60% and the increasing effect was linear. According to the Taguchi analyses, the most significant factors affecting sulphur content of pulp were temperature and dithionite dosage. The more dithionite that was added and the higher temperature that prevailed (the faster the reaction), the more sulphur was covalently bonded to the pulp. Almost identical contributions of factors were observed (**Fig. 4**).

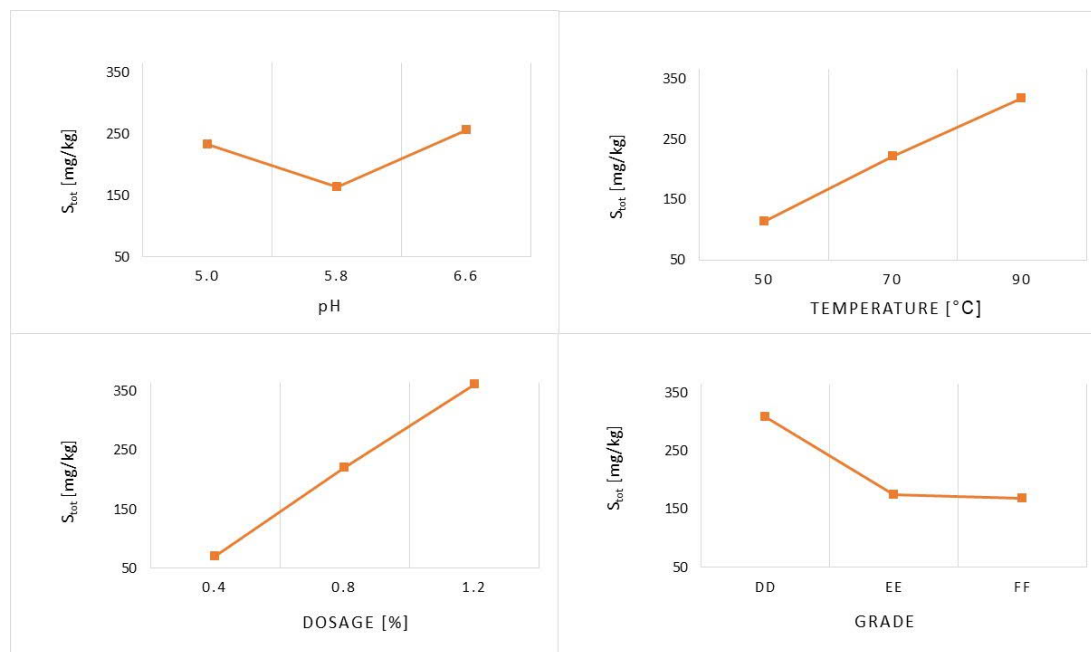


Fig. 4 Sulphur analysis in bleaching of thermomechanical pulp from PM2; the contribution of dosage is 53%, temperature 26% and grade 16%.

The sulphur content and brightness of pulp had a distinct relationship. The pulp brightness increased quite steadily as a function of the sulphur content in the pulp. This led to the conclusion that bleaching reactions increase according to the sulphur content of pulp and represent significant and dominant reactions. Therefore, it seemed that both kinds of reactions—the addition of sulphur and reduction of chromophores via radical reaction—occurred and the proportions of these reaction types were almost constant under each bleaching condition. Otherwise, the sulphur content of pulp and the brightness of pulp should not have so close a relationship.

Mill-scale trials (PM2)

Several bleach liquors and bleaching filtrate samples were collected during the mill trials with varying dithionite grades. The most bleach liquor samples were taken from the mixing unit; in addition to them, some samples were collected from the dithionite dosing points to pulp and the recycled fibres (RCF). Dosages of the grade EE were calculated as powder basis and those of DD as active sodium dithionite.

During the mill-scale trial, it was found that the bleach liquor was properly stored. The concentration of the dithionite liquor varied only slightly (RSD ~3%). The size of variation was extremely low if all the sources of errors, for example, analytical method, sampling and heterogeneous dithionite preparation were taken into account. This led to conclusion that the composition of bleach liquor is constant if the leaching of dithionite is done correctly.

In the mill-scale trial, significant differences between dithionite grades in terms of sulphur compounds were not observed (Figs. 5 and 6). The total sulphur amount in filtrates of the grade DD was higher than noted in the EE experiments because the DD liquor clearly consisted of more sulphate anions. In the case of DD, the total sulphur amount of filtrate was not cumulative as a function of dithionite dosage; therefore, the actual dosages at points 0.6% and 0.92% could have been higher. The thiosulphate anion levels were quite low in all filtrate samples.

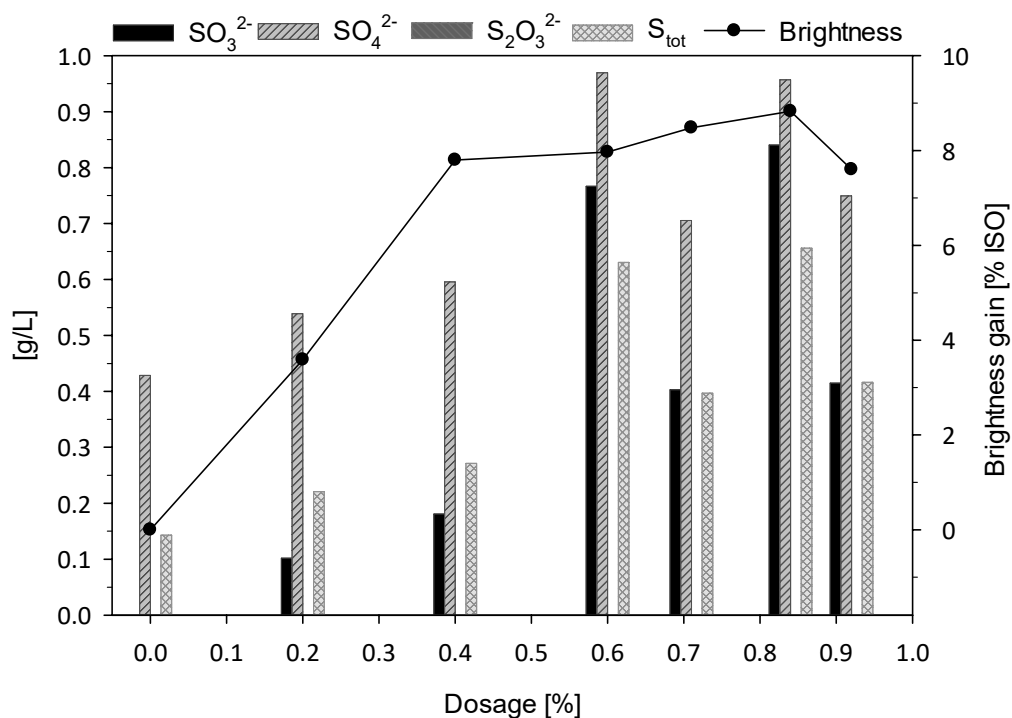


Fig. 5 Filtrate analysis in bleaching of thermomechanical pulp from PM2 with dithionite grade DD.

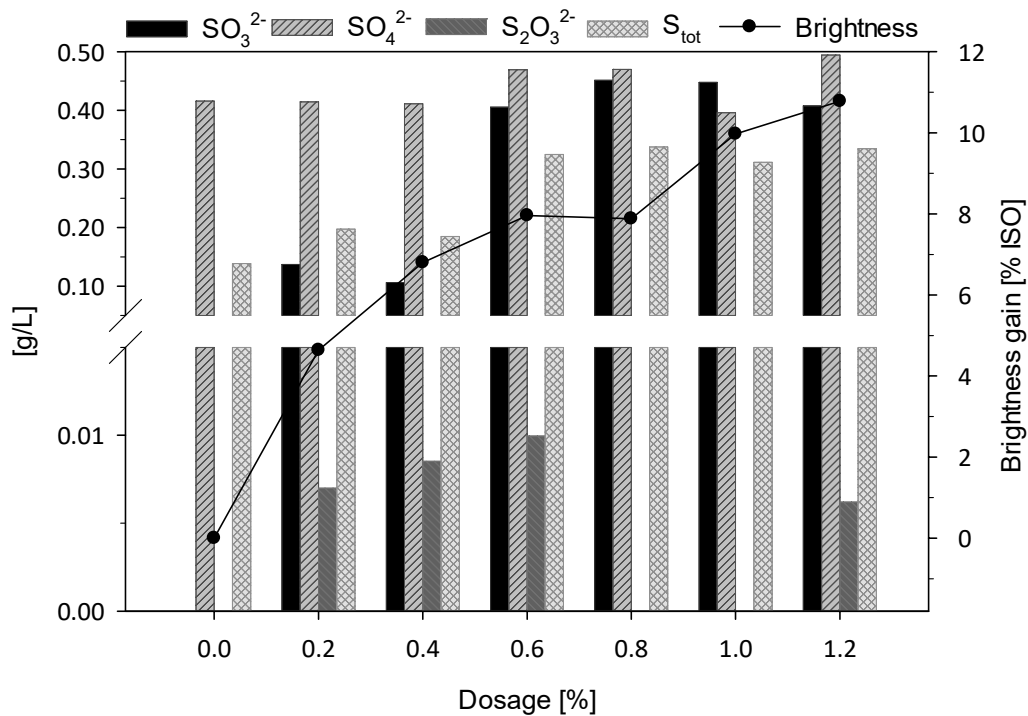


Fig. 6 Filtrate analysis in bleaching of thermomechanical pulp from PM2 with dithionite grade EE.

The sulphur compound levels that were found from the filtrates of RCF bleaching for both dithionite grades were quite identical (Figs. 7 and 8). Again, the sulphate anion levels in filtrates of the DD experiments were higher because of bleach liquor. The sulphur compound concentrations increased almost linearly as a function of dosage. Dithionite was added to the medium consistency (MC) pump after the disc filter. The samples were taken at every dosage level.

Bleaching filtrate samples from the RCF bleaching were collected both from DD and EE runs. Dithionite was added to the MC-pump after the standpipe before the RCF towers and the samples were taken at every dosage level. It was seen that the total sulphur load of the RCF line was much higher than that of the TMP line and the bleaching response (gain) was lower. Furthermore, it was noted that the brightness gain was curved at quite low dithionite dosages. The total sulphur content increased almost linearly as a function of dosage.

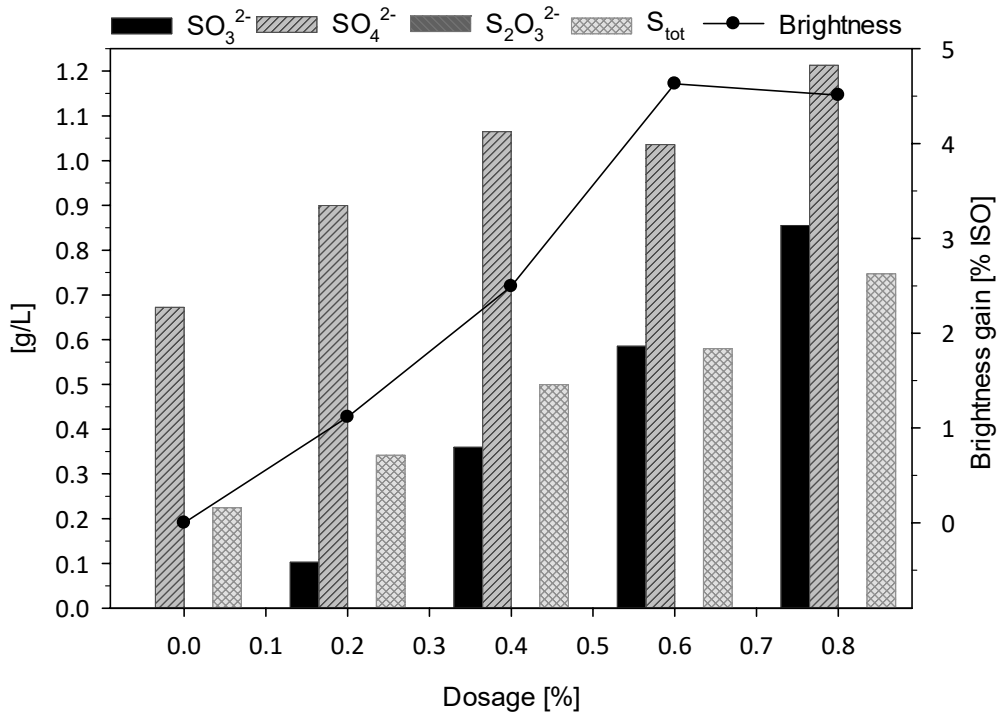


Fig. 7 Filtrate analysis in mill-scale bleaching of RCF from PM2 with dithionite grade DD.

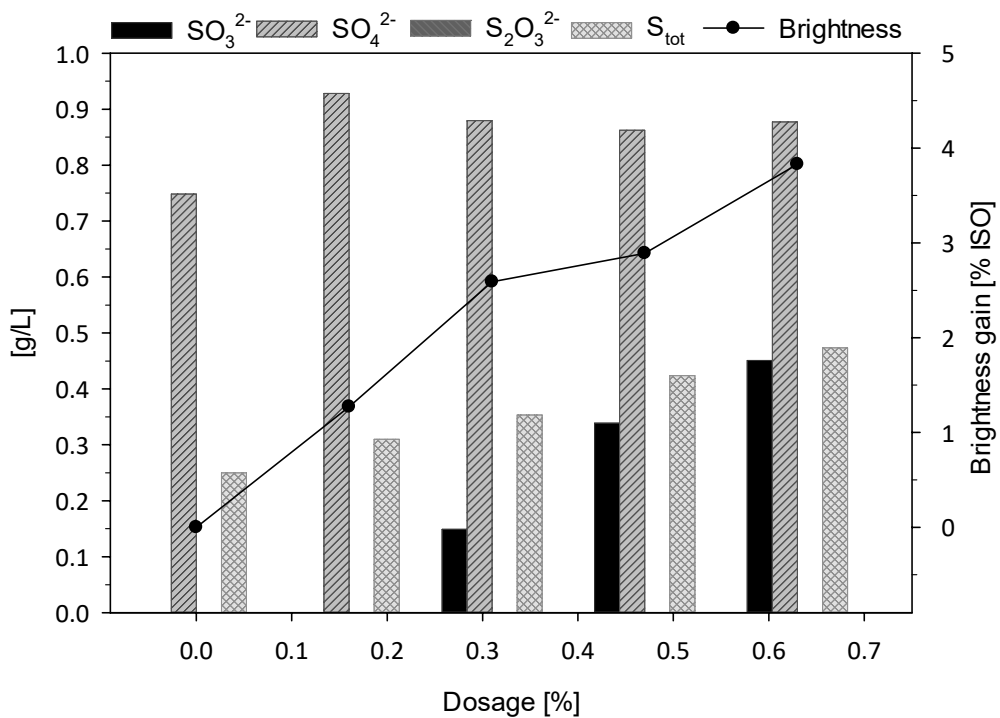


Fig. 8 Filtrate analysis in mill-scale bleaching of RCF from PM2 with dithionite grade EE.

In order to complete the sulphur analyses of the PM2 mill scale trial, the sulphur content of pulp samples was determined. One objective was to find out the effect of the sulphur content on the strength and wettability properties of pulp. It was expected that dithionite bleaching

might affect strength properties because sulphonation reactions take place during bleaching and the hydrophilicity of fibres increases.

In each run, the sulphur contents of pulp samples increased, clearly as a function of dithionite dosage (Table 3). The sulphur contents were similar to those from the corresponding laboratory-scale results. However, no correlation between the sulphur content of pulp and the strength properties were found. The strength properties were fairly similar between the unbleached and bleached samples.

Table 3. Sulphur contents of thermomechanical pulp and RCF samples in the mill-scale trials from PM2

Pulp (grade DD)		Pulp (grade EE)		RCF (grade DD)		RCF (grade EE)	
Dosage [%]	S _{tot} [mg/kg]	Dosage [%]	S _{tot} [mg/kg]	Dosage [%]	S _{tot} [mg/kg]	Dosage [%]	S _{tot} [mg/kg]
0.00	42	0.00	41	0.00	270	0.00	294
0.20	117	0.20	245	0.20	369	0.16	282
0.40	367	0.40	168	0.40	456	0.31	410
0.71	369	0.60	536	0.60	593	0.47	524
0.84	608	0.80	510			0.63	528
0.92	566	1.00	586				
		1.23	565				

A clear correlation between brightness and sulphur content of pulp was observed from all runs. Higher sulphur content of pulp meant normally higher brightness. Especially, according to the brightness and sulphur content curves of pulp bleaching, brightness did not increase after a certain point. In RCF bleaching, this kind of behaviour was not observed and the curve shape would have probably been similar if higher dithionite dosages (over 1.0%) were utilised.

CONCLUSIONS

The effects of various factors on dithionite bleaching using different pulps were investigated using the Taguchi method. It was discovered that combinations built up from factors dosage, grade and temperature, were the most critical factors. An increase in temperature improved the efficiency of bleaching and this was also seen from the total sulphur analysis of pulp. However, the temperature of the mill-scale process could not be elevated excessively because, due to energy consumption, the benefit of better brightness can be lost. In contrast, adding dithionite to a proper point, where the temperature is naturally higher and mixing is efficient, would be a more rational approach.

Dithionite dosage was an essential factor. Typically, the more dithionite utilised, the higher the brightness gain achieved. The optimum dosage level should be carefully examined by taking pulp origin into account. Measured sulphur content and brightness of pulp also had a clear relationship in these experiments

In addition, dithionite grade proved to be a significant factor in laboratory-scale studies, but in mill-scale studies, both dithionite grades (DD and EE) seemed to be equal in terms of brightness response. An actual reason for the different behaviour of dithionite grades

concerning brightness response was not apparent and hence, dithionite grade should be separately optimised for each purpose.

Acknowledgement

The support provided by UPM is gratefully acknowledged.

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III

OXIDATIVE DEGRADATION OF AOX IN SOFTWOOD-BASED KRAFT MILL EFFLUENTS FROM ECF BLEACHING

by

Jukka Pekka Isoaho, Suvi Tarkkanen, Raimo Alén and Juha Fiskari, 2012

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Oxidative degradation of AOX in softwood-based kraft mill effluents from ECF bleaching

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KEYWORDS: Bleach effluent, Kraft pulping, AOX, Chlorinated organic compounds, Fenton, Taguchi

SUMMARY: Softwood-based kraft mill bleaching effluents from the initial bleaching stages D₀ and E₁ (the bleaching sequence being D₀E₁D₁E₂D₂) were treated by the oxidative Fenton method (H₂O₂-FeSO₄) to decompose organic pollutants containing adsorbable organic halogens (AOX). Experiments designed using the Taguchi method were applied to predict the process conditions that would result in a cost-effective and adequate removal of AOX. In addition to the composition and concentration of the reagents (H₂O₂ and Fe²⁺), the main process parameters selected were temperature and reaction time, while pH was adjusted to an approximate value of 4 (the volumetric ratio of the mixed effluents D₀:E₁ was 3:2). The results indicated that an AOX removal of about 70% for this mixture (corresponding to about 50% for the mill) was achieved when the effluent samples were treated for 60 min at 70°C with H₂O₂ and Fe²⁺ at a concentration of 1600 mg/l and 28 mg/l, respectively.

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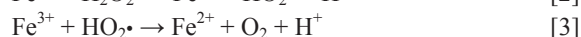
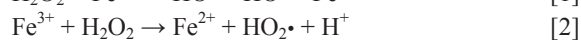
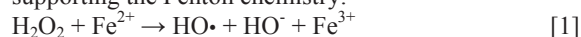
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Bleaching effluents generated by conventional and elemental chlorine-free (ECF) bleaching processes of kraft pulp contain adsorbable organic halogens (AOX, kg per tonne of pulp), mainly in the form of chlorinated high-molecular-mass (HMM, >1000 Da) lignin-derived material (Lindström et al. 1981; Berry et al. 1993; Dahlman et al. 1993; Bajpai, Bajpai 1996; Bullock et al. 1996; Bajpai 2010). There has been considerable concern about the environmental impact of AOX discharged in various effluents, which has led to extensive research on the characterisation of chlorinated organic material in bleach plant effluents (McKague, Carlberg 1996) and to regulations limiting this discharge in several countries (Reeve, Weishar 1990; Reeve, McKague 1991). AOX is expected to comprise substances that are toxic to aquatic organisms and that can bioaccumulate in the fatty tissues of higher organisms or act as carcinogenics. However, the new modified bleaching sequence currently in use (e.g., low chlorine ratio and greater substitution of chlorine dioxide for chlorine or even the use of chlorine dioxide

alone (McDonough 1998)) and the application of oxygen delignification stages (Pikka et al. 1999), together with activated sludge plants (Hynninen 1998), have gradually resulted in a substantial reduction in the formation of soluble chlorinated organics. In spite of these general trends, due to a high global production of ECF-bleached chemical pulp, AOX can still be considered a timely and relevant issue.

The activated sludge process removes chlorinated organic compounds from bleach plant effluents through processes such as biochemical degradation, biotransformation, adsorption onto the sludge (biosorption) and volatilisation (Juuti et al. 1996; Pinkerton 2000; Jokinen 2011). It has been reported that biological treatment removes about half of the AOX in kraft pulp mill effluents (Gergov et al. 1988; Bryant, Amy 1989; Dahlman et al. 1993; Jokela et al. 1993; Mortha et al. 1993). Due to slow microbial degradation or even resistance to biodegradation, the HMM fractions of chlorolignins are very stable. Compared to low-molecular-mass (LMM) chlorinated derivatives, which readily penetrate into microbial cell membranes (Dahlman et al. 1993), the HMM fraction is more stable both during the activated sludge process and later in nature, where it degrades slowly. For this reason, it can be concluded that when decreasing the AOX load of bleaching effluents, it would be advantageous to degrade chlorinated HMM compounds to LMM compounds prior to biological wastewater treatment. In addition, some chlorolignin degradation products are aliphatic compounds which are, compared to aromatics, more amenable to the aerobic bacteria in the activated sludge process (Dahlman et al. 1994).

Various advanced oxidation processes (AOPs) have been applied to ECF bleaching effluents to reduce their AOX loads (Stasinakis 2008). Among the many AOPs that can adequately decrease the AOX load, one of the most attractive approaches is the Fenton method (Goldstein et al. 1993; Stasinakis 2008). This method is based on the significant generation of hydroxyl radicals (HO•) from the decomposition of hydrogen peroxide (H₂O₂) in the presence of bivalent iron (Fe²⁺) salts (Pignatello 1992; Pérez-Moya et al. 2007). Additionally Fe³⁺ can react with H₂O₂ regenerating Fe²⁺ thus supporting the Fenton chemistry:



The hydroxyl radicals can effectively, though non-selectively, oxidise a wide range of organic pollutants. In order to achieve a successful reaction, the pH value of the Fenton's reagent should be in the range of 3-5 (Bishop et al. 1968; Pérez et al. 2002; Pera-Titus et al. 2004; Catalkaya, Kargi 2007; Anon. 2009). The basic advantages of this oxidative method include its high

efficiency, simplicity of use, readily available chemicals and relatively low costs.

AOX is one of the most common conventional ways for describing the organically bound chlorine in bleaching effluents (Dahlman et al. 1998). In this standardised method, the chlorinated organic material in the sample is first adsorbed on activated carbon, which is then washed with a nitrate solution to remove any residues of inorganic chlorine compounds. The activated carbon and the adherent chlorinated organic material are quantitatively combusted (at about 1000°C) with oxygen. The hydrogen chloride formed during combustion is adsorbed in an electrolyte solution and determined by microcoulometric titration. However, this basic method is still under development. The total AOX (EN-ISO 9562:2004) analysis consists of two parts: 1) "stable AOX" (SFS EN 1485), mainly originating from chlorinated lignin structures, and 2) "unstable AOX", from chlorinated hexenuronic acids (Björklund et al. 2002; 2004). For this reason, modified practices for determining both of these AOX parameters have been developed (Järnefelt 2007; Lehtimaa et al. 2010).

Chlorinated phenols, catechols and guaiacols have been found in effluents from bleaching of softwood and hardwood kraft pulps. For these chlorinated aromatics, several analytical procedures based on extraction of the liquor sample followed by the chromatographic analysis have been used (cf., Lindström et al. 1981; Voss 1983; Kringstad, Lindström 1984; Kringstad, McKague 1988; Lindström, Mohamed 1988; Owens, Lehtinen 1996; Dahlman et al. 1998; McKague et al. 1998). However, liquors from the modern ECF bleaching of kraft pulps usually contain only small amounts of a few chlorinated (mainly monochlorinated) phenolic compounds and higher concentrations of other aromatics (non-chlorinated compounds); these may therefore interfere with the determination of chlorinated derivatives. In light of this possible interference, the GC/MS determination of the acetyl derivatives of chlorinated phenolic compounds in liquors from the ECF bleaching using appropriate isotopically labelled standard compounds for peak identification has been applied (Deardorff et al. 1994; Dahlman et al. 1998).

The improvement of any process via experimental tests without systematic test planning is often costly in terms of resources and time (Roy 2001). A tool for test planning is usually needed when there are several factors affecting the process performance and/or product characteristics. Such an approach can reduce the number of experiments required (i.e., a low number of tests can be used to examine the effects caused by a wide range of process parameters).

The Taguchi method is one of the most common methods suitable for full-scale applications that can efficiently combine engineering knowledge and statistical analysis. It was originally developed in the early 1980's by Genichi Taguchi and was based on the statistical test planning ("design of experiments", DOE) developed by Ronald Fisher in the 1920's (Roy 2001). This method makes it possible to achieve almost the same result as that obtained when all trial combinations are studied separately. Furthermore, only certain predetermined tests

are usually necessary and the performance characteristics of experimental work (the results vs. the responses) can be readily predicted by computer-aided calculations.

The Taguchi method is based on the orthogonal matrix by which the effects of principal factors can be found out and used to test the summarisable properties of these factors; it is therefore a way to eliminate various interactive factors of less importance (Roy 2001). The main focus is to experimentally examine process performance and/or product quality parameters by which the desired characteristics can be reached with minimal variation. It is typical for this method to verify the proper operation conditions of the process in the interference-rich environment. To reduce various effects of these interferences, the most suitable parameter combinations can be determined according to the satisfactory signal-to-noise ratio. However, the prerequisite of the procedure is that the quality properties must be carefully measured with reasonable accuracy.

The main objective of this study was to determine the decomposition efficiency of chlorine-contained pollutants in pulp mill bleaching effluents by the Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$). The approach was to predict the realistic process conditions whereby an acceptable removal of AOX could be obtained at a reasonable level of chemical costs (a limiting factor). In addition, the results would reveal useful and versatile data on this application. To minimise the experimental work, the experimental design was developed using the Taguchi method. The principal parameters selected were reagent concentration and composition as well as temperature and reaction time.

Materials and Methods

Chemicals and bleach effluents

All the chemicals used were commercially available. Crystalline ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and hydrogen peroxide (H_2O_2) were used as 0.1 M and 0.36% (w/w) solution, respectively. Ultra high quality (UHQ) water (internal resistance $\geq 18.2 \text{ M}\Omega\text{cm}$ at 25°C) obtained from a Milli-Q Plus water system (Millipore) was used to prepare various solutions.

All of the effluent samples originated from a softwood and hardwood kraft mill with an annual production of about 500,000 tonnes. The samples were collected only when bleached softwood kraft pulp was being produced, either from the bleaching stages D_0 (pH 2.5) and E_1 or from the effluents before (sample BASP) and after (sample AASP) the activated sludge plant. Prior to various analyses or further processing, the samples were stored in a freezer at -18°C. To obtain a suitable pH (~4) for the oxidation treatments, the acidic (D_0) and alkaline (E_1) effluents were mixed in a volumetric ratio of 3:2.

Design of experiments and oxidation tests

The Taguchi experimental design, based on the orthogonal L_9 (3^2) matrix, was carried out considering low, medium and high levels of variables (Table 1). For designing factorial experiments and confirmation tests, the DOE v. 1.3F, Total Quality Software (1994) computer program was used.

Table 1. Experimental variables and levels

Variable	Symbol	Variable level		
		1	2	3
Fe ²⁺ (mg/l)	X ₁	10	20	28
H ₂ O ₂ (mg/l)	X ₂	400	800	1600
Temperature (°C)	X ₃	45	55	70
Reaction time (min)	X ₄	10	30	60

The levels of all four variables were chosen with respect to feasible industrial conditions. For this reason, due to the maximum chemical costs allowed, the highest usable limits for iron (Fe²⁺) and hydrogen peroxide (H₂O₂) concentrations were set at 28 mg/l and 1600 mg/l, respectively. The temperature range (45-70°C) was selected based on the common circumstances within the bleaching process. A reasonable reaction time range was considered to be between 10 and 60 min.

The oxidation experiments of the effluent mixture (D₀ plus E₁; about 300 ml and 200 ml, respectively) were conducted in an Erlenmeyer flask equipped with on-line monitoring of temperature, pH and redox potential. The flask was heated (1.2 °C/min) in a water bath and the solution was continuously stirred (~300 rpm) with a magnetic bar. A predetermined amount (Table 1) of the Fenton's reagent was added to start the reaction when the desired temperature was reached. Redox potential was monitored using a Mettler Toledo 320 meter (with an electrode MC3051Pt) and pH was monitored with an Orion model 410A (with an electrode Mettler Toledo Inlab® 418) meter. Prior to chemical analyses (AOX and chlorinated low-molecular-mass monoaromatics), the samples were stored in a freezer at -18°C.

Analytical determinations

A simplified scheme of the experiments including the analytical determination needed is presented in Fig 1. In each determination two parallel measurements were made and the results were calculated as an average value of these determinations.

According to the practice generally used (Järnefelt 2007; Lehtimaa et al. 2010), 1 M sodium hydroxide (NaOH) was first added to the effluent sample (50 ml) until a pH level of 12.0 ± 0.2 was reached. Subsequently, 0.5 ml of 1 M sodium sulphite (Na₂SO₃) was added and the sample solution was allowed to react at room temperature for 10 min. At the end of the reaction, the sample solution was made acidic (pH <2) with concentrated nitric acid (HNO₃) and then diluted to a known constant volume. The stable AOX determinations (SFS EN 1485) for these pre-treated effluent samples were made by Oy Keskuslaboratorio-Centrallaboratorium Ab (KCL, Espoo, Finland). Once the total AOX contents were determined (EN-ISO 9562:2004), the unstable AOX contents could be calculated as the difference.

The chlorinated phenols, catechols and guaiacols were quantitatively determined by the Institute for Environmental Research (YMTK, Jyväskylä, Finland). In

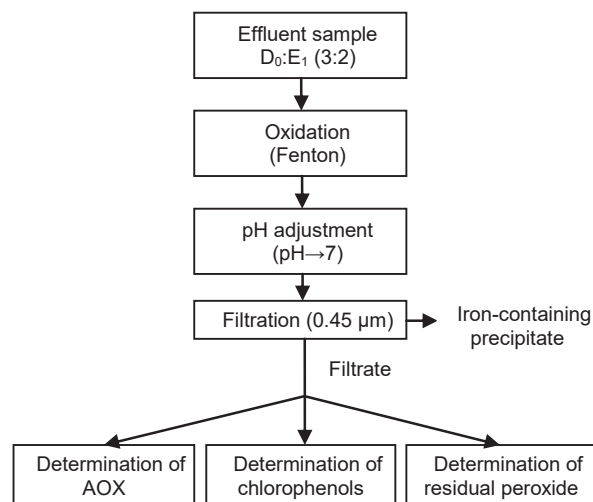


Fig 1. Scheme of the sample treatments and analyses.

these determinations (Mäntykoski 2006), for the GC/ECD (electron capture detection) analysis, the chlorinated compounds were first acetylated by adding acetic acid anhydride to the sample and by shaking at room temperature for about five minutes. A known amount of 2,3,6-trichlorophenol was also added as an internal standard prior to acetylation. The sample was then made 0.1 M with respect to potassium carbonate and was well agitated.

The determination of the H₂O₂ concentration in the Fenton's reagent-treated samples (as "residual H₂O₂") and the commercial H₂O₂ reagent was based on the reaction of H₂O₂ with excess iodide in the presence of an ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O) catalyst. This reaction stoichiometrically produced triiodide ions which were then determined titrimetrically with a standard sodium thiosulphate (Na₂S₂O₃) solution. In this method, 4 ml of 1 M sulphuric acid (H₂SO₄) and 10 ml of potassium iodide (KI) were added to the sample (25 ml) in a 150 ml Erlenmeyer flask and the solution was left to stand for 5 min. Then 50 ml of UHQ water and 80 μl of colour agent (prepared by dissolving 0.10 g (NH₄)₆Mo₇O₂₄·4H₂O in 250 ml H₂O) were added and the solution was immediately titrated with 0.05 M Na₂S₂O₃ solution until the dark brown triiodide colour was reduced to a yellow hue. Finally, 1 ml of a starch indicator solution (5 g starch/1000 ml H₂O) was added and the titration was continued until the blue colour of the solution became colourless. The residual H₂O₂ (RHP, g/l) was calculated by the Eq 4:

$$RHP = \frac{E \cdot c \cdot V}{SV} \quad [4]$$

where *E* is the mass equivalent of H₂O₂ (17.007 g/mol), *c* is the molarity of Na₂S₂O₃ solution, *V* is the consumption of the Na₂S₂O₃ solution (ml) and *SV* is the sample volume (ml).

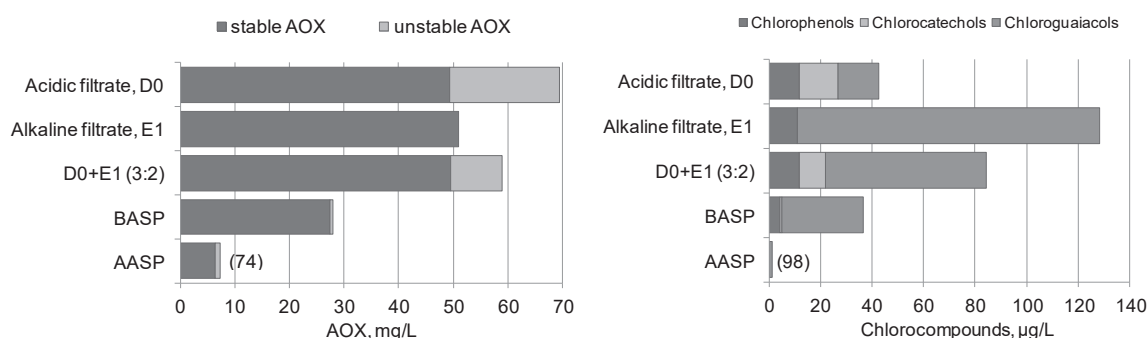


Fig 2. Concentrations of stable and unstable AOX and chlorinated low-molecular-mass aromatics in the effluent samples. The numbers in parentheses indicate the reduction %. BASP and AASP refer to “before activated sludge plant” and “after activated sludge plant”.

Results and Discussion

AOX in the reference effluents

Due to the high concentrations of AOX and chlorinated LMM aromatics in the effluents D₀ and E₁ (Fig 2), it was determined that the best approach was to apply the oxidative treatment directly to these effluents before their dilution by other bleaching effluents (with lower concentration levels of AOX). In this case, the most frugal way to obtain a pH of 4 for oxidation was to mix an acidic (D₀) and alkaline (E₁) bleach filtrate in a proper volume ratio (3:2). This ratio also roughly corresponded to their actual flow rate ratio. After mixing, the approximate values of AOX and chlorinated LMM aromatics in this “synthetic effluent” were 59 mg/l and 84 µg/l (Figs 2 and 3), respectively. In addition, it was noted that a major part of these chlorinated aromatics belonged to chloroguaiacols.

The total reduction of AOX and LMM chlorinated aromatics (cf., BASP vs. AASP in Fig 2) from the mill’s bleaching effluent (the bleaching sequence D₀E₁D₁E₂D₂) in the activated sludge plant without the Fenton treatment was 74% (AOX in AASP was about 7 mg/l) and 98% (chlorocompounds in AASP was about 1.5 µg/l), respectively.

Oxidation experiments

Fig 3 shows the AOX reductions in the oxidation experiments based on the Taguchi L9 matrix (Tables 1 and 2). It could be seen that, with one exception (the combination 10(X₁)-400(X₂)-45(X₃)-10(X₄) performed under the “mildest” condition), the reduction values were above 37%. In all cases, at 70°C (i.e., 10-1600-70-60, 20-800-70-10 and 28-400-70-30), the reduction values were about 55%. The corresponding values for various chlorocompounds under these conditions were 88%, 80% and 65%, respectively. In addition to the combination 10-1600-70-60 (88%), the highest reduction values were obtained in cases 28-800-45-60 (84%) and 28-1600-55-10 (89%), where the maximum amount of Fe²⁺ (28 mg/l) with a high amount of H₂O₂ (800 mg/l or 1600 mg/l) were used.

The relative mass proportions of the different LMM chloroaromatics (i.e., chlorophenols, chlorocatechols and chloroguaiacols) in the different effluents after oxidation

are presented in Fig 4. The mutual degradation rates of these chlorinated compound groups seemed to be similar. However, in the case of 28-400-70-30, a relatively low reduction (65%) as well as a high relative mass proportion of chlorocatechols (47% vs. 3-23% detected for other oxidations) indicated that, due to an unfavourable Fe²⁺/H₂O₂ ratio (i.e., a high Fe²⁺ and low H₂O₂), the redox potential was not high enough to permit effective degradative oxidation of chlorocompounds. As a result, in this case an enhanced formation of various quinones and other undesired products were obtained from chlorocatechols, rather than the desired degradation products (Chamarro et al. 2001). This could be also seen from the quinones-derived brown colour of the oxidised effluent and an intensive decrease in redox potential (425 mV→175 mV, normally between 400 mV and 475 mV during oxidation) along with the progress of reaction. In this case (28-400-70-30), the residual peroxide was about 10% of the initial H₂O₂ charge, whereas for other combinations it was 52-91% of the initial.

This finding suggested that H₂O₂ is the main influence on degradation effectiveness and Fe²⁺ on reaction kinetics. In addition, the combination 28-400-70-30 will interfere with the Taguchi prediction, if only the formation of chlorocatechols is considered.

Taguchi considerations

The Taguchi calculations, based on the analysis of various combinations, suggested (Fig 5) that the most intensive decrease in the mean value of total AOX could be obtained at “level 3”, where all the factors were the

Table 2. Experimental design matrix L9 (3⁴) and the measured responses

Sample	Design matrix				AOX (mg/l)		
	Factors				Measurement		Mean
	X ₁	X ₂	X ₃	X ₄	1	2	
10-400-45-10	1	1	1	1	44.8	45.7	45.3
10-800-55-30	1	2	2	2	37.8	36.4	37.1
10-1600-70-60	1	3	3	3	28.8	24.4	26.6
20-400-55-60	2	1	2	3	34.6	35.2	34.9
20-800-70-10	2	2	3	1	24.8	26.5	25.7
20-1600-45-30	2	3	1	2	30.1	31.6	30.9
28-400-70-30	3	1	3	2	26.5	27.8	27.2
28-800-45-60	3	2	1	3	28.0	32.1	30.1
28-1600-55-30	3	3	2	1	28.1	32.7	30.4

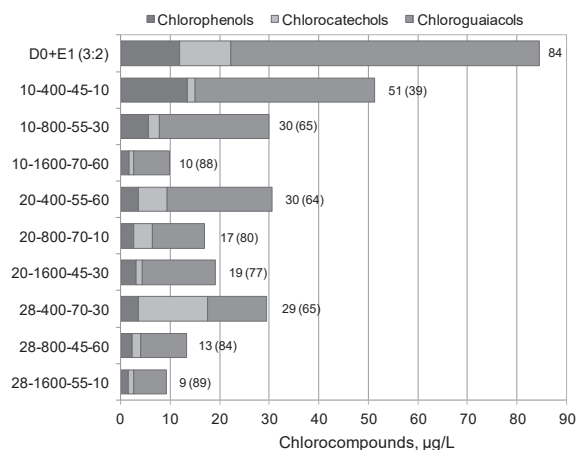
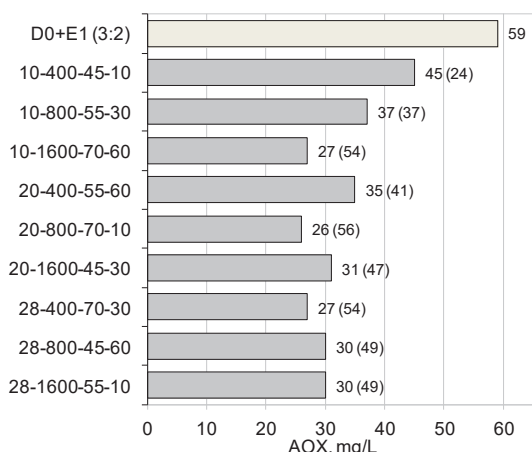


Fig 3. Taguchi experiments of total AOX (left) and chlorocompounds (right). The measurement uncertainty is ±10%. The numbers in parentheses refer to the reduction %.

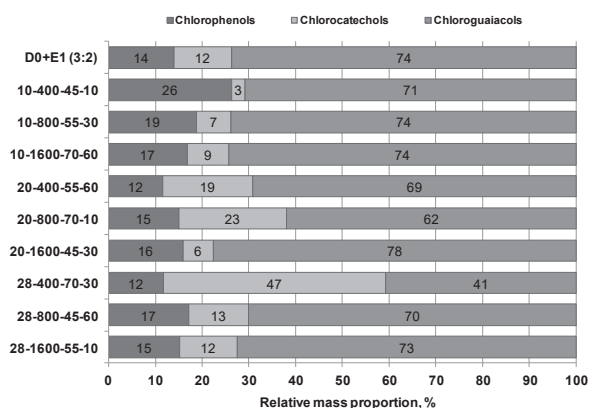


Fig 4. Relative mass proportions of chlorinated LMM aromatics in the effluents after oxidation (see Fig 3).

highest (Table 1). In addition, the significance of these factors decreased in the following order (according to the Taguchi-calculated response values): temperature (X_3), Fe^{2+} charge (X_1), H_2O_2 charge (X_2) and reaction time (X_4). For this reason, variations in temperature within the selected range were the most important impact on the AOX reduction, while those in reaction time were the most insignificant.

The confirmation tests (Fig 6) indicated that, as predicted, the most significant decrease in AOX was obtained with the combination 28-1600-70-60. The predicted values were similar to those found in the supplementary experiments, especially at the highest Fe^{2+} charge (28 mg/l) and at a high H_2O_2 charge (800 mg/l or 1600 mg/l). The effect of the same combinations on the degradation of chlorinated LMM aromatics is given in Fig 7. In the case of 28-1600-70-60 practically all of the residual compounds with low concentrations (about 0.2 µg/l) were chlorophenols. It could be estimated that when applying the Fenton treatment to an effluent mixture of D_0 and E_1 , the AOX emissions would be about half of the initial level.

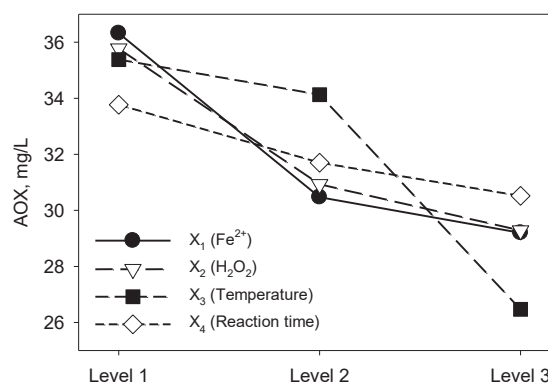


Fig 5. Factor contribution graph of total AOX. For levels, see Table 1.

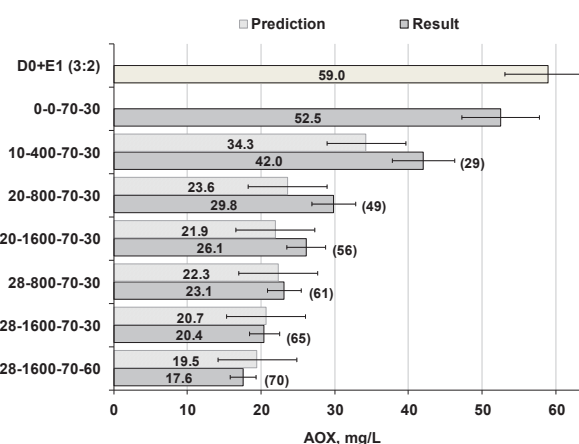


Fig 6. Confirmation tests for total AOX concentrations. For each bar, the line segment describes a measurement uncertainty of ±10%. Prediction level at a confidence level of 95% is ±5.4%. The numbers in parentheses indicate the reduction %.

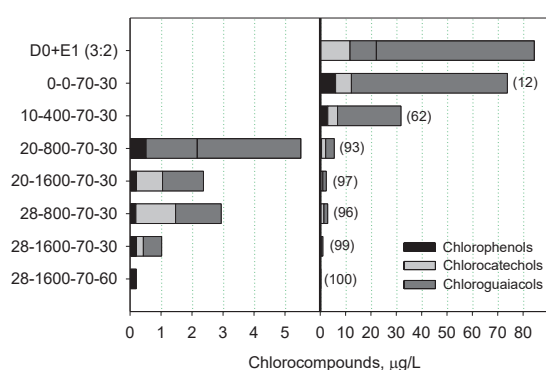


Fig 7. Confirmation tests for chlorinated LMM aromatics. The numbers in parentheses indicate the reduction %.

Conclusions

The results indicated that the Taguchi method was suitable for designing L9 (3^4) matrix experiments to predict oxidative conditions when applying the Fenton method (H_2O_2 - $FeSO_4$) to softwood-based kraft mill bleaching effluents. However, due to practical limitations, only a narrow variation range of each factor could be used. To obtain more accurate determination values for this design method, one element of uncertainty that should be considered is the possible non-homogeneity of the full-scale bleach effluent samples. The general aim of this study was to clarify the influence of each variable of interest on a decrease in AOX, rather than to determine one optimal combination of these variables. In addition, it was noted that the most reasonable approach was to oxidise the mixture of an acidic (D_0) and alkaline (E_1) bleach filtrate with the highest AOX loads in a 3:2 ratio, which resulted in a the suitable pH level of 4 for this oxidative treatment. The most important findings were as follows:

1. Temperature had the most significant effect on AOX reduction.
2. The H_2O_2 charge had the most significant effect on decreasing chlorinated LMM aromatics.
3. Under the “severest reaction condition” (according to the experimental tests — i.e., 28 mg Fe^{2+} /l-1600 mg H_2O_2 /l-70°C-60 min) the AOX reduction was about 70% (corresponding to about 50% for the mill) and the simultaneous reduction of LMM chlorinated aromatics was almost 100%.
4. At the “mildest reaction condition at 70°C” (according to the confirmation tests — i.e., 10 mg Fe^{2+} /l-400 mg H_2O_2 /l-70°C-30 min) the reduction of AOX and chlorinated LMM aromatics was 29% and 62%, respectively.

Acknowledgements

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IV

TOTAL SULPHUR CONTENT OF DITHIONITE-BLEACHED PULP

by

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TOTAL SULPHUR CONTENT OF DITHIONITE-BLEACHED PULP

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The amount of sulphur covalently bound to pulp during dithionite bleaching was determined by means of an energy-dispersive X-ray fluorescence (EDXRF) spectrometer. The method was first calibrated with thermomechanical pulps (TMPs) having a wide range of sulphur concentration (40 - 5900 mg sulphur/kg pulp) and then applied to the determination of total sulphur content in industrial-based washed TMPs (dithionite dosage <1.0% on pulp and sulphur content <700 mg/kg pulp), recycled fibre pulps (deinked pulps; dithionite dosage <0.6% on pulp and sulphur content <600 mg/kg pulp), chemithermomechanical pulps – CTMPs, sulphur content <5000 mg/kg pulp. Finally, the correlations between dithionite dosage and sulphur content and, on the other hand, between dithionite dosage and brightness gain were briefly discussed.

Keywords: sulphur, thermomechanical pulp, X-ray fluorescence spectroscopy, bleaching, dithionite

INTRODUCTION

The determination of sulphur or sulphur-containing anions (especially oxyanions) is important for many practical purposes within the pulp and paper industry. Knowledge of the quantitative sulphur balance and of the migration of different anions is needed when evaluating the efficiency of brownstock washing and the recovery of cooking chemicals in kraft pulping¹⁻⁴ or when clarifying the chemistry of sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$, “hydrosulphite”) bleaching of mechanical pulps.⁵⁻⁷ For example, the reactions of different sulphur-containing anions, formed readily from sodium dithionite during bleaching, with different chromophores of lignin in high yield pulps have not been fully explained.⁸ However, it has been suggested⁹ that chemically bound sulphur (possibly in the form of sulphonic acid groups $-\text{SO}_3\text{H}$) plays an important role, especially in the stabilisation of the brightness reversion of these pulps. For this reason, it is reasonable to conclude that for practical purposes, an efficient method for determining the total amount of sulphur in dithionite-bleached mechanical pulps will be of benefit to the further development of this lignin-preserving bleaching process.

Our previous experiments¹⁰ focused on the determination of total sulphur content in spent liquor (black liquor) after kraft cooking by energy dispersive X-ray fluorescence (EDXRF). This technique, with its high sensitivity and good inherent precision, is used widely to measure quantitatively the elemental composition of solid and liquid materials, since each element has different characteristic fluorescent X-ray energy lines.¹¹⁻¹³ This study reports on the determination of total sulphur content, mainly in thermomechanical pulp (TMP) bleached with $\text{Na}_2\text{S}_2\text{O}_4$ by means of an EDXRF spectrometer. The results were compared to those obtained by the existing conventional method (*i.e.*, Schöniger combustion method/ion chromatographic (IC) analysis described in SCAN-CM 57:99) which, as judged from the expected sulphur balance in many practical applications, seemed to result in somewhat too low amounts of sulphur.

The basic idea of using an EDXRF spectrometer for the determination of total sulphur content in sulphonated chemimechanical pulp (SCMP with an average sulphur content of about 0.5%) has been earlier realised by Rivington¹⁴ who developed a use-

ful method for this purpose. However, in our case a more accurate method was needed (*i.e.*, we used a mini X-ray tube as a radiation source instead of a gamma-ray emitting iron-55 radioactive excitation source¹⁴) since we studied, in addition to high sulphur-containing chemithermomechanical pulps (CTMPs with an average sulphur content of about 0.3%), for example, also low sulphur-containing TMPs with an average sulphur content of about 0.05%. In our forthcoming studies, different sulphur-containing anions in black liquors and bleaching effluents from the dithionite bleaching will be determined in detail by IC.

EXPERIMENTAL

Pulps

Thermomechanical pulp ("basic TMP") was obtained from the full-scale refining stage prior to washing and bleaching and consisted of Norway spruce (*Picea abies*). For the preparation of the sulphur-containing pulp standards (*i.e.*, "basic TMP" was used as a matrix), an aliquot quantity of this TMP (67 g (o.d.)) was washed with ultrapure water (UHQ-water) by diluting to a volume of 2 L. The mixture was kept in a beaker overnight, pressed through a plastic wire and the dry pulp obtained by compression was washed two times with excess of UHQ-water. The pulp sample was

then filtered and centrifuged to a dry matter content of 30–40%. The primary drying was performed by first keeping the pulp sample in an oven at 50 °C for one hour and then storing at room temperature for 4 days. Finally, the air-dried pulp (59 g, dry solids content 92–94%) was milled in a Cyclotec 1093 sample mill.

Industrial-bleached TMP samples and RCF (recycled fibre) pulp samples together with CTMP samples and their fractions, all with various sulphur contents, were used as examples of different pulps for testing the method of determination described in this paper. For these tests, the samples were prepared in a same way as the "basic TMP" (*e.g.*, the samples were analysed after washing). For all pulps, brightness was measured with a Minolta Spectrophotometer CM-3700d.

Sulphur-containing pulp standards

Pulp standards with a gradient in sulphate content were made as follows. Fifteen standard solutions of sodium sulphate (Table 1) were first thoroughly mixed with the "basic TMP". The mixtures obtained were allowed to stay overnight at room temperature and were then dried in a laboratory oven at 80 °C for 1.5 hours. The dried and cooled pulp standards were finally homogenised with an electric rod mixer and were moisture-stabilised overnight by storing at room temperature (atmospheric humidity).

Table 1
Aqueous solutions of sodium sulphate for the preparation of the sulphur-containing pulp standards^a

Sample	Concentration ^b (g/L)	Pulp pellet	
		Amount (g)	Dry solids content (%)
Reference ^c	-	1.422	93.2
1	0.36	1.417	92.2
2	0.71	1.416	93.9
3	1.42	1.419	92.5
4	2.13	1.425	92.7
5	2.84	1.419	93.0
6	3.55	1.420	93.9
7 ^d	4.26	1.423	93.7
8	4.97	1.427	93.8
9	5.68	1.427	93.1
10	6.39	1.428	93.7
11 ^d	7.10	1.424	93.1
12	8.52	1.432	93.7
13	9.94	1.423	92.6
14	11.36	1.432	93.7
15	12.78	1.426	93.3

^a Pulp standards were used in the form of pressed pellets for the EDXRF measurements

^b In preparation of each standard, the initial amount of Na₂SO₄ solution and pulp was 0.25 L and 3.5 g (o.d.), respectively

^c The initial sulphur content of the reference sample was 40 mg sulphur/kg pulp

^d Used only for the Schöniger test

For the EDXRF determinations, equally-sized pulp pellets (diameter 25 mm) consisting of about 1.4 g of the milled pulp (Table 1) were prepared by pressing each pulp preparation for 5 minutes at a pressure of 10-11 tons in a custom-made pellet maker. The dry matter content of the pellets was measured with a Denver Instrument IR-200 moisture meter. The actual concentration of sulphur in the pulp pellets was checked separately. In this procedure, the pellet was dissolved in UHQ-water and, after separating the pulp phase by filtration, the total sulphur in the liquid phase content was measured (*i. e.*, based on the determination of SO_4^{2-} anions by IC). The sulphur content of the washed pulps was checked by EDXRF, resulting in all cases in spectra similar to those obtained for the "basic TMP". In addition, a series of Schöniger combustions (see below) was conducted to determine the amount of sulphur in the "basic TMP" (*i. e.*, 40 mg sulphur/kg pulp).

EDXRF method

Four empirical calibrations, within the limits of the concentration range 0.04-0.9, 0.9-2.5, 2.3-4.0 and 3.7-5.9 g sulphur/kg pulp, were developed for the determination of the total sulphur content in TMP, by means of the sulphur-containing pulp standards, using a Metorex X-MET 920XRT analyser (Oxford Instruments Analytical Ltd., High Wycombe, Bucks, UK). The analyser contained a mini X-ray tube as a radiation source (target material Cu), a titanium filter and a gas-filled proportional counter detector. All the EDXRF determinations were performed by placing the sample pellet on a thin Mylar film (2.5 μm) in a teflon-made sample cup. The measurement was made under helium atmosphere and the measurement time used was 300 s. Due to the nonhomogeneous distribution of fine particles within the sample pellets, they were analysed on both sides and the calculated mean value was used. An example of the X-ray intensity spectra obtained is given in Figure 1.

The calibration equations within each concentration range (Fig. 2) were based on the least squares fit regression analysis and were obtained automatically from the instrument after defining the regression terms. The intensities of sulphur (S) and backscattering (BS) were defined for all four calibrations, and the instrument calculated the factors used to multiply the gross count rates in their measurement windows to obtain the corresponding net count rates ("real amounts") for each calibration. In all cases, however, the "BS terms" were negligible compared to the other terms and were excluded. The complete equations (*i. e.*, sulphur content C_s) in increasing order of sulphur content for the four concentration ranges were as follows:

$$C_s = 93.7 + 4.79 \times S \quad (1)$$

$$(r=1.000, A \text{ in Fig. 2})$$

$$C_s = 5.99 + 5.45 \times S \quad (2)$$

$$(r=0.999, B \text{ in Fig. 2})$$

$$C_s = 88.5 + 5.25 \times S \quad (3)$$

$$(r=0.999, C \text{ in Fig. 2})$$

$$C_s = -774 + 6.51 \times S \quad (4)$$

$$(r=0.995, D \text{ in Fig. 2})$$

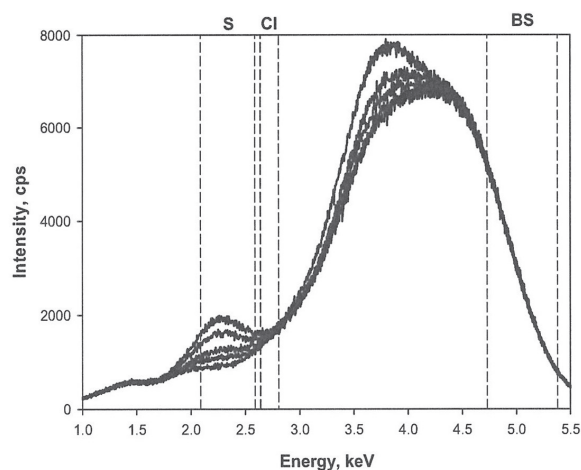


Figure 1: Example of the X-ray intensity spectra (counts per seconds, cps) of the five sample tablets within the concentration range 0.04-0.9 g sulphur/kg pulp. Symbols S, Cl and BS refer to the measurement windows for sulphur, chlorine and backscatter, respectively

The standardized residuals for the calibration lines are given in Figure 3. Σ is the residual divided by the standard error of estimate.¹⁵ It is essentially the standard deviation of the residuals, and is a measure of the variability around the regression line. Since the 95% confidence interval is within ± 2 of the average value (*i. e.*, the suggested value for deletion is more than ± 3), all the values obtained in this study were below this level and thus the calibration seemed to be successful.

IC method

A Dionex (Sunnyvale, CA, USA) model 4500i ion chromatograph equipped with a quaternary gradient pump module (GPM), an anion self-regenerating suppressor (ASRS I) and a pulsed electrochemical detector (PED-2) in conductivity mode, or conductivity detector (CDM-1) was used for the quantitative sulphate analyses. Chromatographic conditions were based on those described by the manufacturer, application notes and column manual.¹⁶ The columns used were AS11 - HC (analytical) and AG11 - HC (guard column), and an alkaline solution (60 mmol NaOH/L UHQ-water) was used as an eluent. For the IC calibration, a standard sulphate solution (1000 mg SO_4^{2-} /L UHQ-water) was first prepared

and then a portion of this stock solution was further diluted to the desired range of concentrations.

Schöniger combustion

A sample pellet was combusted with oxygen in the presence of hydrogen peroxide (SCAN-CM 57:99). In our study, the method was modified, with respect to the chemicals used, to correspond to an initial sample amount of 200 mg. The sulphur-containing compounds were converted during this treatment into sulphate anions, which were then determined quantitatively by IC.

RESULTS AND DISCUSSION

Results of the determinations carried out with the different analytical methods (EDXRF vs. Schöniger) for all the sulphur-containing pulp standards (Table 1 and Fig. 2) are shown in Figure 4.

In all cases, the values obtained by the Schöniger method were about 20% lower (at high sulphur concentrations >1 g/kg pulp) than those obtained by EDXRF; the reason for this discrepancy was not clear.

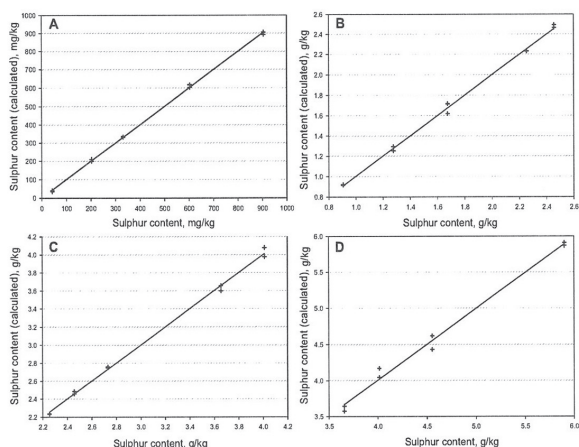


Figure 2: The sulphur content of the standard pulp samples (“sample pellets”, actual values) predicted by the EDXRF determination (calculated values). The standard error of prediction was about 1%. In each case, two measurements (upper and lower sides of the sample pellet) were made. The limits of the sulphur contents: A) 0.04-0.9, B) 0.9-2.5, C) 2.3-4.0 and D) 3.7-5.9 g sulphur/kg pulp

In the Schöniger method organically-bound sulphur is converted into sulphate anions which can then be determined by various methods, especially by IC.¹ Although this very sensitive and versatile technique is much simpler and faster for small samples than the conventional gravimetric method, it

can still be considered a rather laborious analytical method, requiring a high level of skill in practice.

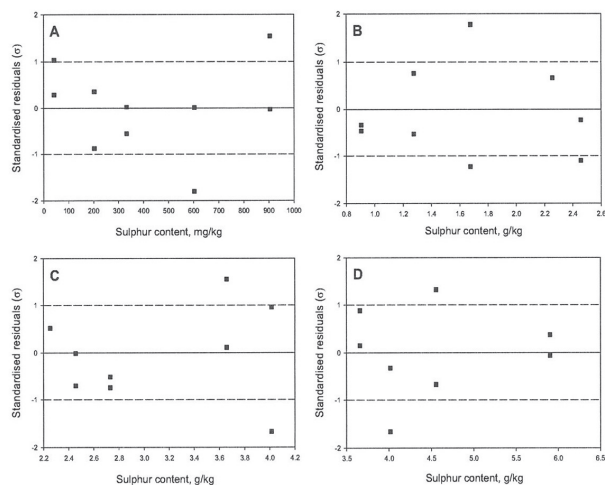


Figure 3: Concentration vs. standardized residual for the sulphur-containing pulp standards (see Fig. 2). Limits of sulphur content: A) 0.04-0.9, B) 0.9-2.5, C) 2.3-4.0 and D) 3.7-5.9 g sulphur/kg pulp

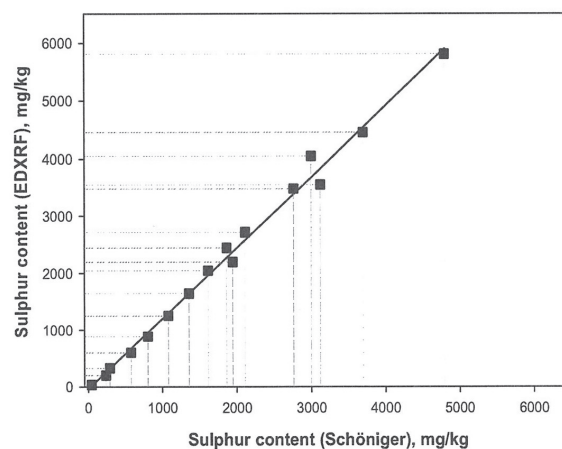


Figure 4: Comparison of the EDXRF and Schöniger methods in the determination of sulphur content in the sulphur-containing pulp standards

In addition, it has been reported that any departure from the standardized procedure, as well as other factors, may affect the final result. In our case, the main reasons, as is generally the case, for the lower values obtained by the Schöniger combustion/IC method were probably incomplete burning and oxidation together with losses in volatile sulphur compounds from the sample during the procedure. However, it should be pointed

out that, owing to the thoroughness of the procedure used here to check the actual sulphur content in the sulphur-containing pulp standards prepared, it is unlikely that the values obtained by EDXRF were too high.

Table 2
Sulphur content (mg/kg pulp) of dithionite-bleached TMP and RCF pulps manufactured with varying dithionite charges (% on pulp)

TMP		RCF pulp	
Dithionite charge	Sulphur content	Dithionite charge	Sulphur content
-	42	-	270
0.20	117	0.20	369
0.40	367	0.40	456
0.71	369	0.60	593
0.84	608		
0.92	566		

In the next phase of this study, the developed EDXRF method was applied to six TMP and four RCF pulp samples which all had a sulphur content of <1 g/kg pulp and were manufactured with a dithionite dosage of <0.92% (TMPs) or <0.60% (RCF pulps) on pulp (Table 2). The total content of sulphur in pulp (after washing) and brightness improvement (brightness gain was for TMP and RCF pulp samples → 8.8% and → 4.6%, respectively) that accompanied the addition of dithionite seemed to be a rather linear function of dithionite charge. Thus, within a dithionite charge range studied, for example, a high sulphur content of pulp generally meant a high brightness value. In our separate experiments, some TMP samples were not washed prior to their analysis and for this reason it was also possible to estimate the actual amounts of chemically - bound and total entrained sulphur in these pulps. The results indicated that 70-90% of the total sulphur detected (estimated to be <10% of the total sulphur charged) was chemically bound (*e.g.*, probably in the form of sulphonate acid groups) to pulp.

Finally, to test further for the applicability of the method, we selected two CTMP samples with a higher average amount of sulphur (*i.e.*, <5 g sulphur/kg pulp) than that present in TMP (Table 3).

These samples originated from the first and second refining stage (in the latter stage the amount of sulphonating chemicals was

higher than in the former case) of a full-scale process and both of them had also been fractionated with a Bauer McNett apparatus.

Table 3
Total sulphur content (g/kg) of chemithermo-mechanical pulp samples and their fractions

Fraction (Bauer McNett) mesh	Sample #1 ^a	Sample #2 ^b
< 28	0.38	2.7
28 < 48	0.42	2.9
48 < 100	0.44	3.0
100 < 200	0.53	3.1
200 <	0.63	3.7
Initial CTMP	0.45	3.1

^a From the first refining stage

^b From the second refining stage

In general, it is known that a chemical pulp contains a smaller proportion of fines (*i.e.*, the fraction passing through the 200-mesh screen) than a mechanical pulp and that the lignin-rich fines primarily originate from the middle lamella and primary layers of the fibre wall.^{17,18} In addition, fines have an average relative surface area several times larger than that of the initial fibre fraction. Thus, it was obvious that, also in our case, an increasing trend in the sulphur content was detected, probably due to an increase in the content of lignin and in the relative surface area, along with the decrease in particle size.

CONCLUSIONS

In this study, the sulphur content of industrial-based pulps with different origin was determined with reasonable accuracy and reproducibility by an EDXRF method. Compared to other known methods used for this purpose, the main benefits of the EDXRF method are simplicity of use, stability of calibration and rapidity of measurement. In addition, there is virtually no sample pretreatment, which means that in practice the method is operator-independent and that reliable results can be obtained across a wide range of sulphur concentrations. Furthermore, the results indicated that only less than 10% of the total sulphur charged in dithionite bleaching is chemically bound to TMP and the sulphur content in pulp has almost a linear effect on its brightness.

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V

DETERMINATION OF THE TOTAL SULFUR CONTENT IN BLACK
LIQUOR BY X-RAY FLUORESCENCE

by

Jarmo Louhelainen, Raimo Alén and Jukka Pekka Isoaho, 2005

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Determination of the Total Sulphur Content in Black Liquor by X-Ray Fluorescence

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The general methods for determining the total sulphur content of black liquor include ion chromatographic, titrimetric and gravimetric analyses. A common prerequisite for these methods is the need to oxidize the various sulphur-containing compounds, e.g., sulphide, thiosulphate, sulphite, polysulphides and sulphur-containing organics to sulphate prior to performing the measurements. In this study, a method for analyzing the total sulphur content of black liquors without any preoxidation by means of an energy-dispersive X-ray fluorescence (EDXRF) spectrometer was developed. This method was evaluated by comparing the results with those obtained by other known methods. Simplicity of use, absence of the need for multistage sample treatment, stability of calibration and rapidity of measurement were considered to be the major benefits of the EDXRF method.

Les méthodes générales pour déterminer la teneur en soufre total de la liqueur noire comprennent entre autres la chromatographie d'échanges d'ions, la titrimétrie, et la gravimétrie. L'une des conditions préalables à ces méthodes est l'oxydation de divers composés soufrés (par ex., le sulfure, le thiosulfate, le sulfite, les polysulfures, les matières organiques soufrées) en sulfate avant de procéder à la détermination. Dans la présente étude, nous avons développé une méthode d'analyse de la teneur en soufre total des liqueurs noires au moyen d'un spectromètre à fluorescence X à dispersion d'énergie (EDXRF), méthode qui n'exige aucune pré-oxydation. Cette méthode a été évaluée en comparant les présents résultats avec ceux obtenus à l'aide d'autres méthodes connues. Les principaux avantages offerts par cette méthode sont l'élimination du besoin de l'échantillonnage en plusieurs étapes, la stabilité de l'étalonnage, et la rapidité de la détermination.

INTRODUCTION

The main active cooking chemicals in the aqueous cooking liquor (white liquor) used in kraft pulping are sodium hydroxide (NaOH) and sodium sulphide (Na₂S). The charged alkali is consumed almost entirely during pulping to neutralize the aliphatic carboxylic acids and the lignin degradation products [1]. It is also known that hydrosulphide ions (HS⁻) react primarily with lignin, whereas carbohydrate reactions are affected by alkalinity only (i.e., HO⁻ ions) [2]. With respect to the sulphur-containing inorganic compounds, the spent liquor (black liquor) after pulping contains, besides the residual Na₂S, sodium thiosulphate (Na₂S₂O₃), sodium sulphite (Na₂SO₃), sodium sulphate (Na₂SO₄) and polysulphides (Na₂S_x). In addition, part of the sulphur originating from Na₂S is bound to the degraded lignin fragments (1–3% of the dry solids) and sulphur-contain-

ing volatile products such as hydrogen sulphide (H₂S), methyl mercaptan (CH₃SH), dimethyl sulphide (CH₃SCH₃) and dimethyl disulphide (CH₃SSCH₃) are formed as well.

Data on the total sulphur content of black liquor and fibre product are important for many practical purposes including, for example, evaluating the efficiency of brownstock washing [3]. The quantitative sulphur and sodium balances of the kraft mill are also useful for understanding the behaviour of these elements during the process [4]. In particular, knowledge of the behaviour of sulphur-containing compounds during the heat treatment, evaporation and combustion of black liquor is needed to make various calculations regarding the balance of materials and energy [5,6]. In general, due to the current trend towards closed process circulations, with the objective of decreasing environmentally harmful emissions, sulphur discharges have clearly decreased while, e.g., the average sulphidity level of white liquor in kraft mills has gradually increased.

There are several alternative methods of determining the total sulphur content of black liquor. These include ion chromatographic (IC), titrimetric and gravimetric analyses [3,7–9]. The prerequisite for these methods is

usually the need to oxidize various sulphur compounds to sulphate prior to performing the measurements. However, preoxidation of sulphur compounds is not needed for methods based on capillary electrophoresis (CE) [10,11] and elemental analysis [12]. It should be pointed out that the CE methods, as well as the IC method described by Easty et al. [13], have been developed primarily for the purpose of analyzing different sulphur-containing anions in black liquor rather than determining its total sulphur content.

X-ray fluorescence (XRF), with its high sensitivity and good inherent precision, is used widely to measure quantitatively the elemental composition of solid and liquid materials, since each element has different characteristic fluorescent X-ray energy lines [14–16]. Thus, XRF spectrometry is a simple method based on the detection of X-ray radiation that is emitted from the sample bombarded first with X-rays. An XRF instrument typically consists of an excitation source or, practically, an X-ray tube that creates an incident X-ray (i.e., an electron of a particular element is ejected from a low energy level leaving a vacancy) and a detection system (i.e., an electron from a higher energy level of this element falls into this space). The

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system measures an energy that is equal to the difference between these two energy levels and each element in the sample will fluoresce (or emit) a secondary X-ray. Then, the instrument software translates this information into the type and amount of each element present in the sample. For this reason, it was concluded that, as a fast and nondestructive analytical technique, XRF offers an alternative approach to determining the total sulphur content of black liquor. Currently, three basic types of XRF spectrometers are available commercially: wavelength dispersive, energy dispersive and nondispersive.

The study reported here had two main objectives. Firstly, to develop a rapid method for determining the total sulphur content of black liquor by means of an energy-dispersive XRF (EDXRF) spectrometer and, secondly, to compare our new method with existing methods by conducting comparative analyses of the sulphur content of various industrial black liquors.

EXPERIMENTAL EDXRF Method

Three empirical calibrations were developed for the determination of the total sulphur content of black liquor using a Metorex (Oxford Instruments Analytical Ltd., High Wycombe, Bucks, UK) X-MET 920XRT analyzer. This EDXRF analyzer contained an X-ray tube as a radiation source (target material Cu), a titanium filter and a gas-filled proportional counter detector. One typical North American industrial kraft black liquor was used for preparing the first calibration curve (Cal 1) by analyzing gravimetrically the sulphur content of this liquor according to TAPPI T 625. Altogether, ten standard samples then were made by diluting this basic black liquor with water (Table I).

The other two calibrations were based on the soda black liquors from the laboratory-scale pulping of softwood and hardwood feedstocks (Cal 2 and Cal 3, respectively). The sulphur content of these liquors was first analyzed by an ion-coupled plasma atomic emission spectrometer (ICP-AES) and known amounts of a sulphur-containing salt (i.e., Na₂SO₄) then were

Calibration	Sulphur concentration of the standard, g/L									
	1	2	3	4	5	6	7	8	9	10
Cal 1	0.90	1.79	2.69	3.58	4.48	5.37	6.27	7.16	8.06	8.95
Cal 2	1.61	3.02	4.49	6.04	7.52	9.39	10.49	11.87	13.57	15.01
Cal 3	1.50	3.00	4.66	5.98	7.47	9.27	10.66	12.15	13.73	14.89

added to these liquors to obtain the standard samples (Table I). Na₂SO₄ was added so that the standard samples contained an equal amount of the original black liquor (90% by volume).

Both standards and black liquor samples were measured for 5 min after pipetting 10 mL of each properly diluted sample (1:1.25–10) separately into a sample cup and inserting this cup to a sample chamber.

Other Analytical Methods

The potentiometric titration method was performed using a lead-ion selective electrode (Orion 9482SC, Oriola Oy, Espoo, Finland) and a reference electrode using an automatic titrator (QC-Titrator, Man-Tech Associates, Guelph, ON, Canada) [7,9]. The black liquor samples were oxidized with 30% hydrogen peroxide (H₂O₂) prior to determination and 0.05 mol/L lead perchlorate (Pb(ClO₄)₂) solution was used as the titrant. The inflection point of the titration curve was determined using the Jandel Table Curve program, Systat Software Inc., Richmond, CA, USA.

The IC analysis was done according to Douek and Ing [3]. H₂O₂ was used to oxidize all the sulphur-containing compounds in the black liquors to sulphate as in the case of the potentiometric titration method. Sulphate was determined after diluting the samples with water (ratio ≈ 1:500) by a Dionex Model 4500i IC equipped with a conductivity detector CDM-1 as well as columns AS11-HC and AG11-HC. An amount of 0.06 mol/L NaOH solution was used as the eluent.

The gravimetric analysis was performed according to TAPPI T 625 [8]. The black liquor samples were oxidized with concentrated nitric

acid (HNO₃) and 70% perchloric acid (HClO₄). The sulphate obtained was precipitated with barium chloride (BaCl₂) as barium sulphate (BaSO₄). The BaSO₄ precipitate was ignited to a temperature of 800°C, cooled and weighed.

The ICP-AES method included black liquor oxidation with either concentrated HNO₃ or 30% H₂O₂ in a microwave oven (CEM Mars 5, CEM Corp., Matthews, NC, USA), dilution with water (ratio ≈ 1:700) and determination of sulphur at 181.975 nm (wavelengths of 180.669 and 182.563 nm were also tested) by a Perkin Elmer Optima 4300DV instrument.

Black Liquor Samples

A general comparison between the various methods of analysis was performed by determining the sulphur amount present with all these methods in a softwood kraft black liquor sample provided by Oy Metsä-Botnia Ab, Espoo, Finland.

A further validation of the EDXRF method was done with four black liquor samples (provided by UPM-Kymmene Corporation, Helsinki, Finland) from various stages of the evaporation plant. The sulphur content of these samples was determined by UPM-Kymmene Corporation with the method, including sample preoxidation in a Schöniger flask followed by the IC analysis [9].

An industrial kraft black liquor was used in testing varying measuring times (1–5 min) needed for the EDXRF method.

RESULTS AND DISCUSSION EDXRF Calibration

The gravimetric determination of sulphur in the industrial black liquor (from North America) was repeated five times with the

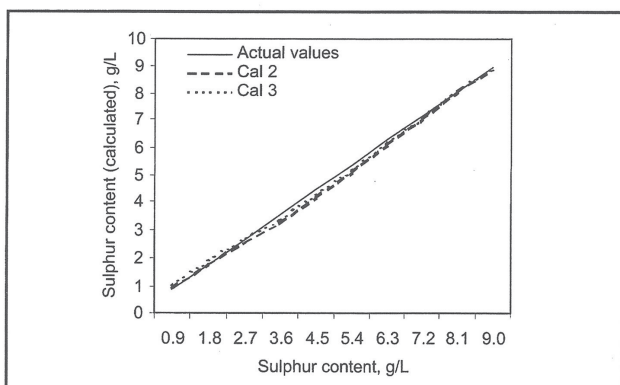


Fig. 1. The sulphur content of the standard samples of Cal 1 (actual values) predicted by Cal 2 and Cal 3 (calculated) in the EDXRF analysis. The standard error of prediction was 0.13 in both cases.

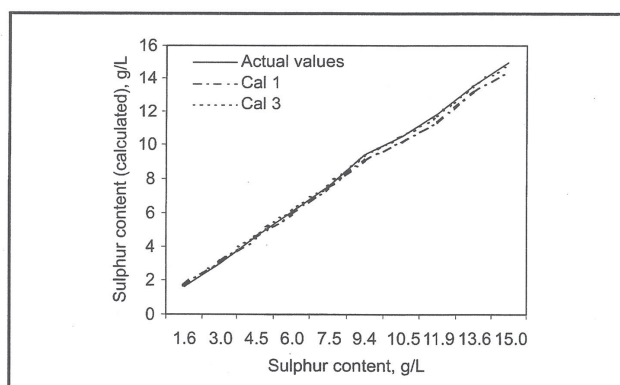


Fig. 2. The sulphur content of the standard samples of Cal 2 (actual values) predicted by Cal 1 and Cal 3 (calculated) in the EDXRF analysis. The standard error of prediction was 0.07 in both cases.

following results for sulphur content: 6.02, 5.94, 6.04, 6.09 and 5.86% of dry solids (mean 5.98, standard deviation 0.09). The sulphur contents in the softwood and hardwood soda black liquors (from laboratory-scale cooks) were very low: 0.05 and 0.03 g/L, respectively.

The calibration equations were based on the least-squares fit regression analysis and were obtained automatically from the instrument after defining the regression terms. The intensities of sulphur (*S*) and backscattering (*BS*) were defined for all three calibrations as the regression terms of the equation $aS + bS/BS$. The complete equations (i.e., sulphur content *C*) were:

$$C = 434 - 2.84 \times S + 8514 \times S/BS \quad (1)$$

($r = 0.9991$) Cal 1

$$C = 199 - 1.04 \times S + 5788 \times S/BS \quad (2)$$

($r = 0.9999$) Cal 2

$$C = 371 - 1.25 \times S + 5791 \times S/BS \quad (3)$$

($r = 0.9998$) Cal 3

For each calibration method, the sulphur content of the standard samples was calculated using the other calibration equations (Figs. 1–3). The predictive power of the calibrations was also checked in this way. The standard errors of prediction were low in all cases (Figs. 1–3), which suggested that, e.g., the black liquor matrix did not affect the results adversely.

In addition, it was observed that the calibrations worked across a large range of concentration. Cal 1 (Figs. 2,3) gave reasonably good results even for those reference samples (standards 6–10 of Cal 2 and Cal 3) not within the limits of its calibration range of 0.9–9.0 g/L.

A separate test of varying measuring times (Fig. 4) indicated that even a time of 1 min could be used in EDXRF for obtaining repeatable results (i.e., maximal values). Thus, it is worth mentioning that the EDXRF calibrations made were not sensitive to measuring time, although they all were made using a constant measuring time of 5 min.

Comparison of the Methods

Results of the determinations carried out with the different analysis methods are shown

TABLE II
SULPHUR CONTENT OF THE INDUSTRIAL SOFTWOOD KRAFT BLACK LIQUOR (FROM OY METSÄ-BOTNIA AB) DETERMINED BY THE VARIOUS ANALYTICAL METHODS

	Sulphur content, % of dry solids							
	Titration	Gravimetry	IC	ICP (H ₂ O ₂)	ICP (HNO ₃)	EDXRF (Cal 1)	EDXRF (Cal 2)	EDXRF (Cal 3)
			5.62			5.55	5.63	5.64
			5.60			5.56	5.67	5.68
	5.79	5.48	5.60	5.96	6.05	5.48	5.57	5.61
	5.82	5.33	5.78	6.07	6.02	5.57	5.67	5.71
	5.61	5.43	5.71	5.94	6.12	5.56	5.57	5.69
	5.66	5.51	5.69	5.95	6.09	5.53	5.56	5.67
Mean	5.72	5.44	5.67	5.98	6.07	5.54	5.61	5.67
Standard deviation	0.10	0.08	0.07	0.06	0.04	0.03	0.05	0.04

TABLE III
SULPHUR CONTENTS (g/kg) AND STANDARD DEVIATIONS IN THE DUPLICATE DETERMINATIONS OF BLACK LIQUORS (BLs 1–4) FROM THE VARIOUS STAGES OF EVAPORATION (FROM UPM-KYMMENE CORPORATION)

Method	BL 1		BL 2		BL 3		BL 4	
	Content	St. Dev.	Content	St. Dev.	Content	St. Dev.	Content	St. Dev.
EDXRF (Cal 1)	49.6	0.57	49.1	0.35	49.2	0.21	28.7	0.49
EDXRF (Cal 2)	50.1	0.64	49.5	0.28	49.5	0.28	27.7	0.49
EDXRF (Cal 3)	50.8	0.64	50.2	0.21	50.5	0.28	29.1	0.49
(Schöniger/IC)	51.3	2.12	50.9	2.62	50.1	6.29	26.3	0.64

in Table II. In all cases, except the ICP method, a relatively close similarity was observed. The ICP analysis was first performed using HNO₃ oxidation and, after comparing these results with those of the other methods, additional analyses were performed using H₂O₂ as the oxidant. In addition, the Na₂SO₄ standard solution was measured as such and after similar treatments with HNO₃ and H₂O₂ as in the case of the black liquor samples. The results for the standard measurements were accurate and independent of the type of pretreatment. Thus, the black liquor matrix was thought to be the main reason for the inaccuracy of the ICP method.

The lowest values were obtained using the gravimetric method, most probably due to the loss of some volatile sulphur compounds during oxidation. Similarly, the lowest values of the EDXRF determinations were obtained

with Cal 1, which was based on the calibration standard obtained originally from the gravimetric determination of sulphur.

The accuracy of the methods was assessed by carrying out replicate determinations. The standard deviations of the content values were fairly small in all cases (0.6–1.8%), indicating the good suitability of the methods for sulphur determination.

All three EDXRF methods seemed to give results higher than those based on gravimetry, but lower than those from titration or IC (Table II). However, the differences were very low. Equivalent results using the EDXRF methods were obtained at three different concentrations (40, 60 and 80% of original liquor by volume, sulphur content of 4.5–9.0 g/L) (Fig. 5), which further proved the reliability of this method over a wide range of concentration.

The EDXRF method was also validated

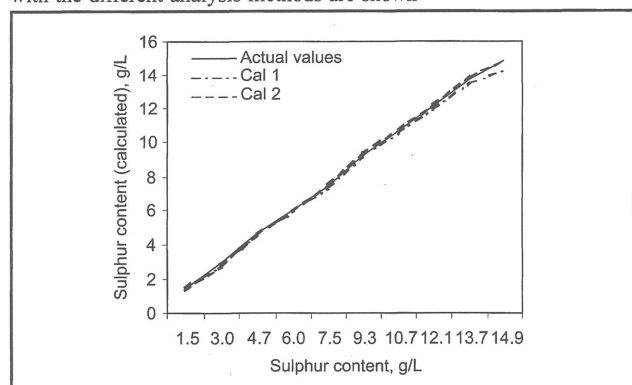


Fig. 3. The sulphur content of the standard samples of Cal 3 (actual values) predicted by Cal 1 and Cal 2 (calculated) in the EDXRF analysis. The standard errors of prediction were 0.12 and 0.09, respectively.

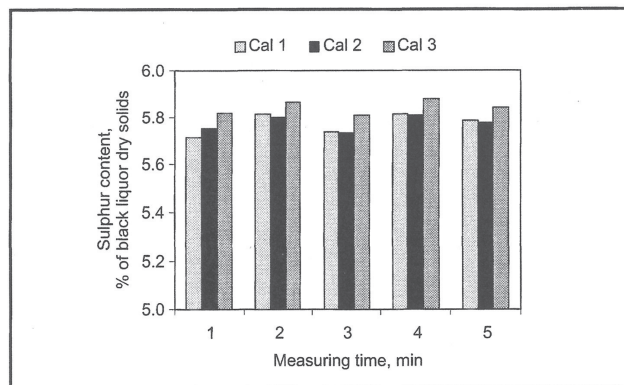


Fig. 4. Sulphur content of the industrial kraft black liquor analyzed using various measuring times. For calibrations (Cal 1, Cal 2 and Cal 3), see Experimental.

by comparison with Schöniger/IC in the results obtained for four industrial black liquors (BLs 1–4, Table III). The results, based on duplicate measurements, were at almost the same level for BLs 1–3 (difference less than 4%), but a slightly greater difference (5–10%) was observed in the case of BL 4 between EDXRF and IC. BL 4 contained insoluble material, which might have impeded the complete combustion of the black liquor in a Schöniger flask, resulting in the lower values found for the IC analysis. In addition, the insoluble material could have interfered with the EDXRF measurement, had it moved down rapidly to the bottom of the sample cup, since the sample was irradiated from below. This phenomena was tested in the EDXRF analysis with a prolonged measuring time (5–20 min). Because slightly lower content values after an analysis time of 10 min were obtained, it seemed that the insoluble material contained less sulphur than the liquid phase of the sample.

Table III shows significantly lower standard deviation values for the EDXRF method. The results indicated that there was actually no need to replicate the analysis, since the deviation was below 2% at its maximum. Again, slightly lower values were obtained using Cal 1 in the EDXRF analysis compared to other two calibrations (Cal 2 and Cal 3), except for BL 4.

General Evaluation of the EDXRF Method

As the results of our study, as well as those of many studies performed by other researchers during the past years, have shown, all the methods for determining the total sulphur content of various black liquors (perhaps except ICP) tested here have reasonable accuracy and reproducibility. However, the costs and the general level of performance required to obtain valid results vary significantly between these methods. The benefits and drawbacks of each method are presented in crude terms in Table IV. As can be seen, EDXRF emerged with the lowest costs and easiest routine operations. Since the CE method and elemental analysis were not included in this study, these methods are not evaluated in Table IV.

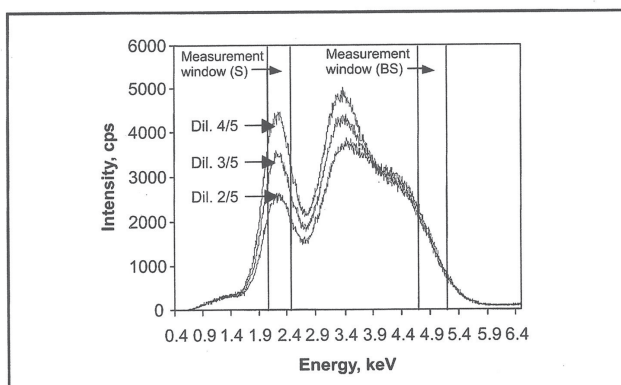


Fig. 5. X-ray intensity (counts per second, cps) spectra of the industrial kraft black liquor (from Oy Metsä-Botnia Ab) measured at three different concentrations (dilution ratios 4/5, 3/5 and 2/5).

TABLE IV
BENEFITS AND DRAWBACKS OF THE ANALYTICAL METHODS TESTED

Aspect	Analytical Method				
	Titration	Gravimetry	IC	ICP	EDXRF
Costs					
Labour	–	–	+-	+-	++
Reagent and glassware	–	–	+-	–	+
Instrument	+	++	–	--	+-
Routine operations					
Sample matrix	+-	+	+-	–	+-
Sample treatment	+-	–	+-	+-	++
Calibration stability	+	no calibration	+	+-	++
Calibration difficulty	+	no calibration	+	+	--
++ very advantageous					
+ advantageous					
+- not advantageous or disadvantageous					
– disadvantageous					
-- very disadvantageous					

CONCLUSIONS

In this study, a new method, EDXRF, suitable for determining the total sulphur (i.e., inorganically and organically bound sulphur) content of black liquor with reasonable accuracy and reproducibility, was developed. Compared to other known methods used for this purpose, the main benefits of the EDXRF method are simplicity of use, absence of the need for multistage sample treatment, stability of calibration and rapidity of measurement. In addition, reliable results can be obtained across a wide range of sulphur concentrations. EDXRF was also found to be insensitive to differences, e.g., in black liquor dry solids.

Although the results obtained indicated clearly that the EDXRF method developed in this study has a sound basis and seems to have potential for the control of sulphur content in black liquor, nonetheless they were based on rather limited amounts of various black liquors. In our forthcoming investigations, the emphasis will not only be on the analysis of black liquors with a more versatile chemical composition but also on the analysis of other substances (e.g., white and green liquors and pulps).

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KEYWORDS: BLACK LIQUORS, X RAY SPECTROSCOPY, SULFUR COMPOUNDS, SPECTROMETERS, FLUORESCENCE, MEASURING INSTRUMENTS, MEASUREMENT, PERFORMANCE EVALUATION.

VI

DITHIONITE BLEACHING OF THERMOMECHANICAL PULP:
FACTORS HAVING EFFECTS ON BLEACHING EFFICIENCY

by

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Dithionite bleaching of thermomechanical pulp: factors having effects on bleaching efficiency

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SUMMARY

The efficiency of dithionite bleaching of Norway spruce (*Picea abies*) thermomechanical pulp was studied by applying various multivariate data analysis techniques to analytical data (temperature, pH, ion chromatographic and energy-dispersive X-ray fluorescence data). In addition, modeling the residual sulfur content of bleached pulp by means of diffuse reflectance UV-vis spectral data from laboratory-scale bleaching experiments was attempted. The results indicated that this lignin-preserving bleaching process could be evaluated by means of the analytical data using either PCR or PLS models. These models also indicated that wavelengths below 400 nm should not be used in measuring the pulp brightness. The residual sulfur content of pulp could not be reliably determined by multivariate modeling of the diffuse reflectance UV-vis spectral data. Copyright © 2000 John Wiley & Sons, Ltd.

KEY WORDS: thermomechanical pulping; dithionite bleaching; ion chromatography; energy-dispersive X-ray fluorescence; multivariate analysis; orthogonal signal correction; projection to latent structures

INTRODUCTION

In 1998 some 13.3 million tonnes of mechanical pulps were produced in Western Europe, of which 9.9 million tonnes alone were produced in Scandinavia [1,2]. Following the development of thermomechanical pulping processes, dithionite has been used to bleach thermomechanical pulp (TMP) and has become the bleaching agent of choice for all (chemi)mechanical pulps, especially in situations where a brightness increase of 4–14 points is required [3]. Although alternative bleaching agents (e.g. hydrogen peroxide) can be used, about 50% of bleached mechanical pulps are currently produced using dithionite bleaching ('hydrosulfite bleaching').

The chemistry of dithionite bleaching is complicated and so far not fully understood. For example, depending on the efficiency of the process, various sulfur-containing species such as sulfite, sulfate and thiosulfate are present at different concentrations in the bleaching filtrate. In addition, some of

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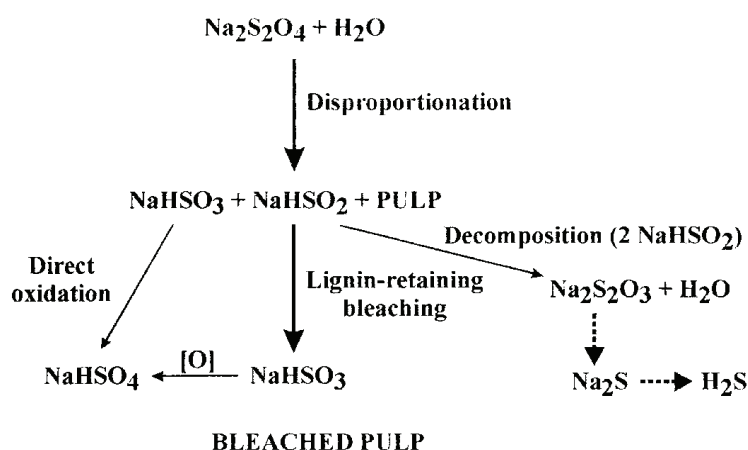


Figure 1. Main reaction pathways for degradation of sodium dithionite during bleaching.

these constituents can be found in pulps. Although earlier work [4] has led to some postulated degradation mechanisms, in this paper a somewhat revised reaction scheme for the degradation of sodium dithionite under these conditions is presented (Figure 1).

The aim of this study was to investigate the efficiency of the dithionite bleaching process by applying multivariate data analysis techniques to the analytical data obtained from laboratory-scale bleaching experiments. Special attention was paid to improving the present analytical methods.

EXPERIMENTAL

Pulp samples

The commercial thermomechanical Norway spruce (*Picea abies*) pulp sample used throughout this work had a brightness value of 64% ISO, a freeness of 45 ml (measured according to the SCAN-C 21:65 standard) and an average fiber length of 1.45 mm. The bleaching experiments under nitrogen atmosphere were done with a Quantum Mini Mixer bleaching apparatus (Quantum Technologies, Inc.) at 4% consistency using a 30 min reaction time. The reaction temperature, pH and sodium dithionite charge were varied as shown in Table I. It should be noted that the dithionite charge was determined by weighing the appropriate amount of 5% sodium dithionite solution (the concentration was determined using ion chromatography).

Ion chromatographic analysis

To determine various sulfur-containing anions, the bleach liquor and bleaching filtrate samples were analyzed in a similar manner using a Dionex 4500 ion chromatographic system (Dionex Corp.) equipped with Dionex VDM-2 UV and Dionex PED-2 conductivity detectors. To prevent the air oxidation of anions, each sample was first introduced to a 2% formaldehyde solution (prepared from commercial 37% solution) and then filtrated through a 0.45 μm membrane prior to ion chromatographic analysis. The chromatographic method was based on mobile phase ion chroma-

Table I. Variations in dithionite bleaching conditions

Temperature (°C)	pH	Dithionite charge (% on wood)
50, 60, 70, 80, 90	5.7, 6.1, 6.8, 7.3	1.30 (± 0.05)

tography (MPIC) and was essentially the same as described previously [5], allowing the quantitative analysis of the following most abundant anions: dithionite ($S_2O_4^{2-}$), sulfide (S^{2-}), sulfite (SO_3^{2-}), sulfate (SO_4^{2-}), thiosulfate ($S_2O_3^{2-}$) and polythionates ($S_nO_6^{2-}$).

Energy-dispersive X-ray fluorescence analysis

The bleached pulp samples were analyzed with a Metorex X-MET 920 (Metorex Corp.) energy-dispersive X-ray fluorescence spectrometer using a mini X-ray tube as a radiation source, a titanium filter and a proportional counter as a detector. A pellet consisting of 1.4 g of the milled pulp sample was measured under a thin polyester (Mylar) film (thickness 2.5 μm) using a 300 s data collection time. The calibration of the spectrometer was accomplished by an addition method using an unbleached pulp sample as a matrix. Each sample was analysed twice and the mean value was used in the subsequent calculations.

Diffuse reflectance UV-vis spectra

A pulp sample was prepared for spectroscopic analysis according to the TAPPI T 218 om-91 standard and measured as described elsewhere [6].

Multivariate data analysis

A mean-centered analytical (temperature, pH and ion chromatographic) data matrix scaled to unit variance was subjected to principal component analysis (PCA) and projection to latent structures (PLS) calculations using singular value decomposition [7]. Various principal component regression (PCR) or PLS regression models were calculated using the mean-centered analytical data scaled to unit variance as an **X** matrix and autoscaled brightness increase values as a **Y** matrix. Also, the mean-centered diffuse reflectance spectral data were used as an **X** matrix in some calculations. The significant ranks of models were determined by cross-validation [8]. All computations were carried out on a personal computer using the MATLAB[®] software package [9].

RESULTS

Brightness increase

As can be seen from Figure 1, the sodium dithionite ($Na_2S_2O_4$) readily disproportionates into sodium bisulfite ($NaHSO_3$, analyzed as sulfite by ion chromatography) and sodium sulfoxylate ($NaHSO_2$), of which the latter, in turn, mainly reacts with the pulp ('lignin-retaining bleaching') to produce sodium bisulfite. Sodium bisulfite is further oxidized to sodium bisulfate ($NaHSO_4$, analyzed as sulfate by ion chromatography). It should also be mentioned that sodium bisulfite may introduce small amounts of sulfonic acid groups into the pulp. It could be concluded that excess amounts of bisulfate and thiosulfate ($Na_2S_2O_3$, formed from sulfoxylate via decomposition) ions in the bleaching effluents may indicate lower bleaching efficiency, resulting in low brightness increase.

The PLS model for the brightness increase (ISO-B) clearly confirmed the proposed main degradation pathways, showing that the excess amount of sulfate in the bleaching system was negatively correlated to the brightness gain, whereas the amount of sulfite— and, to some extent, thiosulfate— was positively correlated, as seen in Figure 2. Also, wavelengths below 410 nm had a clearly different behavior towards the brightness increase than wavelengths above 410 nm. The very minor negative effect of temperature on bleaching efficiency, as seen in Figure 2, is not correct and is suspected to be due to the deficiencies of the temperature measurement in the bleaching reactor. The effect of temperature is typically regarded as highly positive towards the brightness gain.

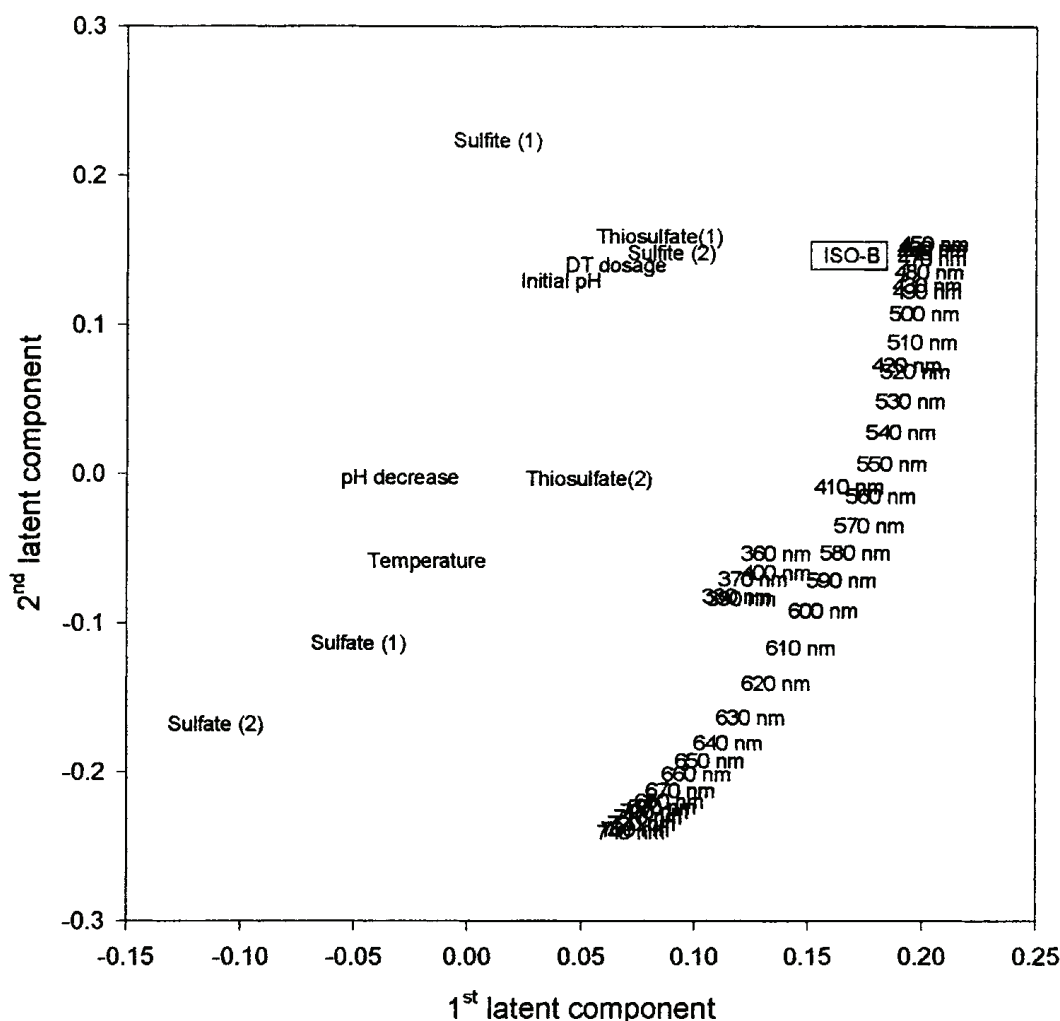


Figure 2. X loading weights and Y loading values (ISO-B) for PLS model of brightness increase: (1) refers to the amount of component in the bleach liquor; (2) refers to the amount of component in the bleaching effluent; wavelengths 360–740 nm refer to the data points in the diffuse reflectance UV-vis spectra; DT dosage refers to the dithionite dosage; ISO-B refers to the brightness increase.

The modeling of brightness increase (ISO-B) yielded a better fit and accuracy of predictions when some interaction terms, in the form of new variables, were introduced to the models. These interaction variables were obtained by multiplying the effective concentrations of (i) sulfite and sulfate, (ii) thiosulfate and sulfite and (iii) thiosulfate and sulfate. It should be pointed out that diffuse reflectance UV-vis spectral data were not used in these calculations. The cross-validated coefficient of determination (Q^2), standard error of prediction (SEP) and rank for the PCR and PLS model with and without interaction variables are shown in Table II. The measured versus the calculated brightness increase (calculated by the PLS model with interaction variables) is presented in Figure 3.

Residual sulfur content of pulp

All the calculated models for the residual sulfur content of the pulp had a rather low Q^2 (38%–50%) and a rather large SEP (up to 32% of the mean for the sulfur content), suggesting that the information

Table II. Cross-validated coefficient of determination (Q^2), standard error of prediction (SEP) and rank for PCR and PLS models of brightness increase (ISO-B) with and without interaction terms (see text for details)

	PCR		PLS	
	With	Without	With	Without
Q^2 (%)	70.1	64.1	95.7	73.1
SEP	0.825	0.905	0.312	0.783
Rank	6	2	4	4

obtainable from the diffuse reflectance UV-vis measurement was not applicable, i.e. sulfur content of the pulp is not seen as color difference. Application of various types of new variables (interaction or squared terms) or orthogonal signal correction calculations [10] did not alter that situation.

CONCLUSIONS

The optimum brightness increase (ISO-B) obtained by the dithionite bleaching process under varying conditions could be evaluated with reasonable accuracy using multivariate models, especially PLS. These models clearly indicated various different effects of analyzed variables (pH, temperature and concentrations of various sulfur anions) on bleaching efficiency. In addition, the effect of sulfate, sulfite and thiosulfate ions on the brightness increase confirmed the proposed primary degradation pathways for dithionite. The PCR and PLS models also indicated that wavelengths below 400 nm should not be used in pulp brightness measurements.

The residual sulfur content of thermomechanical pulp could not be reliably determined by multivariate modeling of diffuse reflectance UV-vis spectral data. Several attempts, such as introducing interaction and/or squared variables to the models, or application of orthogonal signal correction calculations, did not yield any applicable models.

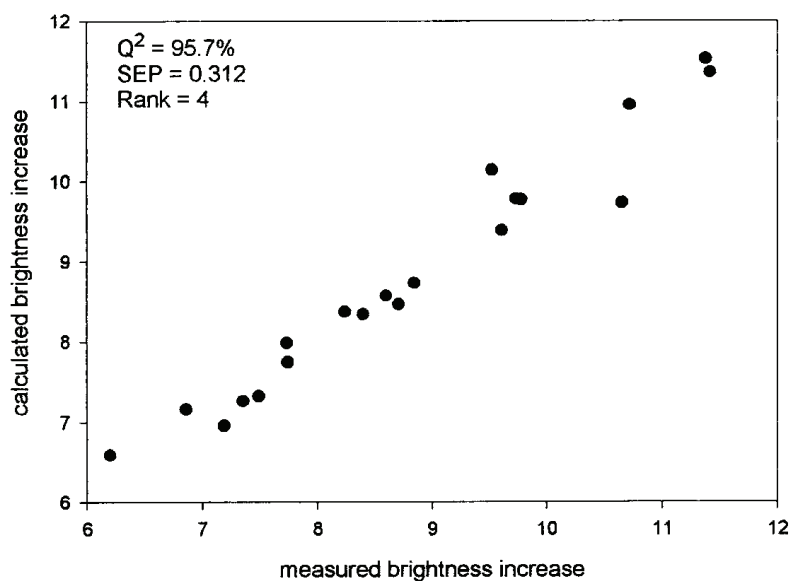


Figure 3. Measured versus calculated brightness increase (PLS model with interaction terms).

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