Impact of wood chip leaching pretreatment on wood chemical composition

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ABSTRACT: The effect of wood chip acid leaching pretreatment on non-process elements removal and its impact on wood chemical components has been examined. Acid leaching treatments were carried out using two different acid pretreatment approaches: (1) acidified water and (2) filtrate from an acidic bleaching stage. Optimization experiments to identify the most suitable leaching conditions with regard to non-process elements removal and chemical oxygen demand generation were performed. The incorporation of an acid leaching stage significantly reduced the non-process elements content in the wood chips. Carbohydrate content and other wood constituents were not negatively affected by the applied pretreatment.

Application: Mills can apply acid leaching pretreatment to the pulping process without degrading carbohydrates and with no major yield loss.

The kraft process is currently the dominant chemical pathway to pulp production. The use of sodium hydroxide and sodium sulfide has a number of advantages over other processes, especially fiber strength and low operational chemical costs. Disadvantages are loss in pulp yield caused by carbohydrate instability and degradation during the alkaline reaction. To minimize these losses, it is important to understand the chemical reactions and the raw material employed in the process. Furthermore, interactions between process conditions and the raw material may be crucial and require special attention.

The harmful action of certain metal ions during the pulping process is of growing concern. These ions may have negative impact on chemical reaction rates, process efficiency, and pulp properties. Wood chips are considered to be the main source of these metal ions (typically referred to as a non-process element [NPE]) that enter the mill [1,2]. Incoming NPEs, such as calcium (Ca), aluminum (Al), silicon (Si), barium (Ba), potassium (K), chlorine (Cl), magnesium (Mg), copper (Cu), iron (Fe), and phosphorus (P), present great potential for mineral scale and deposit formation, recovery boiler corrosion and plugging, increased lime kiln fuel consumption, and pulp quality loss [3].

Ions from the transition metals group of the periodic table generally have deleterious effects in bleaching with hydrogen peroxide because they catalyze its decomposition; this results in reagent waste while triggering the formation of radicals that degrade pulp fiber. Fe and Al restrict brightness development during bleaching and increase brightness reversion in the final bleached pulp [4–11]. Ca has been identified as a delignification inhibitor, which can reduce the rate of wood delignification. One study has even suggested that Ca removal can allow for gains in pulping process yield and pulp viscosity [12].

In the recovery cycle, accumulation of K and Cl causes fouling and corrosion problems while Si, Al, Ca, and Fe increase evaporator fouling. Accumulation of Mg, Si, P, sulfur (S), Mn, Fe, and Al contributes to recausticizing issues, such as poor lime settling and low lime reactivity [13–17].

Considering the damage caused by the presence of NPEs in the wood, it would be desirable to develop alternatives for their removal before they are allowed to enter the pulping process. Removal of NPEs would also offer improvements in the pulping process, pulp bleachability, filtrate recirculation systems, and the chemical recovery cycle. A technique that has shown promise in removing NPEs from wood is acid leaching of the chips before pulping. This approach has potential to reduce the damage caused by NPEs, without negative consequences to the pulp quality. The current work evaluated the impact of wood chip acid pretreatment on wood components and NPE removal.

MATERIALS AND METHODS

Materials

Two contrasting samples of eucalyptus wood chips were employed in this study. Wood A was characterized as a high-quality clone (*Eucalyptus grandis*) for the paper industry because it is easy to pulp and has high pulping yield. Wood B consisted of a mix of inferior-quality eucalyptus clones (*E. urograndis*). The clone quality was based on reported ease of pulping and pulp yield; therefore, easily pulped, high-yield clones were determined to be high quality. Wood A was received as logs from a mill in Minas Gerais, Brazil, and split and processed into wood chips at the Laboratory of Pulp and Paper, Federal University of Viçosa. Wood B was obtained as chips from a pulp mill in Bahia, Brazil.

Leaching conditions and optimization

As suggested by Moreira et al. [18], leaching pretreatment of wood chips was carried out using acidified water at pH 2.0 and temperature at 70ºC. Sulfuric acid (H_2SO_4) was used to reduce the water pH. Experiments were conducted in a factorial 3 × 3 format (three replicates [1, 2, and 3 h] and three liquor/wood [L/W] ratios [4:1, 6:1, and 8:1]). A total of 9 wood pretreatment conditions for each wood sample were evaluated. Experiments were done in triplicate. After treatments, filtrates were collected for NPE content analysis.

Analysis	Method
Metals	TAPPI Standard Test Method T 244 om-88 "Acid-insoluble ash in pulp"
Chloride	TAPPI Standard Test Method T 700 om-93 "Withdrawn - Analysis of bleaching liquors by suppressed ion chromatography"
Wood extractives	TAPPI Standard Test Method T 280 pm-99 "Withdrawn - Acetone extractives of wood and pulp"
Lignin content	Gomide and Demuner [19]
Carbohydrates	Santos et al. [20]
Acetyl groups	Solar, Kacik, and Melcer [21]
Uronic acids	Englyst and Cummings [22]
S/G	Lin and Dence [23]
COD	APHA Standard Test Method 5220 A "Standard method for the examination of water and wastewater"

I. Methods used for analyses in study.

Pretreatment with acidified water and acidic filtrate from bleaching stage

The condition selected from the treatments mentioned previously that was found to partially remove NPEs and to be industrially viable (volume wise) was used to pretreat a larger number of chips using two different leaching approaches. These comparative studies were performed using chips leached with acidified water (leach 1) and acidic filtrate obtained from an acidic bleaching stage (AHT) (leach 2). Nonleached chips (Ref) were used as reference. Acidic filtrate was generated from the bleaching sequence O-AHT(PO)DP. Small pH corrections necessary to bring the pH of the filtrate to about 2.0 were made via the addition of H_2SO_4. After the leaching stage, filtrate was collected and analyzed to quantify NPEs. Chips were then oven-dried and weighed to determine weight loss.

Wood chips and filtrates characterization

Wood chemical composition and NPE removal were evaluated by the methodologies given in **Table I** [19–23].

RESULTS AND DISCUSSION

Leaching conditions optimization

To evaluate the effectiveness of leaching pretreatment, seven major NPEs (Fe, Mn, Cu, Mg, Ca, Cl, and K) were evaluated. **Table II** shows NPE content in the original wood chip material. These NPEs are known to bring negative and positive effects to the pulping process. Negative impacts of Fe, Mn, and Cu are known to be decomposition of bleaching agents, resulting in increased chemical consumption and degradation of fibers. Also, NPE metals Ca, Cl, and K contribute to fouling and corrosion in various sectors of a pulp and paper mill, including digesters and recovery boilers. Positive effect is found when Mn is present because it protects fibers during delignification stages that make use of oxygen derived reagents.

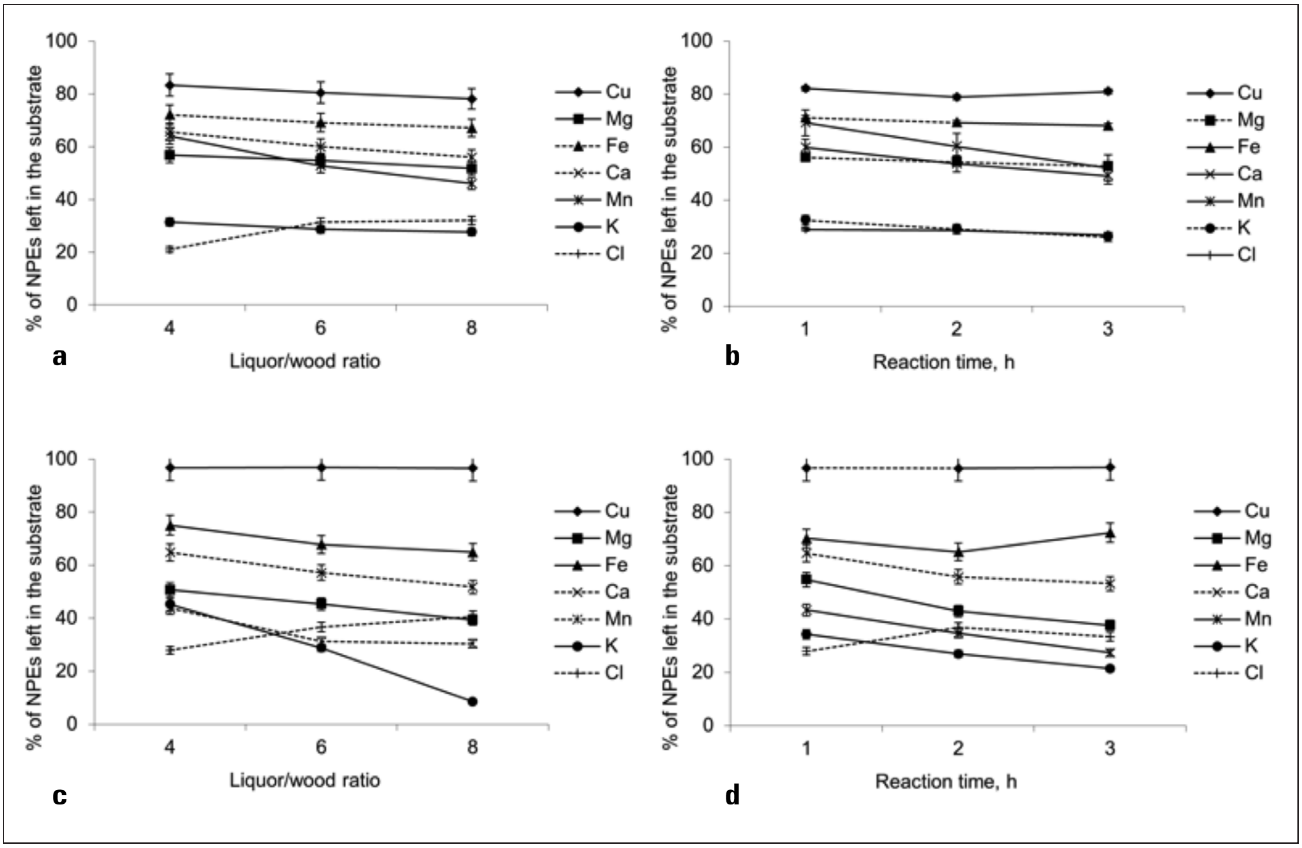
Impact of reaction time and L/W ratio

Wood pretreatment using acidified water was conducted at various times and L/W ratios as described previously. Optimi-

Original Wood Chips	NPE Concentration (mg/Kg)						
	Cu	Mg	Fe	Ca	Mn	K	Cl
A	3.3	96.8	37.6	883.0	33.0	430.9	318.6
B	3.4	84.5	38.7	513.0	52.5	254.0	221.0

Cu = copper, Mg = magnesium, Fe = iron, Ca = calcium, Mn = manganese, K = potassium, Cl = chlorine.

II. Non-process elements (NPE) content of the original eucalyptus chip samples.



1. Impact of liquor/wood (L/W) ratio and pretreatment time on non-process element (NPE) removal for wood A (a and b) and wood B (c and d). Plots a and c are averages of 27 experiments obtained at three levels of reaction time (1, 2, and 3 h). Plots b and d are averages of 27 experiments obtained at three levels of L/W ratio (4, 6, and 8).

zation of the leaching pretreatment was carried out using acidified water. Nine wood pretreatments for each wood sample were performed and evaluated. After each treatment, the filtrate was collected for NPE content analysis according to the methodologies specified in Table I. **Figure 1** shows the metal concentrations remaining in wood samples A and B for each of the leaching times and L/W ratios examined.

Generally, but not for all elements, both the increase in the L/W ratio and the leaching time resulted in enhanced NPE removal. It was also found that increasing the L/W ratio promoted slightly better NPE removal than did increased leaching time.

Other important information to consider from these experiments is the chemical oxygen demand (COD) of the effluent being generated with leaching pretreatment. The filtrate COD results are shown in **Fig. 2**.

Of note, increases in L/W ratio and leaching time both resulted in an increase in the effluent COD. Increased COD is generally undesirable because it results in an effluent with increased organic matter content that needs to be treated before discharge.

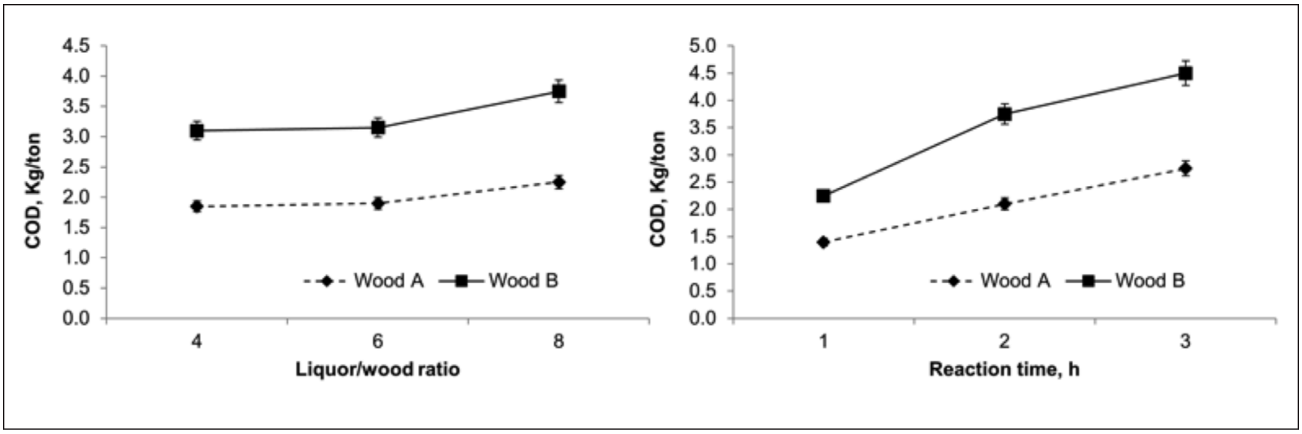
After evaluating the results, the mildest leaching condition was chosen (4:1 L/W ratio and 1 h treatment time). From an NPE removal standpoint, the extreme conditions (8:1 L/W and 3 h leaching) showed better performance. However, from an industrial perspective, the extremes would be unreasonable due to the prolonged operation time required with towers holding unrealistically large amounts of material. The mildest condition also made sense because of its significantly lower COD generation.

Leaching with acidic bleaching stage filtrate

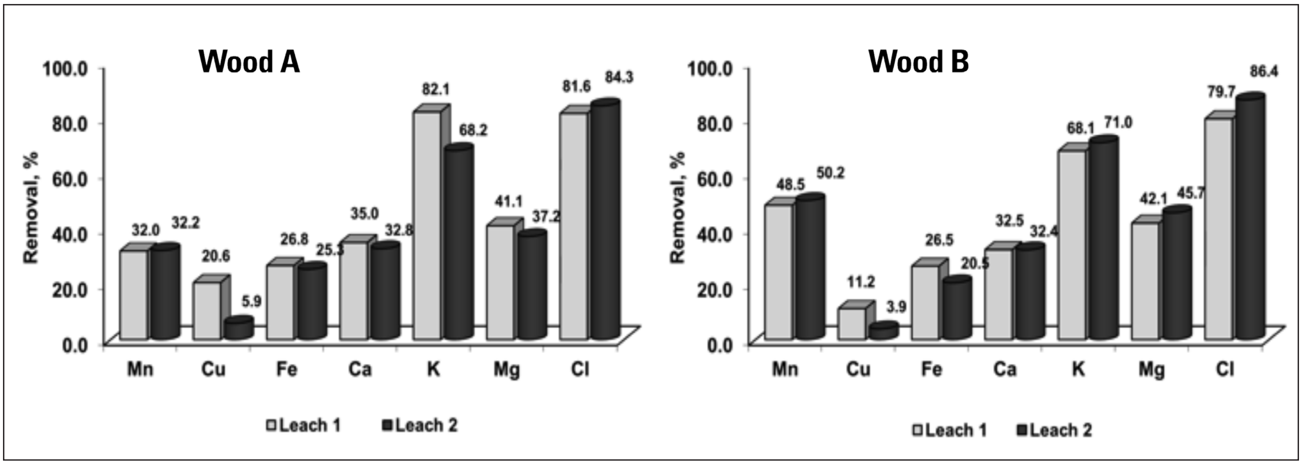
In a mill environment, the use of acidified water to pretreat chips before cooking would result in an undesirable increase in water consumption and a consequent increase in effluent volume. These conditions are contrary to current worldwide policies and practices to reduce water usage in the pulp and paper industry. Thus, the possibility of recirculating effluent from the acidic bleaching stage to pretreat chips was examined.

The conditions used for chip leaching with acidic bleaching effluent were the same as the industrially relevant optimized acidified water conditions determined previously (4:1 L/W ratio and 1 h treatment time). Results comparing the percentage of each of the NPEs removed from the original wood chips for both the optimized acidic water leaching (leach 1) and bleaching effluent leaching (leach 2) experiments are shown in **Fig. 3**.

Potassium removal was good (about 70% for both woods in leach 1 and leach 2). Chlorine concentration was reduced



2. Impact of L/W ratio (average of 27 experiments obtained at three levels of reaction time) and reaction time (average of 27 experiments obtained at three levels of L/W ratio) on effluent chemical oxygen demand (COD) for wood A and wood B.



3. Wood A and B metal removal for leach 1 and leach 2 (4:1 L/W ratio and 1 h treatment time).

by about 85% in the pretreated chips. The significant reduction of both K and Cl should enable the reduction of unplanned shutdowns in the recovery boiler for cleaning and corrosion inspections [3,13,17].

Calcium removal was also significant, amounting to almost 33%. Calcium removal is very advantageous because high concentrations of this metal favor mineral deposit formation (oxalate and calcium carbonate) in the bleach plant, evaporators, and digester [3]. Calcium has also been found to be responsible for a reduction in the delignification rate in the digester, which may lead to losses in yield, viscosity, or both [12].

Manganese and Cu removal were around 40% and 10%, respectively. These two transition metals have a very negative impact on elemental chlorine-free and totally chlorine-free bleaching technology because they catalyze decomposition of oxygen-based reagents [4,5,7,8]. Copper reduction was found to be significantly lower (less than half) for the leach 2 conditions than for the leach 1 conditions.

Magnesium removal provided by leaching pretreatment was also significant (40%). However, it should be noted that Mg removal is not as desirable because its presence reduces carbohydrate degradation during oxygen and peroxide bleaching stages [6]. Nevertheless, it is worth noting that Mg can have a negative impact in the lime kiln by contributing to inert material load increases and consequent rise in fuel usage [14]. High Mg content in lime mud may also cause mud filter pluggage resulting in lower mud solids entering the kiln and a commensurate increase in kiln fuel demand to evaporate the increased water entering the kiln.

Iron removal was one of the lowest in this study (25%), surpassing only the removal of Cu. It must be considered that in wood, Fe is generally present in smaller quantities than other elements. Also, Colodette and others [24] observed that Fe removal is low mainly because it forms a complex with wood components, making it hard to come out in solution.

Removal of NPEs before cooking minimizes their entry into the mill liquor cycle and bleach plant, thus reducing their concentrations in the entire process. As a result, it is reasonable to expect a reduction of deposit formation, corrosion, plugging, and buildup of inert materials in the process.

Effect of acid leaching on wood composition

Removal of NPEs will only benefit the process if wood components are not negatively affected by the acidic pretreatment.

Sample		Wood Composition (% original)										
		Glc	Xyl	Gal	Ara	Man	Extr	Total Lignin	Uronic Acid	Acetyl	Ash	S/G
Wood A	Ref	48.6±0.3	11.5±0.0	0.9±0.0	0.2±0.0	0.9±0.1	0.6±0.0	28.9±0.1	4.7±0.0	2.7±0.0	0.26±0.02	2.80±0.02
	Leach 1	49.6±0.0	12.1±0.1	0.8±0.0	0.3±0.0	1.2±0.1	0.5±0.0	29.2±0.0	4.1±0.4	2.7±0.0	0.18±0.01	2.70±0.05
	Leach 2	48.3±0.3	11.5±0.1	0.9±0.1	0.3±0.0	0.9±0.0	0.6±0.0	29.8±0.2	4.5±0.3	2.7±0.0	0.28±0.02	2.80±0.00
Wood B	Ref	45.9±0.3	12.8±0.2	1.0±0.1	0.2±0.0	1.1±0.1	1.7±0.0	29.5±0.1	5.0±0.4	2.7±0.0	0.18±0.02	2.20±0.02
	Leach 1	46.4±0.2	12.4±0.1	1.1±0.0	0.3±0.0	0.8±0.1	1.4±0.0	29.7±0.5	5.2±0.1	2.7±0.0	0.12±0.02	2.20±0.02
	Leach 2	45.7±0.1	12.5±0.0	1.0±0.0	0.2±0.0	0.9±0.0	1.4±0.0	30.1±0.1	4.8±0.1	2.7±0.0	0.15±0.02	2.20±0.01

Glc = glucan, Xyl = Xylan, Gal = galactan, Ara = arabinan, Man = mannan, Extr = Extractives.

III. Chemical characterization of reference and pretreated samples.

Table III shows the impact of acid leaching pretreatment on wood chemical composition. Some differences between treatments were found but these can be taken as quantitatively minor. The levels of carbohydrates are in accordance with the results obtained by Brelid [25], who found small amounts of carbohydrates in the filtrate of leached wood at 100°C. In a similar study, Moreira et al. [18] reported no changes in the carbohydrates content of eucalyptus after leaching pretreatment. In our study, no measurable yield loss was detected during leaching pretreatment.

Glucan content was higher in chips pretreated with leach 1 for both wood samples; however, this difference was small (0.5% higher for wood B and 1% higher for wood A) and within experimental error (up to 3% for sugar analysis).

Xylan content showed small variations with the acid pretreatments applied. Wood B did not show changes in levels of xylan. Wood A showed a small increase in xylan content for leach 1 that can be assigned by its magnitude to experimental variability. Wood B, which originally had a higher content of xylan, retained this feature after acid leaching.

Galactan and arabinan content was found to be very low and typical for eucalyptus species [26]. Leach 1 and leach 2 did not affect the galactan or arabinan content of either wood A or wood B.

Mannan content was very similar between treatments and wood samples. The results showed no tendency of mannan content to increase or decrease with the application of acid treatments, and the changes observed were minor.

The content of acetyl groups was identical between the original and pretreated woods, clearly demonstrating no influence of acid leaching in the hemicelluloses.

Leach 1 and 2 were both shown to remove slightly more extractives from wood B when compared to the reference. This decrease in extractives level was not observed in wood A, which might be due to the difference in initial extractives content because wood B had three times more extractives than wood A.

Total lignin showed a tendency to increase with the application of acid treatments. This increase was greater with the application of leach 2 (0.6% for wood B and 0.9% for wood A). This increase in lignin with pretreatment using leach 2 may be explained by the existence of dissolved lignin in the acidic effluent where the low pH could have precipitated some of the lignin onto the fiber. It could also be explained by nondetectable yield losses occurring during leaching pretreatment. No changes were observed in the levels of uronic acids with pretreatment; however, both woods differ in terms of uronic acids content with wood B having a higher quantity than wood A.

No changes were detected in the syringyl/guaiacyl (S/G) lignin substructures ratio with the application of these pretreatments (Table III). As discussed earlier, wood A was regarded as of higher quality because of its more rapid delignification rate and better pulping yield. This is confirmed by its higher S/G ratio (2.8 versus 2.2) which results in more reactive and thus easier to remove lignin [20].

The acid leaching pretreatment resulted in a slight decrease in wood ash content, with the exception of leach 2 of wood A, which caused a slight increase of ash. The decrease in ash content was a consequence of the removal of NPEs provided by the pretreatment applied. The slight increase in ash content in the case mentioned previously may be due to the presence of NPEs in the bleaching filtrate.

CONCLUSIONS

Acid leaching of wood chips using acidified water and acidic bleaching stage filtrate considerably reduced the NPE content of the tested samples. Increases in L/W ratio and leaching time resulted in small increases in NPE removal and significant increase in the COD of the effluent. As a result of these results, the mild treatment conditions of a 4:1 L/W ratio and 1-h leaching time were determined to be the industrial significant leaching conditions for NPE removal.

Under the industrial significant treatment conditions, it was determined there were no major differences in the chemical composition of the original and pretreated samples, indicating the leaching pretreatment did not negatively impact the tested samples. No significant differences were noted in the impact of leaching upon high-quality versus lower-quality eucalyptus clones.

Significant differences were noted in the lignin S/G ratio and in the uronic acid content of the higher-quality versus lower-quality clones. The desirable clone had a higher S/G ratio and lower uronic acid content. **TJ**

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ABOUT THE AUTHORS

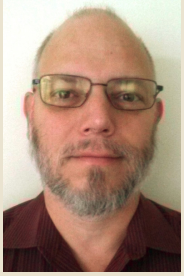
We chose to conduct this research because of an ongoing problem, which is just getting worse as mills tend to reduce the amount of fresh water used. Our work reflects the first time bleaching filtrate was used as a leaching agent.

The biggest challenge we faced was avoiding metals contamination. To address this, the work had to be done using deionized water. We found that acid leaching did not degrade carbohydrates. Furthermore, no major yield loss was detected.

Acid leaching pretreatment can be applied to any pulping process. The next steps are to investigate pulping with leached chips and the process economics.


Santos


Gomide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