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Review

Sustainability of kraft pulp mills: Bleaching technologies and sequences with reduced water use

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ABSTRACT

The Kraft pulp industry is a relevant industrial sector in many countries with a considerable social, economic, and environmental impact. Thus, sustainability is the adequate framework to address this activity sector. This work presents a review of the literature, with a particular focus on the bleaching area and its relevance in reducing water use. The sustainability reports of the most prominent pulp and paper companies were analyzed, considering their specific water utilization and the sustainability targets they have outlined. The most industrially applied bleaching sequences were also addressed and the stages of the state-of-the-art sequences were analyzed (elemental chlorine free – ECF bleaching). Moreover, in this review, a detailed analysis of a sequence used on an industrial scale was carried out, highlighting the washing steps and the measures that are taken to minimize water use. The main limitations to the minimization of water use were identified, being deposit formation the major problem. Measures to overcome these limitations, as well as future perspectives were discussed. Due to the shortage of freshwater nearby some pulp and paper production sites, there will continue to be great pressure in the future to reduce water utilization, especially in the bleaching area.

Contents

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Introduction

Sustainability issues are currently highly relevant to the pulp industry. In addition to the relevance of this sector in economic and social terms, business models must approach environmental sustainability carefully. Nowadays, many pulp industrial plants and corporations periodically prepare sustainability reports, that are made available to the shareholders, stakeholders, and the general public. Many of these reports follow the Global Reporting Initiative (GRI) framework, to "deliver the highest level of transparency for impacts on the economy, environment, and people" [21]. The sustainability reports following GRI standards display the approaches already implemented in each site and future strategies to achieve specific goals. Common tools that have been used to improve the sustainability of the pulp industry, namely for developing environmental sustainability are the standard ISO 14001 (Environmental management systems), EMAS (The EU Eco-Management and Audit Scheme), Ecolabel, ISO 9001 (quality management system), ISO 45001 (Occupational health and safety management systems), ISO 50001 (energy management system), the UN Global Compact, circular economy framework, etc. These tools have made it possible to reach high standards of sustainability that have led some pulp industries to outstanding levels. In particular, some corporations have been considered eligible to integrate the Dow Jones Sustainability (DJSD) Index, which is one of the leading international benchmark indices for world-leading companies in sustainability. Some examples that can be highlighted in this scope are UPM-Kymmene Oyj, Canfor Pulp Products Inc., Chung Hwa Pulp Corporation - Taiwan, Indah Kiat Pulp & Paper Corp Tbk PT, and Japan Pulp and Paper Company Limited. However, UPM has stood out as the only company in its industry sector in the Dow Jones European and World Sustainability Indices for a decade (2012–2022).

Even so, searching the Web of Science database with the words "pulp mill" and "sustainability" in the title, only four results were found, which means that the scientific community has not discussed this issue in depth. One of these studies is related to the "sustainability assessment of integrated forest biorefinery implemented in the Canadian pulp and paper mills" [6]. The other study addressed the "minimization of the environmental impact of kraft pulp mill effluents" [82]. This fact is unexpected, considering that the pulp industry is intensive in energy, water, and wood, and releases very significant quantities of atmospheric emissions, liquid effluents, and solid residues. From the sustainability reports of several pulp industries, it is noticeable that environmental concerns more addressed are water, forest management, biodiversity, waste, and climate issues.

This study intends to contribute to filling this information gap in the scientific literature, focusing on sustainability issues and more specifically on water use in the pulp bleaching stages. In particular, information published in the literature in recent decades on these topics is aggregated, allowing an evolutionary view of the pulp bleaching process, what measures were taken to reduce water consumption, and the impact of applying these measures. Finally, a methodology for modeling and integrated simulation of water consumption in bleaching will be proposed.

Kraft pulp mills process

The kraft process, also known as the sulfate process, allows the conversion of wood into pulp consisting mainly of cellulose fibers, the main raw material for obtaining paper. A simplified scheme of the kraft process is shown in Fig. 1. Globally, the process involves the treatment of wood chips with a hot mixture (white liquor) of water, sodium sulfide (Na_2S), and sodium hydroxide (NaOH), to disintegrate lignin. After the cooking phase, the cellulose fibers are suspended in the dark liquid (black liquor) due to the dissolution of lignin [23]. The fiber and black liquor suspension go through a washing process, making it possible to separate the washed pulp suspension and the weak (diluted) black liquor. Weak black liquor consists of a liquid with a high organic load, resulting mainly from the decomposition of lignin, as well as sodium salts that allow the reconstitution of the main reagents that make up the white liquor. This liquid is concentrated and sent to the recovery boiler for energy recovery from the high organic load. During the combustion of black liquor, a melting mass (the smelt) is formed, especially of Na_2CO_3. The smelt is dissolved in weak white liquor, producing green liquor. This liquid goes through a causticizing cycle, regenerating NaOH and white liquor [79].

The fiber suspension is directed to the bleaching area, which normally requires several bleaching stages to achieve the desired brightness. In the bleaching area, the remaining lignin and chro-

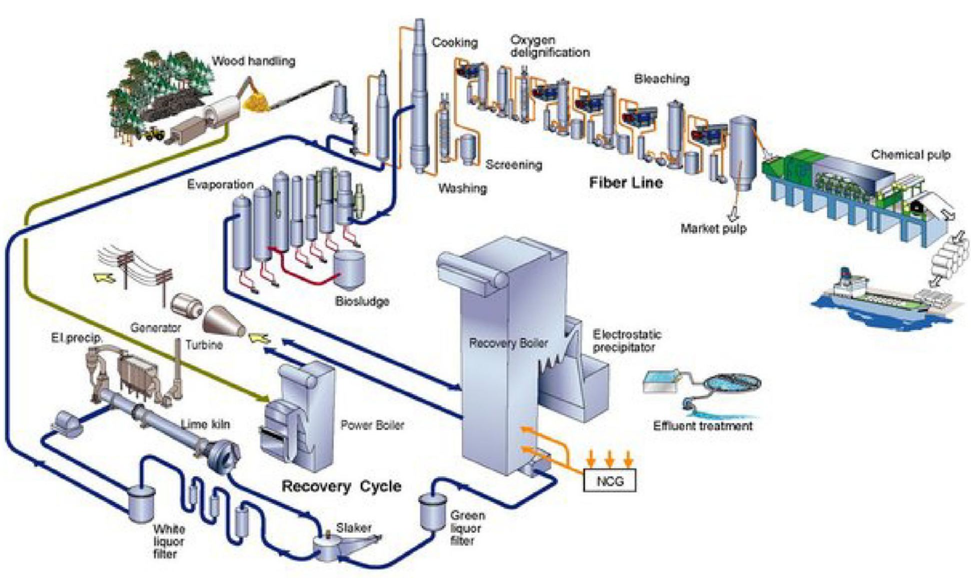

Fig. 1. Overview of a conventional kraft pulp mill © 2008 Kvaerner Pulping [87].

mophore groups are removed from the fibers. The target molecules are oxidized and solubilized and these processes can occur, typically, in two modes: Elemental Chlorine Free (ECF) sequences, which avoid the use of molecular chlorine, replacing it with ClO_2 as the main bleaching agent, and Totally Chlorine Free (TCF) sequences, that avoid totally the use of chlorine. In these types of sequences, the main oxidizing agents are typically oxygen peroxide, oxygen, and ozone. For ECF and TCF sequences, bleaching stages are interspersed with pulp washing stages to remove solubilized compounds [28]. Despite the recycling strategies, this area is responsible for significant freshwater utilization, and for achieving the removal of the chromophore groups from the fiber which results in a high load effluent.

Environmental sustainability

Industrial growth and the high energy intensity from non-renewable energy sources (fossil fuels) have led to consequences that may compromise the needs of future generations. The pulp and paper industry is one of the industrial sectors that has a relevant contribution to resource depletion (namely, wood, chemicals, water, and energy), producing simultaneously high loads of effluents. For these reasons, sustainability practices must be implemented and properly addressed, and communicated. The most common way of reporting sustainability is the so-called "sustainability reports". These reports are generally published annually, and most companies have applied the standards provided by the Global Report Initiative (GRI). GRI provides companies the tools to report the impacts, creating a global common language to report sustainability, helping simultaneously the companies take responsibility for mitigating the impacts. This tool can be extremely relevant for benchmarking [22]. For the pulp and paper industry, most of the sustainability reports include the values of specific water use, water withdrawal, total production, energy consumption, and percentage of water devolution, among others.

Some of the pulp production companies were assessed to integrate the Dow Jones Sustainability Index, which is integrated by companies that, within a given area, present the highest sustainability scores, encouraging improvement in the implementation of sustainable practices (S&P [73]. Another way of evaluating sustainability practices is related to the inclusion of "sustainable development goals"- SDG, to be further implemented according to a strategic plan. Organizations that follow GRI standards generally include in their annual reports the most relevant objectives for achieving sustainability in the industrial ecosystem. Often, specific industrial objectives can be related to some of the 17 SDG established by the United Nations (UN) in 2015 [81]. Table 1 contains a list of the largest pulp and paper production companies that report sustainability documents, where data related to water utilization was also indicated, including specific water use (water per air-dried (AD) ton of pulp), as well as the main SDG addressed in each report. It is important to highlight that 12 out of 17 reports analysed in the present study addressed precisely Goal 6 - *Ensure availability and sustainable management of water and sanitation for all*. Specifically, the pulp and paper industry should handle target 6.3, which is related to "*improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally*".

Analyzing the data gathered in Table 1, it is worth mentioning that most pulp-producing industries followed GRI standards to report sustainability data. As for water use, generally, the range of specific water use (m^3) per ton of pulp varies between 20 and 50, which is in line with the recommendations of the Best Available Techniques for the pulp and paper production industries. In two of the documents analyzed, the specific use of water exceeded 60 m^3/t, since the water used in turbines and the water used in the paper mill were accounted for in this value. In these mills, the specific production of effluent varied between 22 and 36 m^3/t, and most of the water used in the process is treated and returned to the environment. Concerning the reduction of water use, some of these industries have established water use reduction targets for the next decade. Moreover, it is important to highlight that some of these industries were included in the Dow Jones Sustainability Index.

To address environmental sustainability, it is relevant to mention life cycle assessment (LCA) as a valuable tool, which has been used for comparisons between different products and/or technologies. In recent years, some studies have been published in the context of the assessment of the life cycle of various pulp and paper products. These studies were focused on the production of raw materials (eucalyptus), pulp production, paper production, the market, the potential for global warming, etc. For example, Lopes et al. [34] carried out an LCA study for paper production in Portuguese mills, comparing the use of heavy fuel oil or natural gas in the recovery cycle. Although the evaluation of the two cases did not differ in the bleaching, the pulp production step was identified as the largest source of organic matter emission (identified as COD). Pulp production was also identified as the major source of adsorbable organic halogens (AOX) emissions, due to the use of ClO_2 as a bleaching agent. Pulp production makes a major contribution to the eutrophication-related impact category. Samantha-John [67] conducted a study related to the various stages of the paper production process in South Africa. This study does not focus on water utilization, while the bleaching area was identified as a significant contributor to the "summer smog" impact category. Since the bleaching effluent is discharged into the sea, the impact associated with salinization was not relevant. Two production lines were considered in this study, and the total specific use of water and the specific use of bleaching water were identified. In one case, the uses determined were 68.8 m^3/t and 34.9 m^3/t, respectively, and in the other case 33.2 m^3/t and 16.8 m^3/t. In this study, the comparison of South African and Finland mills revealed the existence of higher impact loads in South Africa. González-García et al. [20] performed a study to identify which section of pulp production, from the origin of raw material production, has the greatest environmental impact and the greatest potential for impact reduction. In the case under study, pulp bleaching used a Total Chlorine Free (TCF) sequence. This study identified pulp cooking, washing, and bleaching as the steps that most contribute to the production of wastewater. Ferrari et al. [17] conducted an LCA of different types of paper, focusing on the emission of CO_2 equivalents throughout the life cycle of the products. The bleaching area was identified as one of the operations that contributes the most to the impact of paper, especially regarding the production of bleaching additives. These data are corroborated by the study by Culbertson et al. [14], in which the LCA for the softwood pulp production process is compared to the same process, integrated with lignin extraction. In this study, it is pointed out that the consumption of sodium chlorate to produce chlorine dioxide contributes significantly to most impact categories. The study published by Ma et al. [36] approached the coupling of the life cycle assessment and the assessment of the water footprint of different papers, produced from ECF pulps and C-E-H pulps (C-E-H – chlorine, alkaline extraction, and hypochlorite). In this study, the water footprint is defined as a comprehensive indicator, with geographic and temporal dimensions, used to assess water pollution and its utilization in anthropogenic activities. The results revealed that papers produced from ECF pulps are more environmental-friendly than those produced from CEH pulps. In addition, it was found that water utilization and effluent generation in ECF pulps (32.7 and 27.4 m^3/t,

Table 1
Sustainability data of the most relevant pulp industries.

Company, country	Document, year	GRI	Water: Specific use, targets	SDG from the UN addressed in the report	Reference
Altri - Portugal	Sustainability [61,47,50–51,57]	Yes	Specific water use: 22 m^3/tAD; 83% of the collected water is returned to the environment; Target: reduce the specific water use by 50% by 2030; Target: reduce the effluent organic load by 60% by 2030.	**6**, 7, 8, 12, 13, and 15	(Report [46]
APRIL Group - Indonesia	Sustainability [61,47,50–51,57]	Yes	Specific production of effluents: 31.6 m^3/t (integrated pulp and paper mill); 90% of the water collected is reused; 82% of the water collected was returned to the river; Target: reduce water use by 25% in 2030;Pulp production (excluding energy and paper production) increased by 8% in total water use.	**6**, 7, 8, 9, 12, and 13	(Report APRIL, 2020) [47]
Asia Pulp and Paper Sinar Mas - Indonesia	Sustainability [61,47,50–51,57] Roadmap vision 2030	Yes	Specific water use: 29 m^3/t (integrated pulp and paper mill); In 2020, 13% of the water was reused; Target: reduce the intensity of water use by 30% in 2030, compared to 2018; Achieved in 2020: 8%.	**6**, 12, and 13	[2,48]
Bracell - Brazil	Sustainability [61,47,50–51,57]	Yes	Total water use: 31.7 m^3/tAD; Effluent generation: 23.5 m^3/tAD; 75% of the collected water is returned to the environment.	-	(Report [49]
CENIBRA - Brazil	Sustainability [61,47,50–51,57]	Yes	Specific water use: 38.3 m^3/tAD; Effluent generation: 35.6 m^3/tAD.	**6**, 12, and 14	(Report CENIBRA, 2020) [50]
CMPC - Chile	Integrated [61,47,50–51,57]	Yes	Specific water use: 30 m^3/t (integrated pulp and paper mill);Target: reduction of water use by 25% in 2030 compared to 2018 (reference value: 30.84 m^3/t).	**6**, 7, 12, 13, and 15	(Report CMPC, 2020) [51]
Eldorado Brasil Celulose - Brazil	Sustainability [61,47,50–51,57]	Yes	Total water withdrawal: 44.1 Mm^3; Total effluent discharge: 37.7 Mm^3; 85% of the collected water is returned to the environment; Specific water use: 24.7 m^3/tAD (gradual reduction since 2018).	2, **6**, 8, 9, 11, and 12	(Report [52]
International Paper - USA	Annual Report, 2021 Global Citizenship, 2019	No	90% of the collected water is returned to the environment after treatment; Target: reduce water use by 25% by 2030.	-	[29,53]
Klabin - Brazil	Sustainability [61,47,50–51,57]	Yes	Specific water use has gradually decreased from 2017 (26.65 m^3/t) to 2020 (23.72 m^3/t) (integrated pulp and paper mill); In 2020, effluent discharge was reduced by 3%; Reduction of specific use by 18% (2020); Target for 2030: 30% reduction; Integrates the "Global and Emerging Markets" list of the Dow Jones Sustainability Index.	**6**, 7, 8, 12, and 13	(Report [54]
OJI Holdings Corporation - Japan	Integrated [61,47,50–51,57]	Yes	Specific water withdrawal (2020): 49.3 m^3/t (integrated pulp and paper mill); 95% of the water withdrawn is returned to the environment after treatment; Target for 2020: reduce water withdrawal by 6% compared to 2018; achieved: 4.6% reduction in water withdrawal; Reducing withdrawn water: improving operations and minimizing water use, purifying, and treating it for reuse within the factory.	**6**, 12, 14, and 15	[56]
PT Toba Pulp Lestari - Indonesia	Sustainability [61,47,50–51,57]	Yes	Target: 2020: freshwater use decreased by 13.36% in 2020 compared to 2019; In 2020, freshwater was reused/recycled 4.79 times, before being released into the environment being returned to rivers; The management of freshwater use has improved by 9.39% compared to 2019.	**6**, 8, and 9	(Report Toba Pulp [60]
SCA Pulp - Sweden	Sustainability [61,47,50–51,57]	Yes	Water withdrawal: 63 m^3/tAD, from superficial sources; Emissions to water: minimization (currently: 22 m^3/tAD); Phosphorus emission to effluents: dropped 23 % comparing emissions in 2020 with 2014; Virtually all used water is returned to the environment after treatment.	3, **6**, 7, 8, 9, 11, 12, 13, and 14	(Report SCA, 2020) [57]
Stora Enso - Finland	Sustainability [61,47,50–51,57]	Yes	Water withdrawal: 65 m^3/t (integrated pulp and paper mill); Effluents: 31 m^3/ t; About 97% of withdrawn water is returned to the environment after purification; A decrease in pulp production in 2020 led to slight increases in specific	12, 13, and 15	[58]

(continued on next page)

Table 1 (*continued*)

Company, country	Document, year	GRI	Water: Specific use, targets	SDG from the UN addressed in the report	Reference
			water consumption.		
Suzano - Brazil	Sustainability [61,47,50–51,57]	Yes	Specific use in 2020: 28.6 m^3/t (1.2 m^3/t reduction compared to 2019) (integrated pulp and paper mill); Target: reduction of water withdrawal in the industry by 15% in 2030; 2020 reduction totals 26.7% of the 2030 target achievement; Target: avoid water use of more than 28.6 m^3/t for 2021, optimizing water management. Forecast to change equipment for greater water efficiency and reuse of process water; Part of the Dow Jones Sustainability Index.	**6**, 7, 9, 12, and 13	(Report [59]
The Navigator Company - Portugal	Sustainability Report, 2021	Yes	Specific water use: 20.9 m^3/t of product (integrated pulp and paper mill); 84% of the water collected is returned to the environment; Achieved: 6.7% reduction in specific water use (compared to 2019); Target: reduce specific water use by 33% by 2030 (compared to 2019) ; The Navigator Company was awarded 3rd place by Sustainalytics, among 81 pulp and paper mills.	8, 9, 12, 13, and 15	(Report [55]
UPM - Finland	Corporate environmental and societal responsibility statement, 2020	Yes	Specific water use (pulp): 32 m^3/tAD (2019) and 30.7 m^3/t (2020); Targets: Reduction of effluent the organic load by 40% (COD – chemical oxygen demand) in liquid effluents by 2030; Achieved: 33% compared to 2008; Reduction of wastewater volume by 30% by 2030; Achieved: 10% compared to 2008; In one of the pulp sites, the increase in washing efficiency led to a 9% reduction in the amount of wastewater.	**6**, 7, 12, 13, and 15	(Report UPM, 2020) [61]
Veracel - Brazil	Sustainability [61,47,50–51,57]	Yes	Specific water use: 22.2 m^3/tAD.	-	Report [63]

respectively) are lower than the same parameters in the production of CEH pulps (36.8 and 35.9 m^3/t, respectively). Echeverria et al. [16] focused on the bleaching section, by comparing a traditional bleaching sequence based on the Elemental Chlorine Free (ECF) type, with a TCF sequence, using peracetic acid as the bleaching agent. The LCA demonstrated that the use of a TCF sequence with peracetic acid reduces water use by 14%, effluent production by 16%, and the emission of AOX is eliminated. Furthermore, the energy required is minimized as well as the amount of bleaching agents. The TCF sequence with peracetic acid showed better results than the ECF only for the three impact categories: global warming potential, freshwater eutrophication, and resource depletion fossil fuels. Globally it should be noted that although LCA is an invaluable tool for addressing environmental sustainability, in the area of pulp and paper industry there is room for its use in the future, namely to address issues related to water in the bleaching. In particular, LCA could provide valuable data for deciding which is the best bleaching sequence from an "environmental sustainability" point of view.

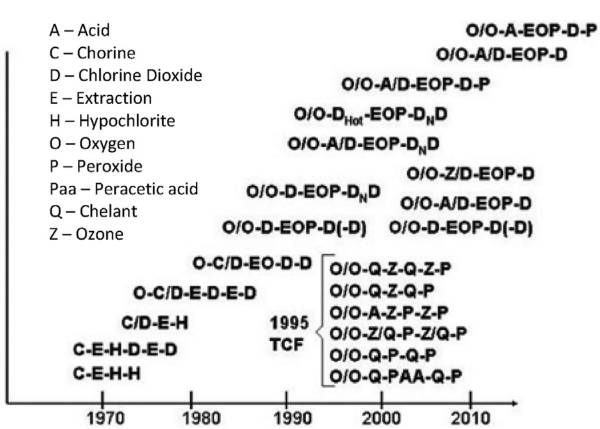

Fig. 2. Evolution of the bleaching sequences [25].

Bleaching technologies and the water reduction

Common bleaching sequence: A historic perspective

The bleaching process has undergone significant development in the last two centuries. In the 19th century, the application of only one chemical compound prevailed – hypochlorite. From the late 1920 s onwards, the use of chlorine as a bleaching agent was introduced, and multi-stage processes were developed, followed by the application of an alkaline extraction stage to remove oxidized lignin. Until the mid-1970 s, the CEH sequence (C-Chlorine, E-Alkaline Extraction, and H-Hypochlorite) and its variants, were the standard bleaching procedure. With the increase in production capacity and environmental awareness, the effects of pollution have become increasingly noticeable. Mills that used chlorine and/or sodium hypochlorite as bleaching agents were discharging higher and higher concentrations of polychlorinated dibenzo-p-dioxins and furans (PCDD/F), as well as other organochlorine compounds into waterways. In the mid-1960 s, the presence of these compounds in effluents, which have toxic, mutagenic, persistent, and carcinogenic effects, was associated with the use of elemental chlorine [4,74]. Since then, pulp mills around the world have phased out the use of elemental chlorine and adopted ECF bleach-

Table 2
Modern bleaching sequences considered BAT [77].

O/O-D-E-D-P	O/O-A-D-E-D	O/O-P-D-Q-PO
O/O-D-E-D	O/O-Z-E-D-D	O-Q-PO-DQ-PO
O/O-D-E-D-D	O/O-A-D-P-Z-P	O-Q-X-O-P/O-D-E-P-D-Paa
O/O-A-D-E-D-P	O/O-Z-D-P	O/O-Q-O-P-D-PO
O-mP-Z-P-Z-P	O/O-Q-OP-Paa/Q-PO	Dhot-EOP-D-P
A/D-EOP-D-D	Dhot-PO-D	D-EOP-D-D

ing sequences or sequences that eliminate chlorine (TCF sequences) [27]. Chemical agents such as oxygen, hydrogen peroxide, or ozone have been introduced as bleaching agents over the years. Fig. 2 represents the historical evolution of the most commonly applied bleaching sequences.

Currently, ECF sequence-based bleaching is the dominant concept, while several combinations can be explored. Indeed, several factors must be considered in the selection, such as raw material, type and load of chemical agents, bleaching performance, water use, effluent emissions, adsorbable organic halogen load, brightness stability, papermaking properties, operating flexibility costs [4]. Due to the high pollution load, the effluents generated in the process of pulp washing are treated through physical (e.g., sedimentation), chemical (e.g., oxidation), and biological processes (e.g., anaerobic digestion) [31].

The pulp and paper industry has made significant efforts to select the best ECF sequences, considering the specific characteristics of the pulp, as well as optimizing the use of chemical reagents from an economic and environmental point of view. When the objective is to produce tissue paper, the bleaching technology is currently well established, with three-stage sequences of the D-EPO-D type being enough to achieve a brightness of 88–90% ISO [10]. On the other hand, for printing and writing paper grades, where it is necessary to achieve high brightness with low reversion, the best bleaching technology is still a matter of debate. However, the use of one or two oxygen stages (O or O/O) followed by four stages of the D-EPO-D-D or D-EPO-D-P type is recommended to assure brightness greater than 90% ISO with reversion lower than 2 % ISO [10].

The inclusion of alternative stages to replace chlorine dioxide (D), such as acid hydrolysis (A or Ahot), hot chlorine dioxide (Dhot), peracetic acid (Paa), and/or ozone (Z) in the sequences of bleaching aims to reduce the consumption of reagents, as well as the environmental impact (ClO_2 load, effluent volume, COD emission) and allow the partial closure of the water circuit in the bleaching process [7]. This happens since the replacement of ClO_2 by other total chlorine-free bleaching agents can allow the valorization of the filtrates in the recovery boiler.

Table 2 summarizes the modern bleaching sequences according to the European Commission's reference document on the best available techniques - BAT [77].

Currently, modern pulp and paper mills consume about 20 – 25 m^3/tAD of water in bleaching [41]. Reducing the utilization of fresh water is advantageous both from an environmental and economic point of view, as it reduces energy consumption and effluent treatment costs. Efforts have been made to close loops of water, for example, by integrating filtrates into recovery systems or increasing their recirculation within the bleaching area. However, a high closure in the water circuit can have negative effects due to the accumulation of dissolved substances and non-process elements (NPE) in the bleaching stages and process cycles, and the later formation of scale deposits in pipes and equipment [28]. Thus, the selection and use of bleaching chemicals properly are extremely important to minimize these problems. Table 3 contains water utilization data for different bleaching sequences, including industrially applied sequences and laboratory-tested sequences. In the following sections, the stages in which greater variations are observed on an industrial scale in Eucalyptus kraft pulp production units will be discussed in greater detail. In particular, issues such as the implementation of oxygen delignification, the replacement of chlorine dioxide in the first bleaching stage, and even variations between the use of D or P at the end of bleaching will be addressed.

From the analysis of Table 3, it appears that most pulp mills focus on eliminating the use of elemental chlorine, except for an Indian industrial unit, where the use of elemental chlorine and hypochlorite is still observed. According to the literature, the water use in the pulp mill is in the range of 20 and 40 m^3/tAD, and the bleaching area is in the range of 11 and 30 m^3/tAD. However, it is important to note that it is very difficult to establish comparisons between different processes and sequences, since many variables affect water consumption in the bleaching, such as the origin of the forest biomass, the yield of the upstream cooking process, as well as the pulp washing efficiency before bleaching. In addition, process conditions such as temperatures, pressures, and concentrations of bleaching reagents have significant impacts on pulp wash water requirements. Lastly, the quality and source of the water used for washing also affect the water flows required in this section of the mill.

Most efficient bleaching technologies

Oxygen delignification

Oxygen delignification is used after cooking aiming at oxidizing and solubilizing lignin before bleaching. It involves the reaction of the pulp with oxygen under alkaline conditions, followed by washing to recover/remove the dissolved lignin [65]. The oxygen delignification technology applied to eucalyptus kraft pulp is typically based on a two-stage system. After the first oxygen stage, the amount of lignin remaining in the pulp is small (representing a low kappa index – an indirect measure of residual lignin content), which is essentially due to the presence of hexenuronic acids (HexA). These compounds are formed in the kraft cooking process and are responsible for increasing the consumption of bleaching chemicals, reversing the brightness of pulp, and forming oxalates that increase deposits and limit the closure of water circuits [70]. Thus, removing HexA at the beginning of bleaching has advantages, and different alternatives have been explored for this purpose. However, oxygen does not react with HexA, and the second stage with oxygen has little impact on the kappa index [83]. The second stage significantly increases brightness, which represents an advantage for the overall process [12].

In addition, oxygen has a greater selectivity when compared to kraft cooking, which makes it possible to preserve the pulp yield. Thus, it is more advantageous to finish kraft cooking at a higher kappa index, using oxygen as a more selective agent to complete delignification and achieve lower kappa numbers. Vuorinen et al. [83] demonstrated that the yield benefit after oxygen delignification was 2 – 2.5% by stopping the cooking at a kappa index of 19, instead of 15.5. The same trend was observed in other studies applied to softwood pulps [11].

The advantages of oxygen stages are both environmental and economic. The effluent from the oxygen stage is free of chloride ions and can be recirculated. Thus, the installation of an oxygen stage considerably reduces AOX, COD, BOD, and color emissions in the effluents, allowing their recirculation and reducing water utilization [8,37]. There are also savings in operating costs through the use of lower amounts of oxidizing agents (D, Z, P, etc.) since oxygen is less expensive. The main disadvantages of oxygen compared to chlorine dioxide stages are lower reactivity and selectivity, as well as the higher capital cost of the installation [5].

Table 3
State-of-the-art bleaching sequences and respective water use and effluent production.

Mill/ country	Pulp	Sequence	Water use bleaching (m^3/tAD)	Total water use (m^3/tAD)	Bleaching effluents (m3/tAD)	Notes	Ref
Brazil	Kraft	O-Dhot-(EP)-D-P	16	40	ni	6 m^3/t of fresh water is used in countercurrent washing with stage jump	[39]
Brazil	Kraft ECF	D-(EP)-D-P	Values tested in the lab: 9, 6 and 3	ni	ni	Lab-scale study; Washing was carried out by mixing filtrates and distilled water; Desired brightness is not achieved when 3 m^3/t is used for washing.	[18]
Brazil	Kraft ECF	O-D-(EOP)-D-P	ni	ni	ni	Through a simulation study, the main conclusions are: replacement of fresh water in the P washer by filtrates from the EOP washer can lead to a reduction of 219 m^3/h (freshwater reduction); This change can lead to 74% water savings.	[40]
CENIBRA, Brazil	Kraft ECF	O-Ahot-(EOP)-D-(PO)	23.67	ni	9.11	Lab-scale study, using oxygen delignification before bleaching; Effluent generation: 9.11 m^3/t; 3.89 m^3/t of filtrates are sent to the washing steps of the causticizing cycle; Washing liquid: 15.67 m^3/t from white waters; 8 m^3/t from condensates; 9 m^3/t reduction in effluent generation.	[13]
Compilation	Kraft ECF	O-D-(EO)-D-D	ni	ni	5.9–18.4	Volatile solids in the effluent: 26–72.7 kg/t	[3]
Compilation	Kraft TCF	O-Z-(EO)-Z-Q-P	ni	ni	5.8	Volatile solids in the effluent: 44–59.6 kg/t	[3]
Husum Mill of MoDo paper AB, Sweeden	Kraft ECF	Includes O, Z, P, and D	ni	ni	5	Countercurrent	(Bajpai, 2012) [4]
India	Kraft	Includes C, H, and D	11.0 16.9	ni	ni	Small mills average water use of around 11.0 m^3/t (production < 100 t/day); some smaller mills use only H stage; Large mills average water use of around 16.9 m^3/t (production > 100 t/day).	[78]
Kymmene, Wisforest	Kraft ECF	O-(ZD)-(O/E)-(ZD)-(EPD)	25	ni	ni		(Bajpai, 2012) [4]
Kymmene, Wisforest	Kraft TCF	O-(ZQ)-(OP)-(ZP)	15	ni	ni	Intention to reduce the water use to 10 m^3/t	(Bajpai, 2012) [4]
Louisiana -Pacific Corporation, USA	Kraft TCF	Q-(EOP)-P-P-P	ni	ni	6.76	Q stage – Chelation stage - is the only one that generates effluent	(Bajpai, 2012) [4]
Scandinavia	Kraft ECF	D-(EO)-D-(PO)	30	ni	ni	Oxygen delignification before bleaching; High water use: lower risk of metal scaling; Washing equipment: wash filter, wash presses, drum displacement, dewatering presses; The company is using process simulation to apply process modifications to reduce water use.	[84]
Stora, Gruvon	Kraft ECF	D-E-D-E-D	ni	ni	12		(Bajpai, 2012) [4]
Union Camp Corporation, USA	Kraft ECF	O-Z-(EO)-D	ni	ni	9.1	Filtrates from O, Z, and (EO) flow in countercurrent, to be recovered. 2.1 m^3/t from Z stage is purged to avoid scaling; D-stage filtrate is discharged to the sewer.	(Bajpai, 2012) [4]
UPM Fray Bentos, Uruguay	Kraft ECF	(AD)-(EOP)-D-P	ni	21.5	ni		[62,77]
Veracel, Brazil	Kraft ECF	A-D-(EOP)-D-P	ni	22.2	ni		(Report [63,77]

ni – not indicated.

First bleaching stage

As aforementioned, the core technology of ECF bleaching of eucalyptus kraft pulp is D-(EPO)-D-D type. However, there are many variations to account for the constraints of each industrial unit, including raw material, etc. Currently, the starting point for bleaching eucalyptus pulp is almost invariably the high content of HexA. These compounds are not removed during the oxygen stage and thus, HexA reaches the first bleaching stage [83,88]. For this reason, many state-of-the-art mills are replacing the conventional first D stage (30 min, 50–70 °C) with an alternative stage [41]. The removal of HexA can be accomplished through an acid treatment (A), an ozone stage (Z), or by increasing temperature in the D stage, Dhot (120 min, 90–95 °C). There are several ways to combine these stages to enhance HexA removal and minimize reagent consumption. Generally, the D stage, when operated at higher temperatures, can also be an Ahot/D combination. The acid stage removes metals that can accumulate and give rise to scale, and are responsible for the decomposition of H_2O_2 in later stages [88].

Ragnar and Lindstrom [43] reported that Dhot technology is more efficient than Ahot/D in terms of reducing reagent consumption, loss of yield, and amount of AOX in effluents and also increasing brightness stability. The comparison of the sequences D-EPO-D, Ahot/D-EPO-D, and Dhot-EPO-D showed a total consumption of ClO_2 as active chlorine (including H_2O_2) of 4.34, 4.14, and 3.74%, respectively. According to this study, the Ahot/D stage achieves a saving of the total active chlorine used in the sequence of about 4.6%, while the saving in the Dhot is 13.8%.

The effects of the Dhot or Ahot/D stages can vary considerably in Eucalyptus kraft pulps, which can be attributed to differences in the composition of the raw material [44]. For similar pulps, D0, Ahot/D, and Dhot technologies showed a similar trend in chemical consumption, with the benefits due to Dhot bleaching technologies being slightly more significant [10]. [42] also reported that the bleaching efficiency with a Dhot stage depends significantly on the type of wood.

Regarding the application of ozone in the first stage, it can be in total chlorine dioxide replacement mode (Z/E) or partial (Z/D) replacement mode [19]. Some variants may include adding an Ahot stage before ozone. Although acid hydrolysis decreases the efficiency of ozone, it has been commercially proven that the introduction of the Ahot stage can reduce the bleaching costs of the Z/EP-D-P sequence [38]. The main motivations for including ozone in Z/EO-D-D and Z/EO-D-P sequences have been the possibility of partially reusing the effluent, the low AOX content of the pulp, and the brightness stability [38]. However, a limited number of mills have implemented Z stages due to low selectivity, which leads to marked degradation of cellulose and consequent loss of viscosity and yield [10]. Additionally, the low efficiency in ozone production has also been an obstacle [37].

Final bleaching stages

After the first bleaching stage, which as mentioned can be D0, Dhot, Ahot/D, or Z, an alkaline extraction (generally EOP) must be followed to remove the oxidized lignin. Regarding the final stage of bleaching eucalyptus kraft pulp, it can be made up of different combinations, typically of the D, Dn/D, D-D, Dn-D, D-, P, or D-E-D type. While the use of three final stages (after the first alkaline extraction) has been popular in the past, the current trend is to use only one or two stages to minimize capital costs. The Dn/D stage is considered just one stage, although it requires an intermediate wash step. Pulps bleached with only one stage have lower capital costs, although they have lower brightness stability and higher operating costs.

Among the two-stage approaches (DD and DP), DP has been considered the most interesting, since it guarantees high final brightness and good brightness stability [15,75,76]. Final bleaching with DP also produces pulp with better refinability and tensile strength compared to DD [26]. Loureiro et al. [35] compared the effects of using D or P in the last bleaching stage of Eucalyptus globulus kraft pulp (D-E-D-D vs. D-E-D-P), concluding that the P stage guarantees lower brightness reversion, better refinability, water retention, and fines.

Washing steps

Pulp washing is a fundamental process in bleaching sequences that takes place in washer equipment and promotes the contact of the pulp suspension stream with the water stream, allowing the dissolved components of the pulp suspension to migrate to the bulk of the solution. The washing stage ends with the separation of the filtrate and the washed pulp, where the consistency of the suspension is one of the washer design specifications. The purpose of the washing steps is to remove NPE as well as dissolved and/or oxidized organic matter during the bleaching stages, since if they remain in the fiber line, the later bleaching stages are hampered, requiring larger amounts of reagents to achieve the same brightness [69]. Thus, the washing steps also prepare the pulp in the best conditions for the next bleaching stage, namely concerning temperature, pH, and composition.

Conceptually, pulp washing is based on 5 basic concepts: dilution, mixing, dehydration, diffusion, and displacement [69]. Dilution consists of decreasing the concentration of NPE and organic matter in the pulp line, by mixing it with a cleaner stream. This allows that when separating the streams at the outlet of the washer, the amount of contaminants transported with the pulp is lower. Dehydration (as well as displacement) involves removing the water from the external pulp solution, and replacing it with cleaner water, to minimize the carry-over of the pulp. In the case of displacement, the water in the slurry is replaced by cleaner water, with the aid of a pressure difference. Diffusion is a mass transfer process, in which the NPE adsorbed on the pulp are removed to the liquid matrix. However, because the diffusion process is slow, the operating residence time is high (~4 hours) [64,69]. At the industrial scale, several configurations of the washing process have been studied, based on countercurrent circulation. The simplest form is the direct countercurrent scheme, but it can also include flow splitting, associated with stage-jump countercurrent washing.

As it requires high amounts of water to wash the pulp, bleaching is the section of the pulp mill with the highest water use, representing up to 50% of the total consumed [18,28], generating about 65% of the effluent produced in the mill [64]. For this reason, it is very crucial to establish efficient washing schemes. To minimize the environmental impact of mills in terms of water utilization, fresh water has been replaced by condensates [28]. These condensates result from the concentration process of the black liquor, by evaporation. Its use in bleaching, as a washing liquid to replace fresh water, has been investigated, especially with regard to pulp quality and the presence of contaminants, such as acetone, methanol, sulfur-based compounds, or volatile organic compounds [86]. Replacing fresh water with condensate did not have noticeable effects on pulp properties, such as brightness, viscosity, and kappa number. It was found that the presence of volatile organic compounds and methanol in the condensates did not significantly affect the COD of the filtrates [85].

Industrial case study

In this section, a state-of-the-art bleaching sequence will be analyzed in detail. The bleaching section follows the sequence O/O-D-E-D-D and the simplified diagram is shown in Fig. 3.

This bleaching sequence begins with two consecutive oxygen delignification (O/O) stages, promoting the extension of the cooking process. This double stage of bleaching promotes an increase in the brightness of the pulp and is followed by washing and pressing [28].

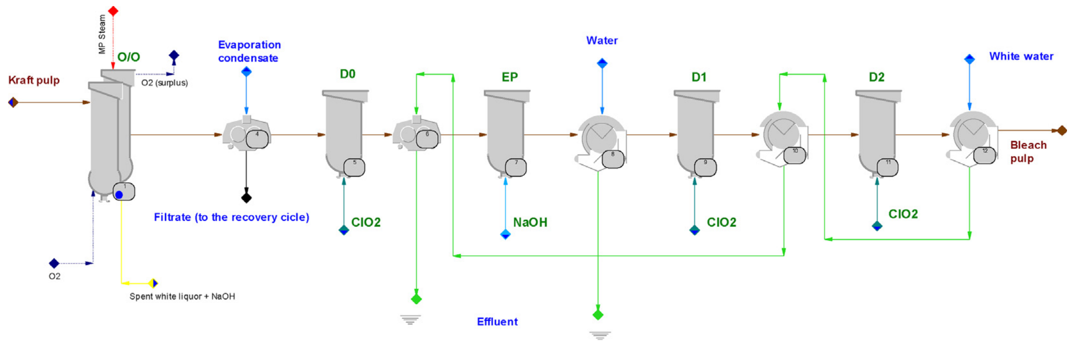

Fig. 3. Industrial bleaching line (case study).

The main aims of washing the oxygen delignified pulp are the removal of organic compounds dissolved in the oxidation stage, as well as sodium (for sodium recovery) and the chemical species that contribute to alkalinity, such as CO_3^{2-} and HCO_3^- anions. The removal of these species is particularly important, since this stream moves to an acid stage, in which the adsorbed NPE tend to migrate to the external solution, with the risk of precipitation of solubility-limited minerals. In the washer equipment after the D0 stage, the objective is to remove and purge the solubilized organic compounds and NPE, to minimize the carry-over along the fiber line. Furthermore, the species that contribute to the acidity of this stream need to be removed, since the presence of these species is associated with corrosion problems in the equipment [80] and excessive use of chemicals in the alkaline stage. After the alkaline extraction stage, it is necessary to remove the organic compounds that were oxidized in D0 and dissolved in the EOP stage. The other target of this washing consists of the extractable constituents of the wood, which remained in the pulp until this stage, such as fats and resins. Most of the lignin present in the fiber is degraded and removed until the alkaline extraction stage, so the last two ClO_2 stages have the function of increasing the brightness stability and attacking the residual lignin, conditioning the pulp for the paper production process. Thus, the purpose of washing after D1 is to remove the compounds that give the pulp acidity, as well as any organic matter that is solubilized. Lastly, the purpose of washing after D2 is to remove chlorides to avoid corrosion problems in the pulp line.

As can be seen in Fig. 3, the pulp suspension from the oxygen delignification is washed with water or condensate and the filtrate continues in countercurrent to the previous washing stage up to the digester. This stage marks the boundary between delignification and the bleaching process itself. The washing liquid from the delignification section is rich in organic compounds solubilized in the cooking and oxygen stages. This filtrate is typically alkaline, and the organic substances present have a high molecular weight [69]. Furthermore, this filtrate is free from chlorides or other organochlorine compounds (potentially formed in chlorine dioxide stages). For this reason, this liquid with a high organic load can be recirculated to the energy recovery boiler. Thus, the formation of AOX is avoided and problems due to scale and corrosion in the boiler are minimized. The condensates resulting from the concentration process of liquid in evaporators can also be reused in other processes, such as washing liquid in the other bleaching stages, allowing the reduction of water utilization. The amount of water to be introduced at this stage must be carefully optimized, to both achieve good washing efficiency and facilitate the concentration process [68].

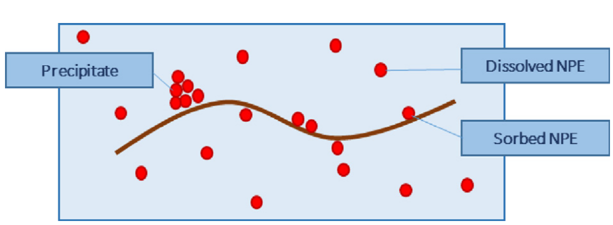

Fig. 4. Scaling and sorption on the fiber wall.

Then, a chlorine dioxide (D0) stage is applied, where the operating pH typically ranges from 2 to 3.5. Chlorine dioxide reacts with the lignin present in the pulp, oxidizing it and giving rise to chlorate (ClO_3^-), chlorite (ClO_2^-), hypochlorite (ClO^-), chlorine (Cl_2), and chloride (Cl^-) species. These species pass to the filtrates in the washing stages, and their concentrations are higher than the recommended chlorinated species content for energy recovery. Therefore, this filtrate must be discharged as liquid effluent.

After bleaching with chlorine dioxide, the pulp goes to an alkaline extraction stage reinforced with oxygen and hydrogen peroxide, where the oxidized lignin is solubilized and can be removed from the pulp stream with a washing process. Alkaline extraction is operated at a pH greater than 10.5. The pH in a basic range promotes the adsorption/ion exchange of NPE on the fiber surface (Fig. 4), as well as the precipitation of minerals such as calcium carbonate ($CaCO_3$), calcium oxalate (CaC_2O_4), or barite ($BaSO_4$). For this reason, the reduction of water use in the washing steps associated with this stage must be done considering the restriction of not reaching saturation for the mentioned and similar minerals [72].

Bleaching ends with two stages of chlorine dioxide. The objective is to remove the chromophore groups present in the pulp. The pH of these stages varies between 3.5 and 5, allowing for the desorption of NPE, as well as the dissolution of some minerals.

The four stages of bleaching are combined with washers. White water from the pulp drying machine is introduced for washing after the last bleaching stage and circulates in countercurrent, to wash all the pulp that leaves a D stage. At the end of this washing line, at the D0 washing equipment, the filtrate is removed from the process, as acidic effluent. This effluent has high concentrations of calcium and other NPE, which are desorbed from the pulp under these acidic conditions. Hot water or condensates from evaporation are used to wash the pulp after the alkaline extraction, resulting in a final basic pH for this effluent, which is discharged separately. These effluents can be treated differently to minimize the possibility of the formation of precipitates or adsorption of NPE on the fibers, since the combination of a high pH (from the washing of EOP) and high concentrations of NPE in the stream to be washed is avoided [28,64].

The selected configuration for the washing has some advantages over the use of direct countercurrent:

- The effluent from the washing of D1 is less loaded than what would result from the EOP if direct countercurrent were used, which increases the driving force in the washing, and, consequently, its efficiency.
- Dividing the filtrate, generating two effluents, minimizes calcium precipitation, as mentioned in Section 1.
- Acid effluent and alkaline effluent can have different destinations depending on the process needs of the mill [69,80].

The evolution of the bleaching sequences led to a significant reduction in water use. The gradual replacement of chlorine-based bleaching reagents with oxygen-based reagents (O, P, and Z) found in TCF sequences, decreased chloride content in alkaline filtrates. Since these filtrates are rich in organic matter and with a low concentration of chlorides, the energetic recovery of the organic load present is possible [30,69].

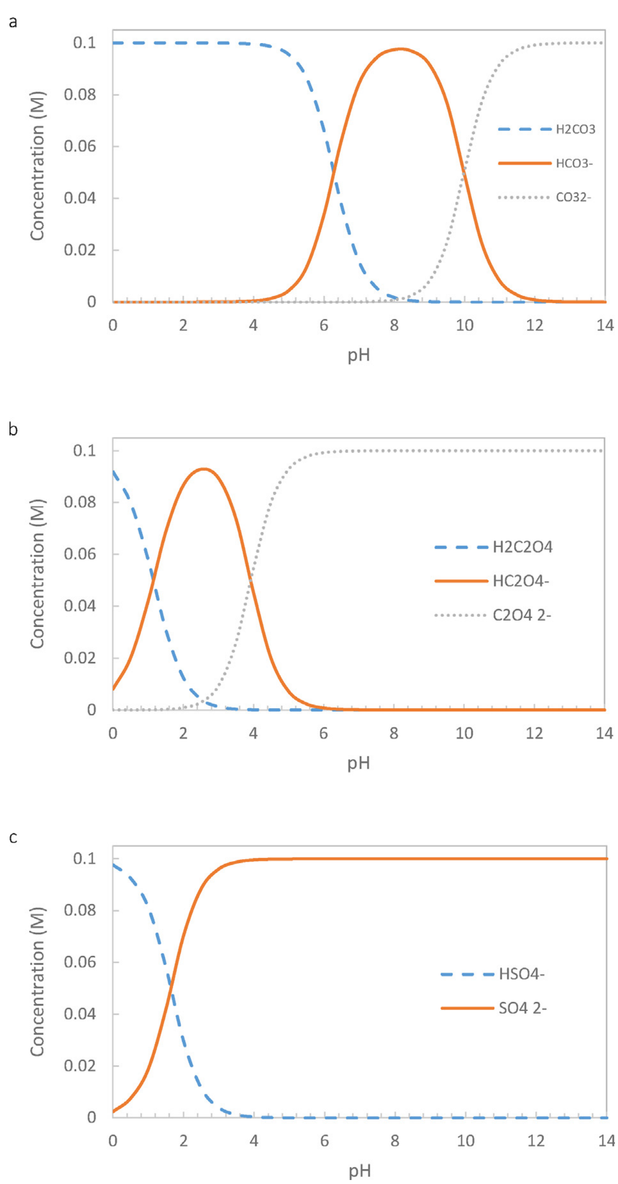

Fig. 5. Speciation of CO_3^{2-} (a), $C_2O_4^{2-}$ (b), and SO_4^{2-} (c) anions in aqueous solution as a function of pH (obtained with Visual Minteq).

Main actions to reduce water use and its impacts

Over the last few decades, the reduction of water utilization in pulp bleaching units has been achieved using a semi-countercurrent pulp washing system. In some situations, fresh water is only used to clean the pulp after the last stage of bleaching. In other situations, the use of fresh water to wash the bleached pulp can be fully replaced by white water, from the pulp drying machine, as seen in the industrial case study (section 4.3, Fig. 3). Furthermore, there has been a reduction in washing flows, minimizing the generation of effluents in the process [28]. However, the reduction of water input in the bleaching sequence has led to an increase in the concentration of organic (from wood) and inorganic species, which end up accumulating in the process. The main NPE that accumulate in the process are calcium (Ca), magnesium (Mg), potassium (K), chlorine (Cl), and barium (Ba) causing several problems in the industrial process [80].

The most relevant organic species with the greatest contribution to the formation of precipitates is oxalate ($C_2O_4^{2-}$), which results from the deprotonation of oxalic acid ($H_2C_2O_4$). Oxalic acid is naturally present in wood, but during the cooking and bleaching process of the pulp, the formation of this species can occur as a result of the oxidation and degradation reactions of lignin [32]. It is estimated that between 250 and 500 g of oxalic acid are formed per ton of pulp in the set of oxidizing stages [66], namely, the stages involving chlorine dioxide and hydrogen peroxide [80]. Among the anionic inorganic species that accumulate in the pulp production process, the sulfate ion (SO_4^{2-}) and the carbonate ion (CO_3^{2-}) stand out.

The accumulation of NPE in pulp production and bleaching plants has negative impacts not only on pulp quality but also on mill operation [28]. The main minerals that can precipitate in a pulp mill with reduced water use are calcium carbonate ($CaCO_3$), calcium oxalate (CaC_2O_4), and barite ($BaSO_4$). $CaCO_3$ tends to precipitate at pH values between 8 and 13, since the carbonate ion is dominant, Fig. 5a, making it possible for its formation and precipitation in the oxygen delignification stages and the stages of alkaline extraction [80]. The carbonate ion appears in the recausticization cycle (associated with cooking), and is available in the process streams for the formation of minerals. Equation (1) describes the formation of calcium carbonate and the solubility product of this mineral in water at 25 °C is 2.8×10^{-9} [71].

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s) \quad (1)$$

In the case of calcium oxalate, the occurrence of this mineral is possible for pH values above 3 and below 12.5. In fact, for pH greater than 3, there is a deprotonated form of oxalate ion in the solution, Fig. 5b. On the other hand, for pH greater than 12.5, all the calcium is mobilized in other reactions [28]. Calcium oxalate can precipitate in various crystalline forms, and the monohydrate form is the most soluble. However, if the pH of the system is lower than 4, the dihydrate form may appear, which is less soluble [24]. Thus, in the bleaching sequence, the highest probability of the appearance of calcium oxalate precipitates occurs in the alkaline extraction stages and the last two stages of chlorine dioxide. Pulp transfer from acidic to alkaline stages, where sodium hydroxide is added, is a critical point where there is a sudden change in the pH, creating the optimal conditions for deposit formation. Thus, it is important to ensure adequate pulp washing to avoid carry-over of the oxalate ion along the fiber line, minimizing the probability of precipitate formation. Equation (2) describes the formation of calcium oxalate and the solubility product of this mineral is 2.7×10^{-9} at 25 °C [71].

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightarrow CaC_2O_4(s) \quad (2)$$

Finally, $BaSO_4$ precipitation can occur for a pH above 2. However, the occurrence of this mineral is less frequent, since the amount of barium in the wood is lower than that of calcium. The sulfate ion is present in the process, resulting from the cooking with sodium sulfate and the use of sulfuric acid to correct the pH in the D stages. When the barite appears in the equipment, its removal is done using "hydro blasting" with caustic detergent and chelating agents, which adds substantial costs to the operation [24]. According to the literature, an approach to minimize the formation of these precipitates involves the efficient debarking of the wood, since several cations are in greater concentration in the bark than in the wood ([4]; [28]. Eq. (3) describes the formation of barite and the solubility product of this mineral is $1.1x10^{-10}$ at 25 °C [71]. Fig. 5c shows the chemical speciation of SO_4^{2-} anions in aqueous solutions as a function of pH. Thus, it can be inferred which precipitates are more likely to form for each pH.

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s) \tag{3}$$

Mineral precipitation can also be prevented by using flocculants or chelating agents, which inhibit the nucleation and growth of mineral crystals. Another alternative involves the use of $Mg(OH)_2$ as a source of alkali, since the Mg^{2+} ion competes with Ca^{2+}, minimizing the formation of oxalates and carbonates [28].

As already mentioned, in addition to precipitation, cations can also interact with the fiber through adsorption processes on its surface. This phenomenon is dependent on the type of ion, and the number of active sites in the fiber. In turn, the amount of active sites in the fiber is dependent on the pH in the solution phase, since under acidic conditions, the carboxylic and phenolic groups tend to be completely protonated, minimizing the existence of active sites for adsorption. Some studies have highlighted the equilibrium of Donnan approach to model the fiber and solution system [72].

One of the limitations of ECF-type sequences is the presence of chlorinated species in the filtrates, which hampers the recirculation of these filtrates to brown stock washing, evaporation, and recovery boiler. Nevertheless, it is possible to reuse alkaline filtrate in the brown stock given some conditions: controlled ClO2 charge in the D0 stage and good washing and purge in D0 washer to results in low chloride content in alkaline filtrate; treatment of recovery boiler ashes and chloride purge to control its content in the circuit and avoid corrosion problems. In the case of TCF sequences, in theory, it is possible to achieve greater reductions in water use, since the filtrates are free from chlorides and can be concentrated and recovered by combustion, resulting in a greater amount of condensate further used as freshwater [28]. However, according to Axegård et al. [3], sequences of the TCF type are less compatible to reduce water utilization, since their reagents are more susceptible to the accumulation of metals and organic species. Despite this, the effluents generated in E sequences can be treated to remove NPE, namely, through precipitation processes with lime or lime mud or by ion exchange [33,80].

Overall, the reduction in the water flow for the washing steps will increase the concentration of NPE in processual streams, which can have two direct consequences: scaling, which leads to frequent plant shutdown (higher operation costs), and sorption on the fiber wall, reducing the fiber quality and the product added

Fig. 6. Negative impacts of closing the water loops in the pulp bleaching section.

value. However, from the interaction with the industrial sector, the authors of this study understood that it may be possible to further reduce the water consumption in the bleaching, if the reduction is applied to strategic points. This can be achieved with process modeling and simulation, which will be detailed in section 5. Fig. 6 represents the direct impacts of water closing in pulp bleaching.

Another way to minimize water use during bleaching is to minimize the amount of NPE that goes through the fiber line as carryover. For this, an efficient debarking of the wood must be carried out, since the concentration of NPE in the green parts (bark, leaves, branches) can be about 10 times higher than in the wood itself [80]. As an example, it is estimated that about 2 t/day of calcium enters a pulp mill together with the wood [24].

Additionally, the utilization of peracetic acid (A) in complement to the O/O delignification stage may have a positive effect on water utilization. In oxygen delignification, lignin degradation occurs mainly, with no attack on the hexenuronic acids present in the pulp, which contribute to its brown color. Peracetic acid can degrade these molecules and may increase brightness before the ClO_2 stages. Thus, the amount of reagents needed for the bleaching itself decreases, also minimizing the amount of water needed for washing [9].

Another possibility to reduce water utilization involves an attempt to take advantage of the alkaline effluent generated, sending it to the recovery boiler. This will only be possible if the chloride content in the effluent is reduced to an acceptable level in the boiler. To this end, some pulp production companies have implemented measures to remove chlorides from this effluent, namely through evaporation followed by electrodialysis, precipitation with lime, acidification or desorption of HCl, and evaporation. However, the efficiency of these processes is not guaranteed [28].

In the case of integrated pulp and paper mills, the replacement of fresh water in bleaching with process water from paper machines, specifically clarified water, has been pointed out by some authors as a measure to achieve further reductions in water use [1] and industrial cases can already be found. This measure is also mentioned among the guidelines of the document on the BAT). Furthermore, this document indicates that measures to reduce water use should be applied gradually, starting with good systematic water management and appropriate treatment of white water, going through saving and replacing fresh water, with advanced treatments and recirculation of white water, and concluding with the in-line treatment of the process water so that it can be recirculated. This document also indicates that there must be good storage capacity to minimize the impact of a possible system crash [77].

In addition, guidelines are indicated on how to operate the bleaching line, to optimize water use, highlighting: i) Oxygen delignification at medium consistency (10–15%) allows for higher selectivity in the bleaching [77]; ii) Use of hydrogen peroxide under optimized conditions for bleaching residual lignin (D2 stage complement) [77].

Future prospects

In addition to the already established BAT, emerging techniques are pointed out, which have been studied at a laboratory or pilot scale, and which are expected to allow additional reductions in water utilization [77], highlighting:

- Leaching the chips with an acidic solution removes the NPE that enters the process through the wood. Thus, it is estimated that the amount of calcium that enters the process can be reduced by about 70%. This measure complements the efficient debarking of wood.

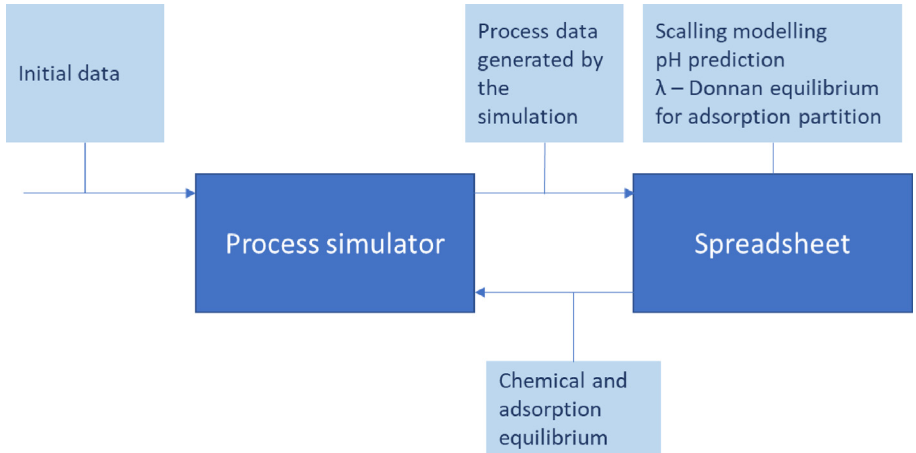

Fig. 7. Methodology proposed by the authors to approach the water minimization in the bleaching area.

- Separation of metal ions from bleaching filtrates through a purge. To this end, ''kidney'' technologies are used, which allow a selective separation of multivalent metal ions. One example is the use of ion exchange processes. Another example involves adjusting the pH of acidic filtrates to the basic range, forming compounds of low solubility that can be removed by filtration or flotation. For the selective removal of organic compounds present in alkaline filtrates, the use of ultra and nano-filtration methods is recommended.

Another alternative for minimizing water use in a pulp production unit involves optimizing the water distribution network for bleaching which was studied by the authors of this review. This hypothesis requires the correct mathematical modeling of the industrial process, so that the water network is properly optimized, allowing identification of the washing configuration that allows the lowest water use, without inducing the adsorption of NPE and the precipitation of minerals. Currently, process software dedicated to the simulation of pulp production units does not predict accurately the pH nor the adsorption and precipitation phenomena. To this end, these simulators must be upgraded with more reliable adsorption models, for example, the Donnan equilibrium model [45], and must be integrated with chemical speciation tools, to allow, in the future, to optimize the water network to be used. Fig. 7 shows an example of integration between a process simulator and an Excel spreadsheet where speciation calculations, pH prediction, and Donnan equilibrium are previously predefined.

Conclusions

In this review, the sustainability data of the most relevant pulp and paper mills were analyzed, with a special focus on water utilization. It was found that most companies follow the rules of the Green Report Initiative (GRI) in the preparation of their sustainability documents. These companies report specific water use in the range of 20–50 m^3/t, which is in line with the BAT document guidelines for pulp and paper production.

Over the last decades, the use of elemental chlorine as a bleaching agent has been progressively replaced by chlorine dioxide (bleaching with D, E, and/or O and P) or other bleaching agents totally free from chlorine. (O, P, Z, and Q).

There has been an effort by the mills to reduce the use of water in bleaching, the main measure has been the washing of pulp in countercurrent and the introduction of an oxygen stage before bleaching. The countercurrent washing scheme allowed the reduction of water consumption by around 50%, compared to the values observed in the 1980 s. Furthermore, the oxygen stage allows the use of filtrates for the boiler, minimizing the need for water for washing the subsequent stages, since these filtrates are concentrated and the resulting condensates can be later integrated into the washing circuits. As the main limitations to the reduction of water utilization, the adsorption of NPE and the precipitation of minerals stand out, once reducing the water flow increases the concentration of the different dissolved species, thus making it easier to reach the saturation product for the different minerals. The water network in the washing (associated with bleaching) can be optimized with simulation tools, to determine the washing configuration that minimizes water use while simultaneously restricting scaling and adsorption. For the reduction of water utilization in the future, further research is required at the lab scale, to refine the implemented models, and then the scale-up is the final step to achieve full scale. LCA can generate valuable data to decide which is the best bleaching sequence in terms of environmental sustainability, and this type of study should be promoted in the future.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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