KRAFT PULPING COMBINED WITH GREEN LIQUOR
PRE-EXTRACTION OF BEECH WOOD

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Beech wood chips were extracted with green kraft liquor at different alkali charges of 1, 2, 3 and 4% on dry wood mass and with hot water. The extractions were performed at 160 °C and different time to achieve 10% wood mass loss. The total content of monosugars in hydrolysed extracts decreased with increasing green liquor charge, but lignin and insoluble solids content increased. The kraft pulp yields from pre-extracted chips with 2, 3 and 4% green liquor charge were similar with those from original wood chips. Effective alkali charges in the pulping process were about 1% to 3.5% lower than in control kraft pulping and reduced with increasing green liquor charge in the extraction process. The addition of AQ in the extraction or pulping process increased pulp yield, especially in extraction. Limiting viscosity numbers of the pulps from chips pre-extracted with green liquor were slightly higher than those of control kraft pulps. Tensile, burst and tear strength of the pulp handsheets from chips pre-extracted with 2, 3 and 4% green liquor charge were the same as or slightly higher than those for original wood chips. The optimal green liquor charge in the extraction process was 2% or 3%, in terms of extraction and pulping process effectiveness.

Keywords: beech wood, pre-extraction, hemicelluloses, kraft pulping, viscosity, strength properties

INTRODUCTION

The conventional kraft pulping technology is focused on the production of papermaking pulps. Lignin, extractives and most of hemicelluloses are dissolved in the kraft black liquor and are an energy source as these components are burned in the recovery boiler in the course of recovery of chemicals.

For economic and environmental reasons, suitable exploitation of all wood components is essential. The pulp and paper industry with its existing infrastructure provides an opportunity to expand the range of products. This can be achieved by transforming chemical pulp mills into integrated forest biorefineries (IFBRs), producing new biomaterials and generating renewable energy, while continuing to meet the growing demand for pulp and paper products. Due to existing infrastructure, the additional costs for realizing a commercial biorefinery can be minimized. In an integrated forest biorefinery, hemicelluloses are partially pre-extracted from wood chips prior to pulping, and can not only offer new feedstock for production of biofuels and chemicals, but also remedy some of the operational problems in pulp and paper mills. The black liquor containing hemicelluloses is currently burnt for producing steam and electricity. The heating value of hemicelluloses is only one half of that of lignin. The pre-extracted wood chips, containing mainly cellulose and lignin can be further delignified. Pre-extraction of hemicelluloses prior to pulping and their conversion to high value added products can improve profitability of pulp production.

In order to realize a biorefinery, the integration of water prehydrolysis of wood chips into the kraft pulping process was suggested. A prerequisite of a successful application of biorefinery is the removal of the desired hemicelluloses, avoiding the degradation of these components and of the final pulp. Much effort has been undertaken to investigate the possibility of hemicelluloses removal prior to alkaline pulping of papermaking pulps. Hot water pre-extraction of wood chips is an effective method of separating fermentable sugars from wood prior to pulping. However, the acidity of the extract leads to significant loss in pulp yield and strength of the final papermaking pulp. These losses can be a result of cellulose degradation, removal of a bulk of hemicelluloses or hemicelluloses of key importance or removal of selected carbohydrates.
susceptible to alkaline degradation. Extraction conditions must be optimized for each wood species to maximize the recovery of monosugars and minimize the degradation of pulp quality. At present, water prehydrolysis for production of papermaking pulp is not commercially utilized, because of cellulose degradation, as well as high investment and energy costs of a water prehydrolysis step.\textsuperscript{11,13}

Other methods of hemicelluloses extraction prior to pulping include near-neutral aqueous pre-extraction at elevated temperatures\textsuperscript{13-14} and alkaline pre-extraction at moderate temperatures.\textsuperscript{15,16} Near-neutral and alkaline pre-extractions are suitable for hardwoods only, as xylan, the main hemicellulose in hardwoods, is dissolved in oligomeric form and can be isolated from the alkaline process liquor, while the softwood galactoglucomannan is rapidly degraded by the peeling reaction during a hot alkaline treatment and, therefore, is lost for further valuable utilisation.

The importance of the biorefinery concept has been well recognized in the pulp and paper industry. However, relatively little work has been performed on extraction and utilisation of hemicelluloses prior the kraft pulping process, besides the commercially used prehydrolysis dissolving pulp process.

The objective of this work was to assess the composition of the hemicelluloses extract and investigate the influence of green liquor charge in pre-extraction on kraft pulping results and pulp properties at 10% wood mass loss in pre-extraction.

EXPERIMENTAL

Materials

Beech wood (\textit{Fagus sylvatica} L.) mill chips were used in this study. Natural dirt was removed (Tappi test method T 265 cm-09) and the chips of 20x20x3 mm dimensions were used for laboratory pre-extraction and kraft pulping experiments.

Method

Hemicelluloses pre-extraction

Wood chips were extracted with hot water and kraft green liquor (GL) at different alkali charge (expressed as Na\textsubscript{2}O) of 1, 2, 3 and 4% on oven dry wood weight (ODW). Green liquor with total titratable alkali (TTA) of 121.7 g Na\textsubscript{2}O/L (156 g Na\textsubscript{2}CO\textsubscript{3}/L, 35 g Na\textsubscript{2}S/L and 3.5 g NaOH/L) was received from a kraft pulp mill. Pre-extraction experiments with green liquor were carried out also with addition of AQ (0.05% on ODW). The extraction experiments were performed in a series of six laboratory autoclaves, each of 0.75 L volume. The autoclaves were filled with 100 g ODW screened beech wood chips. The liquor-to-wood ratio was 4:1. The time to maximum extracting temperature (160 °C) was constantly 60 min and the dwell time at this temperature was in the range of 25 to 45 min. The H-factors of pre-extraction were changed from 220 to 352 h. The H-factors were calculated by the application of the Arrhenius equation, combining the effect of time and temperature similarly to H-factor in kraft pulping.\textsuperscript{17} Under these conditions, 10% of wood mass was removed. After pre-extraction, the residual chips and liquor were separated on a 200 mesh nylon filter. The extraction liquor was collected and stored at 4 °C for further analysis, while the residual chips from one laboratory autoclave were thoroughly washed with tap water and air-dried for determination of wood mass losses. After determining the mass of the extracted chips and the solids, the extraction yield (%) on original chips was calculated. The difference between mass of original and pre-extracted chips was the wood mass loss (%).

Kraft pulping

The pre-extracted beech wood chips from the other autoclaves were pulped after draining the extraction liquor without washing the chips. The volume of residual extraction liquor in the chips was about 1/3 of the total liquor. The kraft pulping experiments were performed similarly to the pre-extraction. White liquor of 25% sulphidity plus fresh water was added to obtain a liquor-to-wood ratio of 4:1 at the required effective alkali (EA) charge. Kraft pulping was performed also with addition of AQ (0.05% on ODW). Effective alkali charge was 11.5 to 14% in kraft pulping experiments on pre-extracted chips and 15% (all as Na\textsubscript{2}O) in control kraft pulping. The control kraft pulping experiments of original beech wood chips were carried out at 170 °C. The heating time to this temperature, from 100 °C, was constantly 90 min and the dwell time was in the range 30-60 min. The corresponding H-factors changed from 432 h to 1122 h. The kraft pulping experiments on pre-extracted wood chips were performed at a constant temperature of 170 °C. The dwell time at this temperature was in the range of 15 to 60 min, and the corresponding H-factors were in the range of 230 h to 918 h.

The pulps were disintegrated in a laboratory pulper and thoroughly washed. The wet pulps were placed in a refrigerator for measurement of total pulp yield. Reject content, kappa number and strength properties of pulps were determined after screening on a laboratory screen with 0.25 mm slots.

Analyses

The pH of the hemicelluloses extracts was determined. To remove insoluble solids, the extract was centrifuged for 60 min at 4500 rpm and the supernatant was collected for analysis. The mass of
insoluble solids in the extract was determined after drying at 105 °C. The original hemicelluloses extract and the extract after one hour hydrolysis with 4% H$_2$SO$_4$ at 121 °C in an autoclave was analysed for monosugars content (xylose, arabinose, glucose, galactose, mannose) by the HPLC method with a refractive index detector (Philips PU 4026), using a cation-exchange resin in Pb form as stationary phase, water (80 °C) as mobile phase. The lignin content of hemicelluloses extract was measured by UV-Vis absorbance at 280 nm, using an extinction coefficient of 20.3 L.g$^{-1}$.cm$^{-1}$ for hardwood. The content of furfural in the extract was determined by a spectrophotometric method.

White liquors were prepared and analysed according to TAPPI test method T 624 cm-85. The effective alkali concentration of the final black liquor was determined according to ISO 302:2004 standard. Limiting viscosity numbers of the pulps were determined according to ISO 5351/1 standard. The kraft pulps were beaten in a laboratory Jokro mill to 30 °SR. The beating degree of the pulps was determined according to ISO 5267-1 standard. The handsheets (80 g/m$^2$) were prepared on a Rapid Köthen sheet former according to ISO 5269-2 and were tested for tensile index (ISO 1924-2), burst index (ISO 2758) and tear index (ISO 1974).

RESULTS AND DISCUSSION
Pre-extraction of hemicelluloses

The conditions of pre-extracting beech wood chips with different charges of green liquor (1, 2, 3 and 4%) and with hot water (0% GL) were selected according to our previous study. The wood mass loss was 10% in all pre-extraction experiments. This is the quantity of the removed wood substance before the kraft pulping process, for which yield and strength properties were approximately equal to those of a control pulp produced using original wood chips.

The extract liquors contain dissolved hemicelluloses, lignin, insoluble solids (condensation products), acetic acid, gluconic acid, furfural, hydroxymethylfurfural, organic degradation products, and residual salts of the used green liquor. The total content of dissolved monosugars (xylose, arabinose, glucose, galactose and mannose), as well as of the xylose and glucose detected in the extracts after hydrolysis, decreases with green liquor charge, as shown in Fig. 1.

The content of total monosugars in the hydrolysed extracts decreased with green liquor charge. The highest content of monosugars was in the hot water extract. The most significant decrease of monosugars content was in green liquor charges of 1% and 2%, when the content was lower by 28.2% and 55.2%, respectively, compared with hot water extraction. At 3% green liquor charge, the content of monosugars was lower by 63.4%, while at 4% green liquor charge, it was lower by 73.2%. With increasing green liquor charge, the hemicelluloses content decreased; this correlates with the increasing pH of the final extracts from 4.1 to 6.7. One of the reasons why degradation reactions under these conditions are more intensive is the formation of saccharinic acids and other products.

Xylan, the major polysaccharide present in hardwood hemicelluloses, was the main component of hemicelluloses extracts (70-75%). The amount of xylose in the extracts decreased with increasing green liquor charge analogously as the total content of monosugars in the hydrolysed extracts (Fig. 1). Pre-extraction with hot water greatly favours the extraction of xylan, while pre-extraction with green liquor favours the splitting off of acetyl groups from the wood and dissolution as sodium acetate.

The glucose content (Fig. 1) was the highest in the hydrolysed hot water extract (0.53% on ODW). With increasing green liquor charge, the glucose content decreased and at 4% green liquor charge, it decreased to 0.22% on ODW. The decrease of the glucose content in the hydrolysed extracts is connected mainly with the increase of the extract pH from 4.1 to 6.7.

The reason is that the acetic acid formed by splitting acetyl groups of hemicelluloses during hot water extraction leads to more intensive hydrolysis and dissolution of glucomannan. Another source of glucose detected after hydrolysis of the extract is starch. Alkaline conditions promote degradation of dissolved glucomannan and glucan or starch, which reduces the amount of glucose detected in alkaline extracts.

Lignin was simultaneously extracted with hemicelluloses as shown in Fig. 2, because a lignin carbohydrate complex was present in wood. The lignin content in extracts increased with increasing green liquor charge. The lignin content in the hot water extract was 0.95% on ODW and at 4% green liquor charge – 1.7% on ODW. The solubility of lignin increased with an increasing pH of the extracts.

The content of insoluble solids in the extracts increased with increasing green liquor charge.
(Fig. 2). Insoluble solids represent condensation products of high molecular degradation products of dissolved lignin. A higher content of insoluble solids was formed for up to 3% green liquor charge. The content of insoluble solids was the lowest in the hot water extract (0.28% on ODW). In green liquor extracts, the content of insoluble solids was about four times higher.

![Figure 1: Total monosugars, xylose and glucose contents in hydrolysed extracts versus green liquor charge](image1)

![Figure 2: Lignin, insoluble solids and furfural contents in extracts versus green liquor charge](image2)

During extraction of hemicelluloses, pentose sugar monomers may dehydrate to furfural and hexose to hydroxymethylfurfural. Furfural and hydroxymethylfurfural content in the extracts depends on the applied extraction agents and extraction conditions. Xylose is the main product of the hydrolysed beech wood extracts. Fig. 2 shows the relationship between furfural content in the extracts and green liquor charge. Furfural content was the highest (0.04% on ODW) in the hot water extracts. With increasing green liquor charge, furfural content in the extracts decreased to 0.01%.

**Kraft pulping**

Hemicelluloses are dissolved in the black liquor during the kraft pulping process. Typically, almost half of the xylan and mannan polymers are lost. Our objective was to utilize these polymers as component sugars, while maintaining the...
composition of the pulp similar to that obtained during conventional kraft pulping with equal pulp yield and strength properties.

The pre-extracted chips (approximately 10% of wood mass loss) were used for subsequent kraft pulping under similar conditions as original beech wood chips, but the charge of effective alkali was lower.

The relationship between the total yield and kappa number of the kraft pulps prepared from original beech chips (control kraft pulping) and those of the chips pre-extracted with hot water (0%) or 1, 2, 3 and 4% green liquor charge (on ODW) is shown in Fig. 3.

With increasing green liquor charge in the pre-extraction of the chips, pulp yields significantly increased. At 4% green liquor charge, the yield of the pulps with the same kappa number was 0.1% higher than that of the control kraft pulp yield. At kappa number 20, the pulp yield from the chips pre-extracted with hot water was 44.2%. In pulping the chips pre-extracted with increasing green liquor charge (1%, 2%, 3% and 4%), the pulp yield in kraft pulping increased gradually from 46.3% to 47.9%, 48.2% and 48.5%. At this kappa number, the yield of the control kraft pulp was 48.4%. The yields of the pulp prepared from chips pre-extracted with hot water were significantly lower than the yield of the control kraft pulp (by 4.2%). The yield of the pulps from the chips pre-extracted with 2% and 3% green liquor charge were about 0.5% and 0.3% lower than the yield of the control kraft pulp (Fig. 3).

Pulp yield increased in the case of green liquor aqueous solutions used for pre-extraction in comparison with hot water. Pulp yield increased especially at about 2% green liquor charge. The yield in the pulping process decreased as a result of carbohydrate removal. Even so, a lower decrease was observed for the pre-extracted chips with green liquor, compared to those with hot water. The total pulp yield, including both pre-extraction and pulping, was obviously lower due to the extracted material in the pre-extraction stage. A significantly lower total pulp yield was obtained for hot water pre-extracted chips.

The pulp yield decrease correlates with the pH of the extracts, which increased with green liquor charge from 4.1 to 6.7. There is a significant loss in the pulp yield when pulping chips are pre-extracted with hot water (0% GL). The hot water extract had the lowest pH and the pulp yields were lower by about 4.2% than the control kraft pulp yields (Fig. 3). Similar results were achieved in our previous experiments. Acid pre-extraction causes random chain cleavage in cellulose and hemicelluloses. The extracted wood components have a lower degree of polymerization and more reducing end-groups. The subsequent kraft pulping conditions of the pre-extracted chips promote increased solubility, peeling reactions and significant yield loss.

Effective alkali charge in kraft pulping was reduced with increasing green liquor charge in the pre-extraction of chips (Fig. 3). The hot water pre-extracted chips were delignified with 14% EA charge, whereas the chips pre-extracted with 4% green liquor were delignified with 11.5% EA charge only. In the control kraft pulping of original beech chips, the EA charge was 15%. Lower EA charge in kraft pulping was applied as due to 10% wood mass loss in pre-extraction, the initial mass of the chips before pulping was lower. Additional reasons for lower EA charge in pulping include higher pH of green liquor extract (approximately 1/3 of the extract in the dissolution of hemicelluloses volume enters pulping) and lower lignin in the pre-extracted chips. At the same kappa number, pulp yields were higher, which led to lower alkali consumption for dissolution of hemicelluloses.

The total monosugars content in the hydrolysed extracts significantly decreased with increasing green liquor charge in pre-extraction (Fig. 1). With regard to kraft pulp yield, the amount of utilisable monosugars, organic and inorganic ballast material, the optimal charge of green liquor in pre-extraction was 2% to 3% on ODW.

The limiting viscosity number of pulp provides an indication of cellulose average degree of polymerisation and about the relative degradation of cellulose in the pre-extraction and in the pulping process. Fig. 4 shows the dependence of limiting viscosity number on kappa number of kraft pulps prepared from original chips (control kraft pulping), from the chips pre-extracted with hot water (0%) and with green liquor charges of 1, 2, 3 and 4% on ODW. The limiting viscosity number of pulp decreased with the decrease of pulp kappa number. Minimal differences were found between the limiting viscosity number of the pulps obtained from control kraft pulping and that of the green liquor pre-extracted wood chips. The conditions of beech wood chips pre-extraction influenced the limiting viscosity number. At the same wood substance removal in the pre-extraction process the pulps prepared from
chips pre-extracted with hot water had the lowest limiting viscosity number. This is related to the highest degradation of the cellulose fraction. On the contrary, the limiting viscosity number of the pulps prepared from chips pre-extracted with green liquor at the same kappa number was higher than that of the pulps prepared from original beech chips (control kraft pulp). A higher limiting viscosity number is related to the lower hemicelluloses content in the pulp, which is confirmed by lower pulp yields (Fig. 3). In the pre-extraction of the chips with green liquor, due to the higher pH, cellulose is not degraded to the same extent as in pre-extraction with hot water.

The limiting viscosity number decreases with increasing H-factor and decreasing kappa number of the pulp. This can be explained in terms of the three phases of delignification. There are several types of reactions of carbohydrates that occur during kraft pulping. Two of them, which damage cellulose to the greatest extent, are alkaline hydrolysis of β-glycosidic bonds and alkaline peeling reaction (removing of end units of the macromolecules of cellulose). Both of them result in the decrease of the polymerization degree and of the limiting viscosity number.
Application of AQ in kraft pulping

Anthraquinone (AQ) is an important catalyst that has been widely used in alkaline pulping for its effectiveness in acceleration of delignification and preserving pulp yield. AQ was added into kraft pulping of original chips (control kraft pulping), into pre-extraction of chips with 2% green liquor charge and into kraft pulping of chips pre-extracted with 2% green liquor charge (Fig. 5).

Figure 5: Total pulp yield versus kappa number of pulps prepared from original beech chips and chips pre-extracted with 2% green liquor charge, followed by kraft pulping with and without addition of AQ in pre-extraction or pulping

Figure 6: Total pulp yield versus kappa number of pulps prepared from original beech chips and chips pre-extracted with 3% green liquor, followed by kraft pulping with and without addition of AQ in pre-extraction or pulping

The results confirmed the positive effect of AQ in protecting the polysaccharides component of wood. The pulp yield of the control kraft pulp at kappa number 20 was 48.4%, whereas with AQ addition the yield was 49.3%. The pulp yield from the chips pre-extracted with 2% green liquor was 47.9%, by addition of AQ into pre-extraction, the pulp yield increased to 49.0%, whereas AQ addition into kraft pulping increased yield to 48.6%. The yield was higher by 0.4% if AQ was added into the pre-extraction process. The yield of the kraft pulp prepared with addition of AQ into pre-extraction was higher by 0.6% than the yield of control kraft pulp prepared without AQ.
The influence of AQ addition into pre-extraction of beech chips with 3\% green liquor charge and into pulping is presented in Fig. 6. The pulp yield from pre-extracted chips at kappa number 20 increased by addition of AQ into the pulping process by 0.5\%, whereas by addition of AQ into pre-extraction by as much as 1.1\%. The yields of the pulps from chips pre-extracted with AQ addition were the same as the yields of control kraft pulp prepared with AQ addition and by 0.9\% higher than the yields of control kraft pulp prepared without AQ.

These results clearly indicate that the presence of AQ in green liquor pre-extraction minimizes the subsequent removal of additional wood polysaccharides in kraft pulping. The yields of the pulps prepared with AQ addition (0.05\%) in pre-extraction were higher approximately by 0.4\% and 0.6\% than the yield of the pulps prepared with addition of AQ in the pulping process.

**Handsheets properties of kraft pulps**

Handsheets were prepared from kraft pulps from beech chips pre-extracted with hot water (0\%) or with 1, 2, 3 and 4\% green liquor charge and from control kraft pulps without pre-extraction. The plots for tensile index, burst index and tear index of the handsheets prepared at a beating degree of 30 °SR at different kappa numbers are shown in Figures 7, 8 and 9, respectively.

The tensile index of the kraft pulps increased with kappa number (Fig. 7). The results show that the tensile index of the kraft pulps (kappa number 20) prepared from green liquor pre-extracted chips are higher or slightly lower (for 1\% charge green liquor by about 1.5\%) than that of the control kraft pulp. On the other hand, the tensile index of the kraft pulps from hot water pre-extracted chips was approximately 12\% lower than that of the control kraft pulps at the same kappa number. Thus, it appears that the tensile index of the pulps prepared from hot water and green liquor pre-extracted chips correlates roughly with the total pulp yield and, consequently, with hemicelluloses content (Fig. 3). The tensile index is a function of interfiber bonding strength.

The burst strength depends on bonding degree and fibre strength, but it is predominantly a function of interfiber bonding degree. The burst index of kraft pulps prepared from pre-extracted chips has a similar development as that of the tensile index. The burst index of the pulps (kappa number 20) prepared from chips pre-extracted with hot water (0\%) and with 1\% green liquor charge was 18\% and 6\% lower than that of the control kraft pulp at the same kappa number (Fig. 8).

![Figure 7: Tensile index versus kappa number of pulps at a beating degree of 30 °SR, prepared from original beech chips and chips pre-extracted either with hot water (0\%) or with 1, 2, 3 and 4\% green liquor charge, followed by kraft pulping](image)

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The slightly higher values of the tensile and burst indexes of the kraft pulps prepared from pre-extracted chips with a higher charge of green liquor indicate that mild alkaline pre-extraction has no negative effect on the bonding ability of the hemicelluloses in pre-extracted pulps. The lower charge of effective alkali in the pulping process has a positive effect on these strength properties, in comparison with the control kraft pulp.

Tearing resistance is known to be dependent on three properties: the total number of fibres participating in sheet rupture, fibre length, and number and strength of fibre-to-fibre bonds. The tear index of kraft pulps decreases with an increasing kappa number (Fig. 9). The tear index of the pulp (kappa number 20) prepared from hot water pre-extracted chips is lower by about 3% than that of the control kraft pulp. The slight gain in the tear index of the kraft pulps prepared from
pre-extracted chips with green liquor may be attributed to the lower hemicelluloses content and lower degradation of cellulose in pre-extraction. These results correlate with the limiting viscosity number of the pulps (Fig. 4).

The results show that the strength properties of the pulp are not altered significantly by pre-extraction with green liquor. However, the negative impact of hot water pre-extraction on tensile, burst and tear strength was confirmed.

CONCLUSION

Pre-extraction of hemicelluloses from beech wood can be used prior to kraft pulping with a green liquor charge higher than 2%, since the near-neutral conditions prevent acetic acid from causing autohydrolysis of cellulose. Hot water extraction releases a higher amount of hemicelluloses, but does so at the expense of the kraft pulp yield and strength properties.

With the same amount of organic matter in the extracts, the hemicelluloses content decreased and the content of lignin and insoluble solids increased with increasing green liquor charge in the pre-extraction of beech wood chips. The most significant was the decrease of hemicelluloses content with up to 2% green liquor charge in pre-extraction (by 55%), when compared with hot water pre-extraction. Pre-extraction of hemicelluloses with green liquor charge higher than 2% had no significant influence on kraft pulp yield, viscosity and handsheet strength properties. The results confirmed that pre-extraction of hardwood with green liquor is a better option than pre-extraction with hot water.

The potential benefit of hemicelluloses pre-extraction with green liquor is the reduction of alkali charge in the pulping process from 15% to 12% EA. The pre-extraction with addition of 0.05% AQ increased pulp yield by about 0.6-0.9%, compared with control kraft pulp.

The advantages of green liquor pre-extraction include the absence of significant degradation of polysaccharides in the extracted wood chips, the availability of green liquor from the recovery cycle of a kraft pulp mill and lower alkali charge in pulping.

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