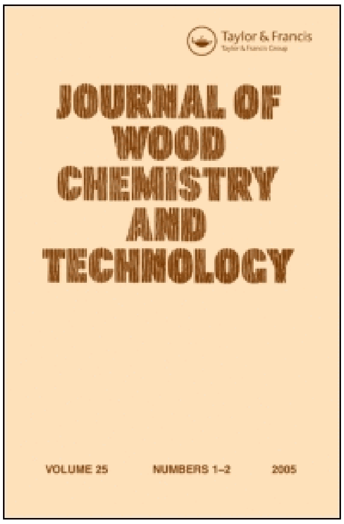

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Effects of Alkaline Treatment on Dissolved Carbohydrates in Suspensions of Norway Spruce Thermomechanical Pulp

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EFFECTS OF ALKALINE TREATMENT ON DISSOLVED CARBOHYDRATES IN SUSPENSIONS OF NORWAY SPRUCE THERMOMECHANICAL PULP

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ABSTRACT

The effects of alkaline treatment on dissolved carbohydrates in suspensions of Norway spruce thermomechanical pulp (TMP) were studied by agitating 1% consistency TMP suspensions at different pH values (5.4 to 12) for 3 h at 60°C, followed by acidification and centrifugation to obtain water samples for analysis. It was found that at pH values above 8, dissolved galactoglucomannans were deacetylated, resulting in their substantial adsorption onto the TMP. Galacturonans began to dissolve from the TMP at pH values greater than 8. The amount of arabinogalactans apparently remained constant throughout the various alkaline treatments. At pH values above 10, arabino-(4-*O*-methylglucurono)xylans began to dissolve from the TMP.

The amount of dissolved and colloidal substances (DCS), measured by TOC, could be substantially decreased by alkaline treatment of filtrate from the 1% consistency suspension, followed by acidification and remixing the filtrate with its original pulp. At 10 m^3/t specific water consumption, the TOC of laboratory-prepared circulation water dropped about 20% due to the alkaline treatment. The decrease in TOC was attributed mostly to the adsorption of deacetylated galactoglucomannans. Alkaline treatment of fiber-free mechanical pulp circulation water may be a useful technique to reduce the amount of organic substances circulating in process waters and leaving the pulp or paper mill in the effluent stream.

INTRODUCTION

In a previous paper[1] we showed that alkaline peroxide bleaching caused significant changes in the sugar composition of carbohydrates released from Norway spruce TMP. Dissolved *O*-acetyl-galactoglucomannans were deacetylated due to the alkaline conditions of peroxide bleaching and were, to a great extent, adsorbed onto the TMP. Anionic polysaccharides were found to be released from the TMP in pulping and peroxide bleaching operations. A major part of the anionic polysaccharides dissolved in unbleached suspensions were heartwood arabinogalactans. The anionic arabinogalactans apparently survived alkaline peroxide bleaching. Furthermore, anionic arabino-(4-*O*-methylglucurono)xylans and galacturonans were released from the pulp due to alkaline peroxide bleaching. Apart from representing a potential yield loss, these anionic polysaccharides can be considered as potential "anionic trash" or "detrimental substances" that may interfere with papermaking operations through complexation with cationic papermaking polymers[2-5].

Acetic acid, formed by deacetylation of dissolved and fiber-bound *O*-acetyl-galactoglucomannans, is probably the most abundant degradation product released from fibers in alkaline peroxide bleaching of Norway spruce mechanical pulp[6-9]. The adsorption of the deacetylated galactoglucomannans represents a potential yield gain that reduces the net yield loss caused by alkaline peroxide bleaching. The adsorption of deacetylated and acetylated glucomannans onto cellulose has been thoroughly studied[10,11]. It is also known that addition of glucomannans to chemical pulp increases sheet strength properties[12]. The purpose of this study was (i) to determine the effects of pH on the carbohydrates dissolved in Norway spruce TMP suspensions and (ii) to determine whether alkaline treatment could be useful in increasing Norway spruce TMP yield by deacetylating dissolved galactoglucomannans, leading to their adsorption onto the TMP.

EXPERIMENTAL

Preparation of Pulp Suspensions and Sampling of DCS

Two different Norway spruce (*Picea abies*) TMP samples (samples 1 and 2) were studied. Both samples were collected from the same point in a pulp mill in March

1990 and 1992, respectively, and stored at -24°C. The consistency of the samples were 41% and 29%, respectively. Sample 1 has been used in previous studies at this laboratory[4,5,8,9,13,14]. Sample 2 was used in a previous study[1] to prepare dirty circulation water from unbleached and peroxide bleached TMP for analytical fractionation of the dissolved polysaccharides. Suspensions (1% consistency) and dissolved and colloidal substances (DCS) were prepared and sampled as described previously[1].

Effects of pH and Alkaline Treatment Time on Dissolved Carbohydrates

In some experiments, suspension pH was controlled during the 3 h and 60°C agitation by using an automatic titrator with 1M NaOH. Suspension pH was always adjusted back to the normal pH range of 5.2-5.5 with HCl prior to centrifugation of the suspension. The resulting supernatant was pipetted off and designated as the DCS sample. The effect of alkaline treatment time was studied by adding 2.75 mmol NaOH (the total NaOH dose used to maintain pH of the suspension at pH 9 in the 3 h constant pH experiments) instantaneously to a 1-L suspension. After different treatment times, 100-mL samples were removed from the suspension, immediately acidified to normal pH, and stirred for an additional 90 min at 60°C. DCS samples were then obtained in the usual manner by centrifugation.

Alkaline Treatment of TMP Suspensions and Filtrates

A 1% consistency TMP suspension and its filtrate were treated with different NaOH charges as depicted in Figure 1. The filtrate was prepared by vacuum-assisted dewatering of the 1% suspension through a paper machine wire, resulting in a pulp mat thickness of 2-3 cm. The filtrate was then passed back through the mat to remove as much fines as possible. Additional water was removed from the mat by squeezing. The final thickened pulp was crumbled and stored 16 h in a closed bag to equilibrate the moisture content. The suspension and filtrate were then treated with NaOH in separate sealed bottles at 60°C and 90°C for 30 min. The initial concentrations of NaOH in the suspension and filtrate samples were 0, 0.2, 2, or 20 mM. After the alkaline treatment, the samples were removed from the hot water baths and acidified to normal pH. The thickened pulp was added back to the filtrate samples to give a 1% consistency suspension. The suspensions were then agitated at 60°C for 90 min and centrifuged to obtain DCS samples for analysis.

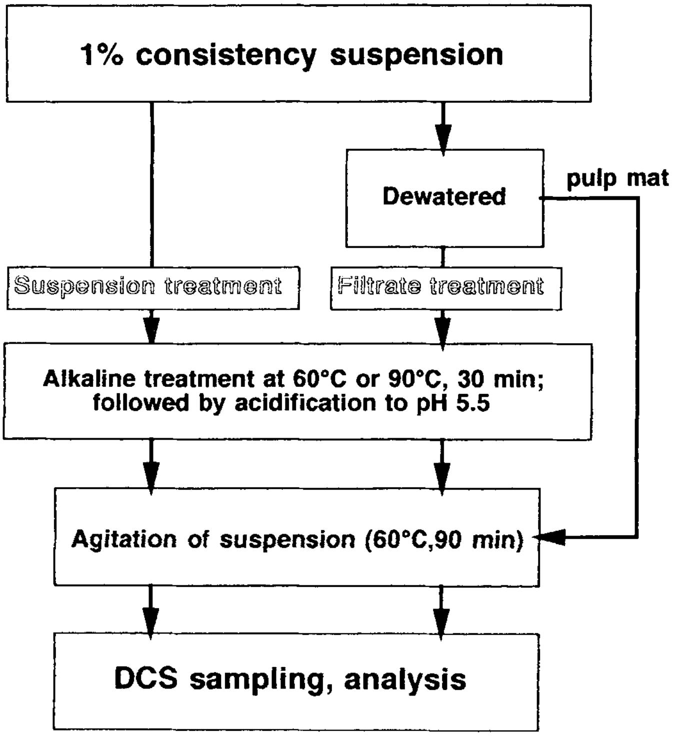

FIGURE 1. Method used to study alkaline treatment of TMP suspensions and filtrates.

Alkaline Treatment of Laboratory-Prepared Circulation Water

The dirty circulation water prepared in a previous study[1] from unbleached TMP was first centrifuged to remove the fines and then treated with 1M NaOH at pH 11 for 30 min at 60°C. The fines were added to the mixing tank, with the next batch of fresh high-consistency TMP, and the acidified filtrate was used to make another 1% consistency suspension. After the suspension was agitated for 30 min at 70°C, a sample was taken and centrifuged to obtain a DCS sample for circulation number 1. The suspension was then dewatered as described previously[1] and the filtrate centrifuged to remove the fines to prepare the next water sample for alkaline treatment. This procedure was repeated without taking samples until the fourth suspension was prepared. DCS samples representing circulations 0, 1, and 4 were then analyzed. The specific water consumption was held at about 10 m^3/t throughout the circulations.

Analysis of DCS Samples

All DCS samples were analyzed according to the methods thoroughly described in the previous paper[1]. Carbohydrates were analyzed using methanolysis of freeze-dried DCS samples, followed by silylation and analysis by GC. Low-molar-mass acids were also analyzed using GC. TOC was measured for all of the DCS samples.

RESULTS AND DISCUSSION

Effects of Suspension pH on Dissolved Carbohydrates

The amount of organic DCS present in the 1% consistency TMP suspension increased with increasing suspension pH (Figure 2). As seen from the increase in acetic acid, deacetylation of the *O*-acetyl-galactoglucomannans appeared to begin at pH values above 8. The amount of carbohydrates present in the DCS samples subsequently decreased but increased for suspensions agitated at higher pH values. Formic acid, probably originating from the degradation of lignin or lignin-like substances[6,7], was liberated to a greater extent in the suspensions prepared at pH values above 10.

The initial decrease in carbohydrate concentration at pH values above 8 can be explained by the adsorption of deacetylated galactoglucomannans onto the TMP (Figure 3). The amount of mannose (Man) units comprising the dissolved carbohydrates decreased considerably when the suspension was prepared at pH 9. At the same conditions, the concentration of galacturonic acid (GalA) units comprising the dissolved carbohydrates increased and steadily rose as suspension pH increased, indicating the release of anionic galacturonans[1]. At higher pH values the amount of mannose and glucose (Glc) units comprising the DCS samples decreased further. The increase in concentration of arabinose (Ara) and xylose (Xyl) units at pH values greater than 10 suggests the release of arabino-(4-*O*-methylglucurono)xylans. Although not presented in Figure 3, increased concentrations of 4-*O*-methylglucuronic acid were

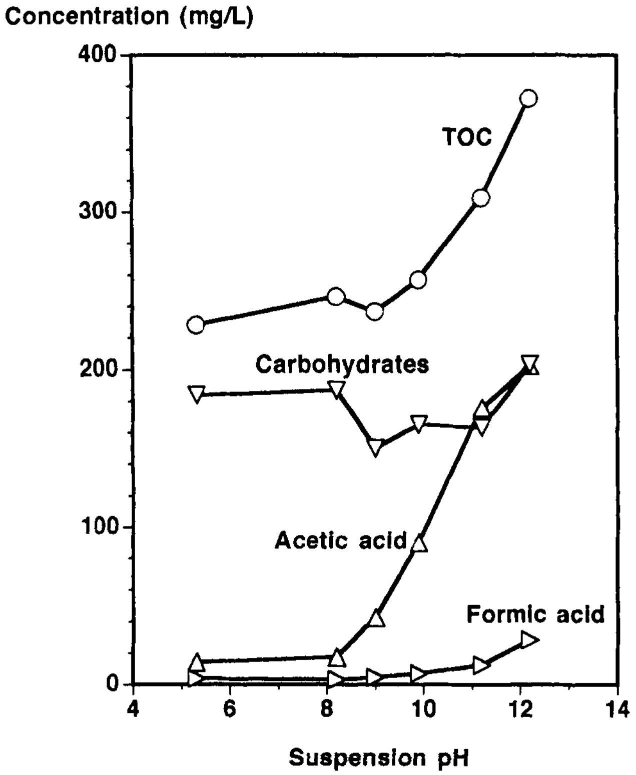

FIGURE 2. Effects of pH on dissolved and colloidal substances (DCS) in TMP suspensions (sampled after acidification to normal pH (5.2-5.5)).

detected in the carbohydrate analysis at the higher pH levels. The amount of galactose (Gal) decreased only slightly over the entire pH range suggesting no change in the solubility of the arabinogalactans. Even at the highest pH values, substantial amounts of mannose were detected in the DCS samples. In general, the trends shown in Figure 3 were in agreement with those reported in our previous study[1].

It is known that isolation of polysaccharides from lignified softwood is very difficult and that arabino-(4-*O*-methylglucurono)xylans are the most difficult to isolate[15]. Usually a delignification step is necessary prior to the alkaline extraction. After KOH extraction of $HClO_2$-delignified wood (*holocellulose*),

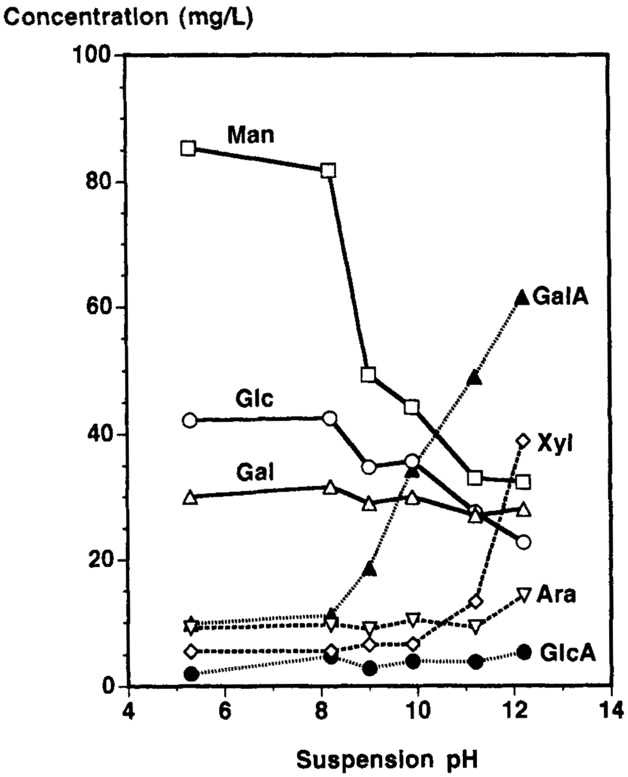

FIGURE 3. Effects of pH on the concentration of sugar units comprising carbohydrates in DCS samples from TMP suspensions (sampled after acidification to normal pH).

galactoglucomannans (Man:Glc:Gal ratio of 3:1:1) and arabino-(4-*O*-methylglucurono)xylans could be isolated from the high-pH extraction liquor[15]. The isolated galactoglucomannan was then referred to as "water-soluble". The material that was not extracted, yet certainly deacetylated by the KOH extraction step, was then extracted with NaOH and borate. From the extraction liquor a galactose-poor galactoglucomannan, referred to as "alkali-soluble", was precipitated with $Ba(OH)_2$ and the Man:Glc:Gal ratio was about 3:1:0.1. Data presented by Sjöström[16] show the Man:Glc:Gal ratios as 3:1:1 and 4:1:0.1 for fractions analogous to those described by Timell[15]. The former galactose-rich galactoglucomannan amounts to 20-50% of the total galactoglucomannans in softwoods[16]. The Man:Glc:Gal ratio for Norway spruce *O*-acetyl-galactoglucomannan isolated from holocellulose with DMSO has been reported as 3.7:1:0.1[17], probably representing a mixture of the two types of galactoglucomannans described by Sjöström[16].

When considering the present results obtained for Norway spruce TMP, the solubility terminology used to describe the different types of galactoglucomannans should be somewhat modified. The thermomechanical pulping process evidently released "water-soluble" *O*-acetyl-galactoglucomannans that upon deacetylation separated into "alkali-soluble" and "non-alkali-soluble" galactoglucomannans. The ratio of the net decrease in Man:Glc:Gal between pH values 8 and 9 was 4.2:1:0.3. About 40% of the mannose units remained in solution at pH 11 and 12, corresponding to the amount of mannose units remaining after peroxide bleaching[1,8]. Perhaps this behavior was due to the presence of two galactoglucomannan fractions similar to those previously reported[15,16]. Larger amounts of galactose-side units would tend to prevent the adsorption of the galactoglucomannan onto the cellulosic areas of the pulp fibers. In our previous paper[1], the ratio of Man:Glc:Gal for the neutral polysaccharides remaining in solution after alkaline peroxide bleaching was 3.4:1:1.4, while prior bleaching the ratio was 4:1:0.6. In both cases, some of the galactose may have been due to neutral arabinogalactans or galactans. Even so, these values are similar to those of the two types of galactoglucomannans described by Sjöström[16]. Isolation of these neutral polysaccharides will be necessary in order to fully understand their sorption behavior and composition in mechanical pulp suspensions.

The dissolution of galacturonans is particularly interesting because of their possible detrimental affects in papermaking[4,5]. It appears that their dissolution begins at the same general pH as the deacetylation of the galactoglucomannans. Native pectic substances are comprised primarily of galacturonic acid units, some of which are methyl esterified[18]. Neutral sugar units such as galactose, arabinose, and rhamnose are typically found in pectic substances. Galacturonans are usually only obtained from pectic substances as subfractions of pectic acid preparations[18]. Like other natural pectic substances, the native pectic substances present in wood are probably partially methylated. The presence of calcium in wood raises the possibility that the pectic substances also exist as calcium salts, known to be insoluble in water[19]. It has been suggested that pectins and calcium together play an important role in lignification of wood cells[20].

Methylated pectic substances are degraded in alkaline solutions by β-elimination reactions which occur side by side with demethylation[18]. The initial release of galacturonans at pH values above 8 suggests that their release is somehow linked to demethylation. The mechanism resulting in the dissolution of galacturonans from TMP at alkaline conditions is uncertain and, based on the previous discussion, is probably complex.

Effects of Alkaline Treatment Time on Carbohydrates in DCS Samples

The NaOH charge chosen in this experiment was the total amount of NaOH needed to maintain the suspension pH at 9 for 3 h in the previous set of experiments. This charge was thought to be a good approximation for the minimum amount of NaOH needed to cause sufficient deacetylation of the dissolved galactoglucomannans. The overall amount of organic DCS in the TMP suspension increased with alkaline treatment time (Figure 4). At 60°C, about 5 min of treatment time was sufficient to cause deacetylation of the galactoglucomannans, resulting in their substantial adsorption onto the TMP (Figure 5). Galacturonans dissolved from the TMP during the course of the alkaline treatment. Compared to the adsorption of the deacetylated galactoglucomannans, the dissolution of the galacturonans proceeded rather slowly.

Improving Mechanical Pulp Yield by Alkaline Treatment of TMP Filtrate

Based on the TOC data presented in Figures 2 and 4, it appears as though no net yield gain can be achieved by treating the entire TMP suspension with alkali (a yield gain would be seen by a decrease in TOC). In order to avoid fiber yield losses, it is probably necessary to first remove the fibers before alkaline treatment of the water containing the *O*-acetyl-galactoglucomannans. The approach used in these experiments was to first deacetylate the dissolved galactoglucomannans using an appropriate NaOH charge. The alkaline-treated filtrate was then acidified back to the normal pH and mixed with its original pulp so that adsorption of the deacetylated galactoglucomannans would occur. As a comparison, alkaline treatment of the entire suspension was included in the experiment. It was found that treatment of the TMP filtrate in this manner resulted in an organic DCS concentration 25% lower than that obtained in the untreated case (at the highest NaOH charge, Figure 6). The 60 mg/L decrease in TOC for the DCS sample, assuming a carbon content of 40%, corresponded to about 1.5% of the original dry weight of the TMP sample.

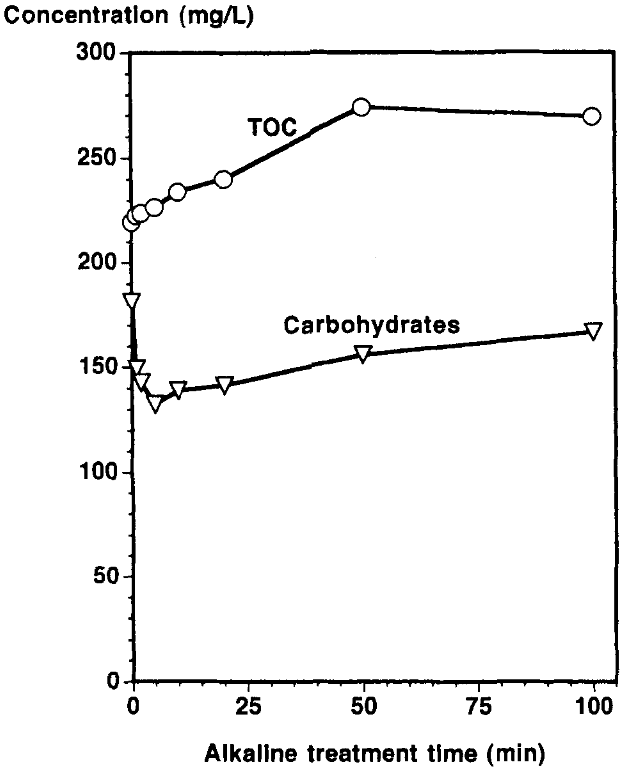

FIGURE 4. Effects of alkaline treatment time on DCS in a TMP suspension treated with 2.75 mM NaOH (final concentration). The suspension was acidified to normal pH and stirred for 90 min before DCS sampling.

Galactoglucomannans were adsorbed onto the TMP due to alkaline treatment of the filtrates (Figure 7) and suspensions (Figure 8). For treatment of the filtrate, the decrease in galactoglucomannans amounted to 72 mg/L (about 0.7% yield increase) and the Man:Glc:Gal ratio for the adsorbed galactoglucomannans was 4:1:0.4, similar to the value reported earlier for neutral polysaccharides present in a DCS sample from unbleached TMP[1]. For alkaline treatment of the suspension, the decrease in galactoglucomannans amounted to 82 mg/L and the Man:Glc:Gal ratio for the adsorbed galactoglucomannans was 3.7:1:0.3, identical to the value reported in our early studies on the effects of peroxide bleaching on organic DCS in TMP suspensions[8]. About

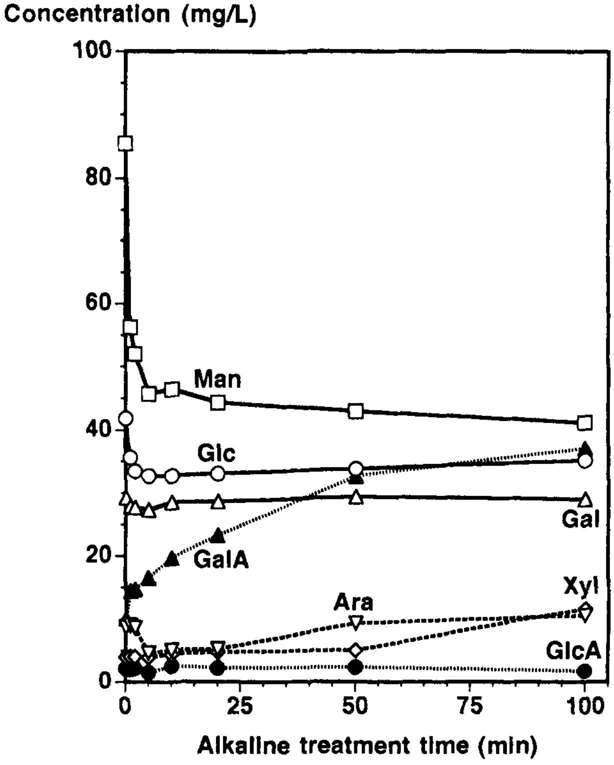

FIGURE 5. Effects of alkaline treatment time on the concentration of sugar units comprising carbohydrates in DCS samples from a TMP suspension treated with 2.75 mM NaOH (final concentration). The suspension was acidified to normal pH, and stirred for 90 min before DCS sampling.

30% of the mannose units remained in solution after alkaline treatment of the suspension, also similar to that presented in our earlier study[8]. As would be expected, the concentration of xylose and galacturonic acid units increased due to the alkaline treatment of the suspension (Figure 8).

The TOC data show a greater potential yield gain than the carbohydrate data. The differences may be explained by the co-adsorption or aggregation of non-carbohydrate substances due to this treatment. In papermaking systems, aggregation of DCS may improve overall process yield because aggregated DCS will be more likely to

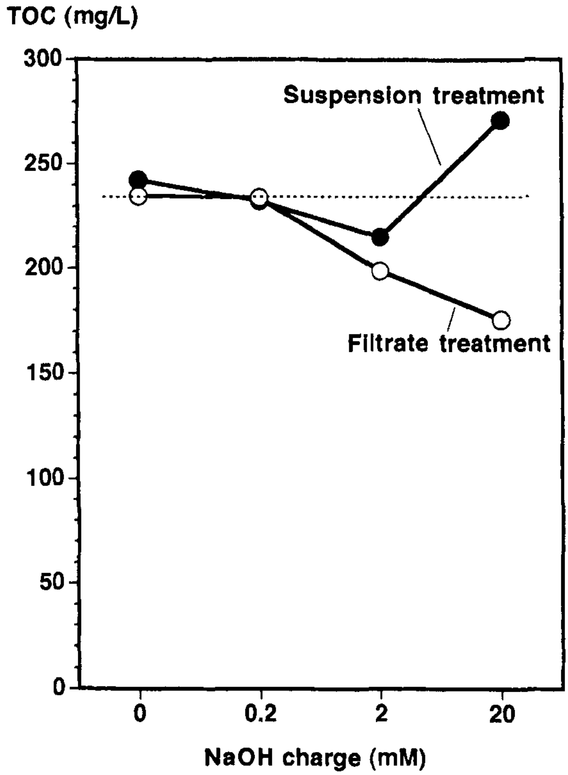

FIGURE 6. Effects of NaOH charge on the amount of organic DCS sampled from TMP suspensions. This is a comparison of the effects of alkaline treatment of the suspension, or its filtrate, prior to final DCS sampling.

be physically retained in the final sheet than non-aggregated DCS. In the present study, the turbidity of the DCS sample, known to be caused mostly by colloidally stable lipophilic extractive droplets[13,14], decreased 40% due to the alkaline treatment of the filtrate sample at the highest NaOH charge. Furthermore, upon addition of 10 mM $CaCl_2$ (molarity calculated based on the final concentration), the turbidity measured after centrifugation dropped to 20% of the value obtained for untreated DCS. This behavior was in agreement with recent observations showing calcium- and lanthanum-induced aggregation of colloidal substances from alkaline peroxide bleached TMP[14]. In the same study, in agreement with earlier results[21], it was found that DCS from

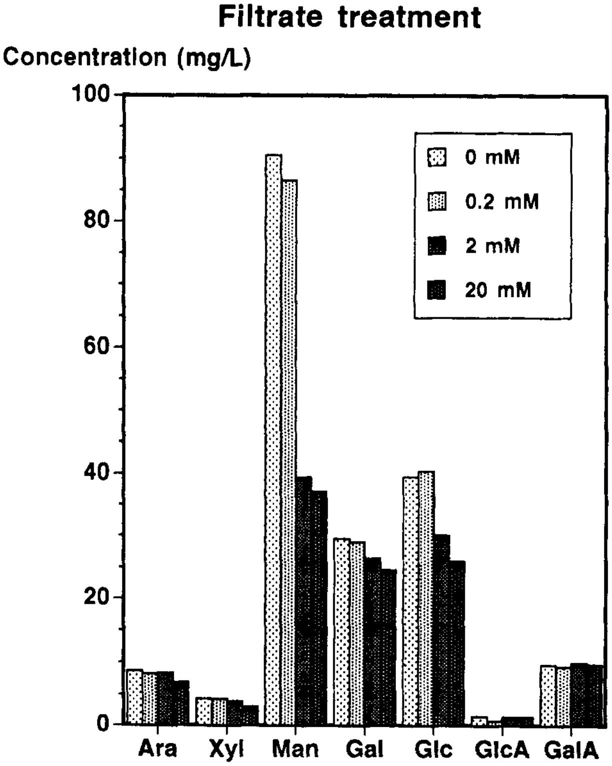

FIGURE 7. Concentration of sugar units comprising carbohydrates in DCS samples obtained via alkaline treatment of filtrates from TMP suspensions.

unbleached TMP were relatively stable in the presence of Ca^{2+}. It is known that water extracts from mechanical pulp can sterically stabilize latex particles[22]. It is possible that changes in the wood polysaccharides caused by alkaline conditions may be responsible for changes in the stability of colloidal substances in mechanical pulp suspensions.

The data obtained for treatment of the filtrates and suspensions at 90°C are not presented because it was found that at the highest alkali charge, substantial carbohydrate degradation took place forming degradation products not detectable by methanolysis. For the highest alkali charge, the amount of carbohydrate degradation at 60°C and 90°C was 9% and 30%, respectively. Also, it was found that addition of 20

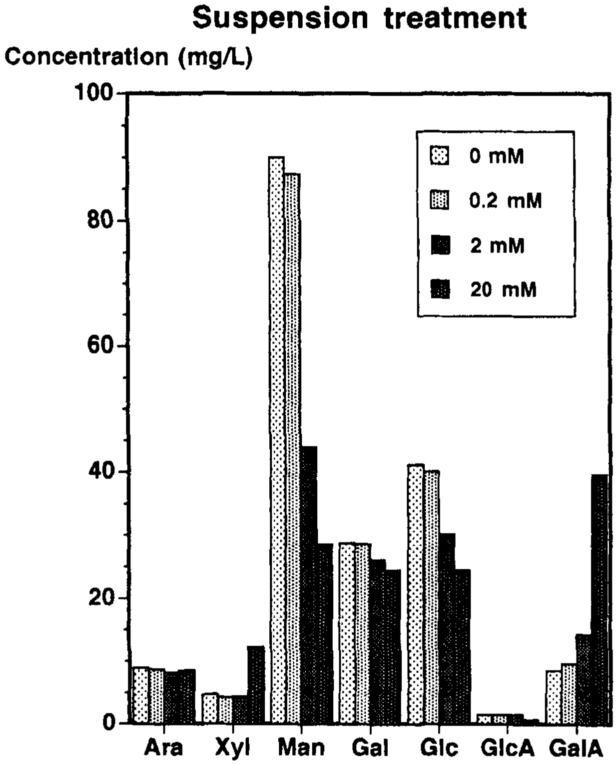

FIGURE 8. Concentration of sugar units comprising carbohydrates in DCS samples obtained via alkaline treatment of TMP suspensions.

mM NaCl resulted in a 9% decrease in detected carbohydrates, demonstrating that the methanolysis analysis was only slightly affected by the presence of salts formed upon acidification of the alkaline-treated samples.

Alkaline treatment of dirty circulation water representing pulp mill water at 10 m^3/t specific water consumption resulted in substantially decreased TOC values (Figure 9). The circulation water TOC dropped about 20% due to repetitive alkaline treatment of the circulation water. The decrease in TOC was due mainly to the decrease in carbohydrates (Figure 9). As expected, the concentration of acetic acid increased with the treatment. The DCS carbohydrates decreased to 65% of their original concentration,

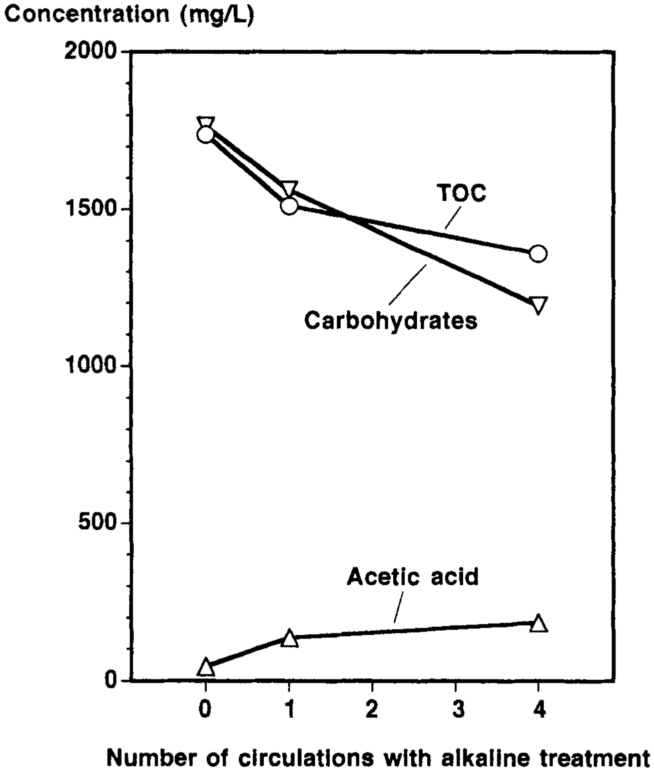

FIGURE 9. Effects of successive alkaline treatments of laboratory-prepared circulation water on DCS circulating in the laboratory water system. Specific water consumption was held at 10 m^3/t throughout the circulations.

mainly due to the adsorption of galactoglucomannans (Figure 10). More than half of the mannose units comprising the circulation water sample remained in solution after the four circulations using the alkaline treatment. It is not certain how low the carbohydrate concentration may have gone if more circulations were carried out, however, it is clear that even after four circulations there was a substantial decrease in dissolved and colloidal substances, probably signifying a pulp yield gain.

This alkaline treatment may be useful for reducing the amount of organic substances leaving mechanical pulp and paper mills in the effluent stream.

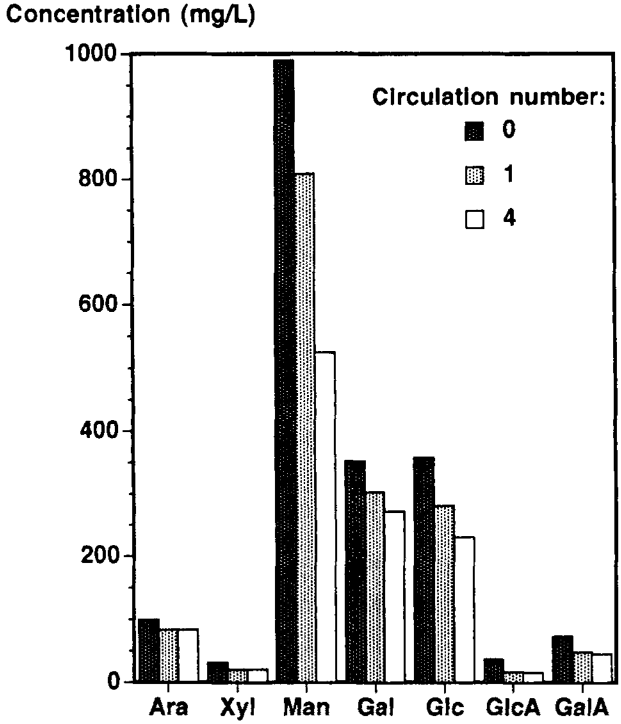

FIGURE 10. Concentration of sugar units comprising carbohydrates in circulation water samples taken before, during, and after the successive alkaline treatments presented in Figure 9.

Furthermore, recent work at this laboratory has shown that a similar alkaline treatment, resulting in deposition of galactoglucomannans onto unbleached mechanical pulp, can result in improved strength properties of the pulp[23]. This may be of particular importance to integrated newsprint mills where required paper strength properties are often obtained by the addition of chemical pulps. Pilot- or mill-scale studies should be done to evaluate the effects of this potential treatment on wet-end chemistry, papermaking parameters such as drainage and retention, and paper properties such as brightness and strength.

CONCLUSIONS

At pH values above 8, dissolved *O*-acetyl-galactoglucomannans are deacetylated and substantially adsorbed onto the fibers in the TMP suspension. Galacturonans begin to dissolve from the TMP at a similar pH. Arabino-(4-*O*-methylglucurono)xylans begin to dissolve from the TMP at pH values above 10. The concentration of arabinogalactans appears to be unaffected by even extreme alkaline conditions. The mechanisms causing these phenomena are not seen from the data presented in this study. However, it is clear that mechanical pulp yield can be increased by galactoglucomannan adsorption without the release of the potentially detrimental anionic substances such as galacturonans and arabino-(4-*O*-methylglucurono)xylans. This can be done by treating fiber-free filtrates from TMP suspensions with sufficient alkali, followed by acidification and remixing the treated filtrate with its original mechanical pulp or fresh mechanical pulp. This simple treatment may be useful for improving mechanical pulp yield and reducing effluent load and may result in improved mechanical pulp strength properties.

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