Effect of Residual Alkali Level in Softwood Kraft Cooking

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Abstract

In washing of softwood pulp, pH is reduced to such low levels that re-precipitation of dissolved lignin may result. It was hypothesized that the lower the residual alkali after cooking, the higher the risk of lignin re-precipitation, which in turn would affect the subsequent oxygen delignification stage negatively. To test the hypothesis, kraft cooks were performed to different residual alkali levels, ranging from 5 to 15 g/l and the delignified chips were subjected to different washing strategies and then oxygen delignified.

However, the results show that even at low residual alkali, lignin stays in solution and only minor amounts of lignin re-precipitate during washing. The amount was irrespective of the residual alkali level in the cook and amounted to 1-2 kappa number units. No effect of residual alkali level was observed on the performance of the oxygen delignification stage.

The residual alkali level affected the lignin concentration in the lumen after cooking. At the low residual alkali level, the lignin concentration in the lumen liquor was equal to the free liquor and as the residual alkali level increased, the lignin concentration in the lumen increased, while the lignin concentration in the free black liquor remained on the same level at all residual alkali levels.

Introduction

Lignin dissolved in the kraft process will re-precipitate when the pH decreases below 10 (Alén et al. 1979; Heijnesson and Grén 2004). The pH at which precipitation occurs depends on concentration and type of metal cation present. For example, above a sodium concentration of 0.5 M, lignin starts to precipitate at pH 9, while precipitation occurs at pH 11 already at calcium concentrations below 0.005 M (Sundin and Hartler 2000). In the washing stage, pH will decrease as the alkaline black liquor is displaced by washing liquor, which can be either water or a slightly alkaline liquor. It can be assumed that dissolved lignin in the entrapped liquor within and surrounding the delignified chips will re-precipitate inside the fibres as well as on fibre surfaces. The lignin concentration is much higher on the fibre surface than in the fibre wall (Heijnesson et al. 1995; Laine 1997; Heijnesson and Paulsson 2003; Jansson and Brännvall 2014). This strongly indicates that lignin dissolved in the black liquor re-deposits onto fibre surfaces. Furthermore, lignin solubility is negatively affected by lower alkali concentration and higher ionic strength and it has been shown that higher sodium ion concentration or lower alkali concentration during cooking increases the concentration of lignin on the fibre surface (Jansson and Brännvall 2014). It has been suggested that lignin originating from the fibre surface is easily leachable by alkali whereas the lignin in the fibre wall is more resistant to leaching. This is based on studies on leaching of unbleached pulp which have shown two phases of lignin leaching; an initial fast removal followed by a phase with slower lignin removal (Favis and Goring 1994; Eriksson and Grén 1997). Increasing the alkali concentration in the leaching increases the rate of lignin removal (Li and MacLeod 1993; Smith et al. 1993; Vilpponen et al. 1993). The fibre wall swells in alkali, due to deprotonation of acid groups in pulp constituents. However, the reason for improved removal of lignin with alkali is not due to the improved porosity by swelling of the fibre wall (Smith et al. 1993; Vilpponen et al. 1993; Sundin and Hartler 2000). The improved solubility of lignin in

alkali is the main reason. An increased alkali concentration reduces the adsorption forces between dissolved lignin molecules and/or breaks up lignin complexes. The colloidal stability of lignin is important, and precipitation of lignin is proceeded by aggregation of dissolved lignin (Norgren et al. 2001). Norgren et al. (2002) have pointed out the importance of having conditions in the digester that promote lignin solubility and avoid irreversible lignin aggregates to deposit on and within fibers. It can be hypothesised that with decreasing residual alkali, the pH will drop faster in the washing stage and should thereby lead to more lignin precipitation affecting the subsequent bleaching stages.

The aim was to study the effect of residual alkali on re-precipitation of lignin in the washing stage and how this affects the subsequent oxygen delignification stage. The goal was to obtain a more efficient oxygen delignification by controlling the residual alkali in the cooking stage and the washing of the pulp.

Materials And Methods

Dried spruce chips, moisture content 8%, were used in the trials. Steel autoclaves were used for the cooking and oxygen delignification trials. Batches of 100 g chips were soaked in deionized water over night and excess water removed prior to cooking. A high sulfidity was chosen, 47%, to ensure that hydrosulfide ions were not the limiting factor. Kraft cooking was performed with the aim to get pulp with kappa number 28 and residual alkali at high (15 g/l), medium (10 g/l) and low (4 g/l) level. Effective alkali and cooking time were varied to reach the desired kappa number and residual alkali levels, see Table 1. The liquor-to-wood ratio was 4.5 L/kg. The temperature profile was an increase in temperature from 25°C to 110°C by 3°C/min. The autoclaves were left to remain at 110°C during 20 min to allow proper impregnation of chips. Subsequently, the temperature was ramped by 3°C/min to cooking temperature 156°C for high and medium level of residual alkali and to 158°C for low residual alkali. When cooking trials at higher ionic strength were performed addition of sodium carbonate was added to the cooking liquor to obtain a concentration of 0.5 M Na₂CO₃.

Table 1
Conditions in kraft cooking. Sulphidity was 47% and liquor-to-wood ratio 4.5 l/kg.

Residual alkali level	EA, %	[OH ⁻]	[HS ⁻]	Addition Na ₂ CO ₃	[Na ⁺]	Temp, °C	H-factor
Low	18.3	1.02	0.31	No	1.32	158	1850
				Yes	1.83		
Medium	21.5	1.19	0.37	No	1.56	156	1310
				Yes	2.06		
High	24.5	1.36	0.42	No	1.78	156	1000
				Yes	2.28		

Washing of delignified chips

Normal lab washing, Fig. 1, was compared to a short wash with either water or 0.1 M NaOH, Fig. 2. The aim was to compare a slow dilution with water (normal lab wash) with a faster dilution with washing liquor. In the normal lab wash of a batch of delignified chips, water is sprayed on top of the chips, slowly rising the water surface from the bottom of the chip column. This is hypothesized to result in an inhomogeneous washing, as the pH probably varies along the chip column as the water rises. With a short wash, a more homogeneous washing should be accomplished, as all delignified chips simultaneously encounter the washing liquor. The fractionation of free, lumen and fiber wall liquors were achieved by pouring delignified or washed chips into a sieve and left to drain for 30 min, thus obtaining the free black liquor. The liquor from within the lumen was obtained by subsequent centrifugation for 10 min at 3500 rpm. The volume of liquor removed by centrifugation and the weight of the delignified and centrifuged chips were recorded. The centrifuged chips were leached with 0.5 M NaOH for 24h to obtain the concentration of dissolved lignin in the fibre wall liquor. Subsequently the leached delignified chips were washed for 10 h with deionized water, dried and the weight was recorded.

Washing of pulp fibres

Washing after cooking was also performed in a more realistic manner, comparable to mill practice. After cooking, the black liquor was separated from the delignified chips by draining. The delignified chips were divided in two portions and transferred to a disintegrator. To one portion, 1500 ml of deionized water was added as washing liquor and disintegration was performed for 1000 revolutions. The other portion was disintegrated with 1500 ml of 0.1 M NaOH. The wash liquor was separated by a funnel and pH and concentration of alkali and lignin were measured. The washing was completed by displacement washing, three times with 800 ml of deionized water. pH and lignin concentration were measured after first displacement.

Oxygen delignification

Oxygen delignification was performed by a two-stage procedure, resembling OxyTrac™ but adapted to lab scale. Oxygen is added in both stages, whereas alkali is only added to the first stage. The aim was to reach a final kappa number of 10-15.

Unbleached pulp samples were placed in polyethylene bags and NaOH, MgSO₄ (2 kg/odt) and water were added, resulting in a pulp consistency of 12%. The bags were closed by heat-welding, kneaded by hand initially and then in a vibrational paint-shaker for uniform mixing of the chemicals. After the mixing, the pulps were removed from the bags and placed in Teflon-coated autoclaves. The autoclaves were closed, pressurized with O₂ to 1 MPa, measured at room temperature, and then placed in an electrically heated glycol bath at 85°C. After 20 min, the autoclaves were removed from the bath and cooled in a water bath. Then they were pressurized with O₂ to 0.5 MPa, measured at room temperature, and placed in the glycol bath, now at 110°C. After 75 min, the oxygen delignification was terminated by cooling in a water bath.

Results And Discussion

Kraft cooking to different residual alkali levels

Kraft cooking was performed aiming at pulp with kappa number 28 and residual alkali at high (15 g/l), medium (10 g/l) and low (4 g/l) level. Effective alkali, cooking time and cooking temperature were varied to reach the desired kappa number and residual alkali levels. Conditions in cooks and the average results from three cooks at each level are presented in Table 2.

Table 2
Conditions in and results from kraft cooking without addition of Na₂CO₃ to cooking liquor. Results are average of 10-11 cooks.

Residual alkali level	Kraft cook			Black liquor			Pulp	
	EA, %	T, °C	H-factor	NaOH, g/l	Lignin, g/l	Dry solids, %	Kappa no.	Yield, %
Low	18.3	158	1850	4.7 ±0.6	64.6 ±1.2	14.2 ±0.3	29.6 ±1.4	49.4 ±0.4
Medium	21.5	156	1310	9.9 ±0.4	64.4 ±1.0	15.6 ±0.6	27.9 ±0.4	49.4 ±0.2
High	24.5	156	1000	15.6 ±0.9	65.3 ±1.0	16.8 ±1.0	27.8 ±0.7	49.1 ±0.4

The effective alkali charge and thereby the residual alkali level had no significant effect on yield. Ribeiro et al. (2019) reported a lower yield when cooking was performed to higher residual alkali level. However, their study was on eucalyptus, which has much higher xylan contents compared to spruce, and with higher alkali charge more xylan is dissolved (Jansson and Brännvall 2011).

The residual alkali level had no effect on the lignin concentration in black liquor. Similar lignin concentration in black liquor was obtained at all levels of residual alkali.

The lignin concentration in the entrapped liquor (lumen and fibre wall) was also analysed. The liquor from the lumen cavities was acquired by centrifugation and the liquor in fibre wall by leaching, according to Brännvall and Rönnols (2021).

As seen in Table 3, the alkali concentration in the lumen liquor was similar to the alkali concentration of the free liquor. The alkali concentration in the liquor after leaching with 20 g/l of NaOH decreased with decreasing residual alkali level. The decrease is not easily explained. The leaching was performed at room temperature and no delignification reactions should occur. Due to the Donnan effect, the alkali concentration is expected to be lower in the fibre wall compared to lumen and free liquor and the fibre wall liquor would thereby dilute the leaching liquor. However, the decrease is larger than what would be obtained by dilution.

Table 3

Alkali and lignin concentration in different liquor fractions, results from one trial at each residual alkali level.

Residual alkali level	Lignin concentration, g/l			Alkali concentration, g/l		
	Black liquor	Lumen	Fibre wall	Black liquor	Lumen	Fibre wall*
Low	64	65	39	4.4	3.4	11.8
Medium	65	71	33	10.2	10.2	13.4
High	66	75	42	15.9	15.4	15.3
*concentration in leachate after leaching with NaOH 20 g/l						

The lignin concentration was lowest in the fibre wall liquor, which is consistent with Brännvall and Rönns (2021). They showed that the lignin concentration in lumen liquor was higher than in fibre wall and free liquor at all degrees of delignification. The results from the present study imply that alkali concentration affects the lignin concentration in lumen as a higher residual alkali concentration resulted in higher lignin concentration in lumen. Consequently, the difference in lignin concentration between lumen and free liquor decreased with decreased residual alkali, so at the lowest level, the concentration in the lumen was equal to the concentration in the free liquor. The diffusion of dissolved lignin from the fibre wall thus seems to be improved when the alkali concentration is higher in the cook.

Washing of delignified chips

The effect of residual alkali in the kraft cook on re-precipitation of lignin in the washing stage was studied by using different washing strategies of delignified chips or defibrated delignified chips. Washing of delignified chips prior to defibration resembles the washing in the washing zone in a digester.

In the normal lab washing procedure of delignified chips, the chips are placed in a washing cylinder and water is sprayed on top of the chips. The water surface slowly rises from the bottom of the chip column until all chips are submerged in water. This should result in an inhomogeneous washing, as the pH probably varies along the chip column as the water rises. With a short wash, with a smaller defined volume of water, it was assumed that a more homogeneous washing would be accomplished, as all delignified chips simultaneously encounter the washing liquor.

After the short washing, the lignin and alkali concentration in the different liquor fractions (free, lumen and fibre wall) were analysed and the results are presented in Table 4. The lignin concentration in the fibre wall was reduced by 50% by washing, going from a level of approx. 40 g/l to below 20 g/l. As in the case after kraft pulping, the concentration of dissolved lignin was higher in the lumen than in free and fibre wall liquor, but after washing the lignin concentration in the lumen was similar at all levels of residual alkali, whereas after cooking the level varied with residual alkali level. Using water or 0.1 M NaOH in the washing had the same effect on the concentration of dissolved lignin in the lumen liquor.

Table 4

Alkali and lignin concentration in liquor fractions after washing with water for 30 min, results from one trial at each residual alkali level.

Residual alkali level	Wash liquor	Lignin concentration, g/l			Alkali concentration, g/l		
		Wash water	Lumen	Fibre wall	Wash water	Lumen	Fibre wall*
Low	H ₂ O	13	33	17	0.7	1.4	11.4
Medium	H ₂ O	12	30	19	1.7	1.6	13.5
	0.1 M NaOH	13	33	15	3.5	3.3	11.1
High	H ₂ O	13	30	18	4.0	2.0	11.8
*concentration in leachate after leaching with NaOH 20 g/l							

The alkali concentration of the entrapped liquor will be affected by the alkali concentration of the washing liquor added. When pulp cooked to a high residual alkali was washed with water, alkali from the lumen and fibre wall were washed out resulting in an alkali concentration of 4 g/l in the water after washing. This is similar to the alkali concentration in the liquor after washing the pulp cooked to a medium residual alkali level with 0.1 M NaOH.

As in the case after kraft cooking, leaching of lignin from the fibre wall using alkali with a concentration of 20 g/l resulted in a much lower alkali concentration in the leachate than what would be expected by dilution of the fibre wall liquor volume. However, the alkali concentration was not dependent on the residual alkali level, the concentration in the leachate was 11-13 g/l in all cases.

In Fig. 4, the distribution of lignin in pulp and dissolved into fibre wall, lumen and free liquor is schematically shown. At a kappa number of approx. 28, the free black liquor contains half of the lignin originally present in wood, one third is in the lumen cavities and 10% in the liquor within the fibre wall. Washing, by dilution with water for 30 min, decreases the amount of dissolved lignin in the fibre wall and lumen liquors by half. Consequently, of the lignin dissolved by cooking, the main part is removed from the pulp in the black liquor and wash liquor and about 20% would remain in the pulp and enter the next washing stage.

The washing procedure after lab cooking is a slow dilution with a large volume of water and it was hypothesised that this would result in an inhomogeneous washing. Adding a much smaller volume of wash liquor was consequently expected to lead to a more homogeneous washing and to a higher pH level within the chips, as all delignified chips simultaneously encounter the washing liquor, and a drastic decrease in pH locally is avoided. Accordingly, less lignin is expected to re-precipitate when a short washing stage is employed compared to standard lab washing procedure.

However, as seen in Table 5, no significant difference in kappa number was obtained whether washing was performed according to standard lab procedure or with a short washing stage with a smaller volume of washing liquor. The assumption that standard lab washing results in more re-precipitation of lignin than washing with a smaller volume is thus not true. Washing with 0.1 M NaOH had no significant effect on the kappa number of the pulp.

Table 5

Effect on kappa number of residual alkali level and treatment after pulping. Average of 1-3 trials at each residual alkali level.

Kappa number									
Residual alkali level	Normal lab wash			Short wash water			Short wash alkali		
	After wash	After leaching	ΔK -no	After wash	After leaching	ΔK -no	After wash	After leaching	ΔK -no
Low	30.6	29.7	0.9	31.0	27.3	3.7	-	-	-
Medium	28.5	26.1	2.4	27.2	26.9	0.3	28.7	26.6	2.1
	28.3	25.4	2.9	26.2	24.2	2.0	-	-	-
High	28.1	25.0	3.1	28.2	26.6	1.6	-	-	-

However, the kappa number determined on pulps after leaching with 0.5 M NaOH for 24 h to obtain the lignin concentration in the fibre wall was significantly lower compared to the kappa number after washing. The leaching is performed at room temperature no delignification reactions should occur. The decrease in kappa number is thus assumed to reflect the amount of lignin re-precipitated during washing in the fibre wall. On average, the difference in kappa number of pulps after washing and after leaching was only two kappa number units. This suggests that very small amounts of lignin re-precipitate during washing. The difference in kappa number was not related to the residual alkali level in cooking.

Washing of pulp fibres

The effect of residual alkali in the kraft cook on re-precipitation of lignin in the washing stage was also studied by different washing strategies performed on defibrated delignified chips, i.e. pulp.

In Table 6, results from washing with water or 0.1 M NaOH at room temperature are shown. Washing with alkali did not affect the concentration of dissolved lignin in the liquor after the first washing step. It was similar whether water or alkali was used as washing liquor. Naturally, the alkali concentration in the liquor was higher when NaOH was used in the water. However, although the pulp was diluted to a consistency of only 1.6% in the washing, the pH of the liquor was 12 to 12.6 when water was used as washing liquor. This should be a sufficiently high pH level for lignin to stay soluble.

Table 6

Effect of washing with 0.1 M NaOH or water at room temperature on the alkalinity and lignin concentration in washing liquors and the kappa number of the washed pulp. Displacement washing was performed with water in all cases. Results from one trial.

Residual alkali level	Washing	Liquor after washing			Displacement liquor		Kappa number	Δ kappa with NaOH
		NaOH, g/l	pH	Lignin, g/l	pH	Lignin, g/l		
Low	H ₂ O	-	12.0	4.6	11.3	0.5	33.3	
	0.1 M NaOH	3.2	12.9	5.3	12.3	0.6	32.1	1.2
Medium	H ₂ O	0.5	12.4	4.4	11.9	0.6	28.2	
	0.1 M NaOH	3.9	13.0	4.6	12.5	0.6	27.6	0.6
High	H ₂ O	0.5	12.6	4.9	11.9	0.7	27.8	
	0.1 M NaOH	3.7	13.1	4.6	12.5	0.6	27.0	0.8

In the second washing stage, a displacement stage, the pH of the displacement liquor was in the range of pH 11.3-11.9 when water was used in the washing and pH 12.3-12.5 when alkali had been used in the first washing stage. The kappa number was 0.5-1 unit lower when washing was performed with alkali. The difference in kappa number is not statistically significant, but a difference was seen at all residual alkali levels, suggesting that washing with alkali has a beneficial effect albeit small.

The diffusion of dissolved lignin from the liquor within the lumen and the liquor surrounding the fibres has been shown to be a rapid process (Andersson et al. 2003). The results from the present study support this, as the kappa numbers of pulps washed as delignified chips, Table 5, or as pulp, Table 6, were similar.

Same washing procedure was performed using a washing liquor with a temperature of 60°C and the results are presented in Table 7. Results from washing of pulps cooked at higher ionic strength (accomplished by addition of sodium carbonate to the cooking liquor) are also shown. Washing temperature had no effect on lignin removal. The lignin concentration in the liquor after washing was similar whether washing was performed at room temperature, Table 6, or at 60°C, Table 7. As in the case when washing was performed at room temperature, washing at 60°C resulted in a reduction of kappa number by 0.5 units when washing was performed with alkali compared to water.

Table 7

Effect of washing with 0.1 M NaOH or water at 60°C on the alkalinity, lignin concentration and kappa number of the washed pulps. The higher sodium ion concentration at each residual alkali level is from a cook with added sodium carbonate to the cooking liquor. Results from one trial.

Residual alkali level	[Na ⁺] in cook	Washing	Liquor after washing			Displacement liquor		Kappa number	Δ kappa with NaOH
			NaOH, g/l	pH	Lignin, g/l	pH	Lignin, g/l		
Low	1.32	H ₂ O	0.1	12.2	4.9	11.5	0.5	25.2	
		0.1 M NaOH	3.2	13.0	5.3	12.2	0.5	24.5	0.7
	1.83	H ₂ O	n.a.	12.0	5.3	11.3	n.a.	27.0	
		0.1 M NaOH	4.4	13.0	5.7	12.3	n.a.	26.7	0.3
Medium	1.56	H ₂ O	0.4	12.4	4.9	11.8	0.8	27.7	
		0.1 M NaOH	3.7	13.0	5.3	12.3	0.7	27.2	0.5
	2.06	H ₂ O	1.0	12.3	5	11.7	n.a.	29.0	
		0.1 M NaOH	3.4	12.9	4.8	12.3	n.a.	28.5	0.5
High	1.78	H ₂ O	1.2	12.6	4.7	11.9	0.6	26.3	
		0.1 M NaOH	3.8	13.0	4.4	12.4	0.6	26.0	0.3
	2.28	H ₂ O	1.3	12.5	4.3	11.9	n.a.	29.2	
		0.1 M NaOH	3.8	12.9	4.3	12.3	n.a.	28.6	0.5

The pulps produced by cooking at higher ionic strength to same H-factor resulted in a slightly higher kappa number, since delignification rate is decreased by increased ionic strength. However, higher ionic strength during cooking did not affect the washing stage.

The results from the washing study show no significant impact of the level of residual alkali on lignin precipitation. There is no effect of residual alkali on the difference in kappa number between pulps washed with water or alkali. As shown by Gomes et al. (2001), pH actually needs to be quite low, < pH 7.5, for lignin precipitation to occur during washing to such an extent that kappa number is affected. The present study showed that the pH remained well above pH 10 even after dilution followed by displacement. This is sufficient to keep dissolved lignin in solution and washing can remove most of the dissolved lignin. Washing with alkali enabled the removal of an additional amount of lignin,

corresponding to one kappa number unit or less. Lignin remaining in the fibre wall liquor requires longer time to diffuse out from the fibre wall.

The difference in kappa number between pulps washed with alkali or water, corresponding to one kappa number unit or less, can be compared to previous research where alkali-leachable lignin was analysed by treating pulp with alkali at 100°C for 60 min. Colodette et al. (2002) reported an effect of residual alkali on the amount of alkali leachable lignin, amounting to 1-2 kappa units higher for eucalyptus pulps cooked to low residual alkali level, 0.1 g/l, compared pulps cooked to high residual alkali level, 10 g/l. Andrade et al. (2013) decreased the kappa number of eucalyptus pulps by 0.5-1.5 units when alkali leaching was performed at 90°C for 90 min. For spruce pulps, a kappa number reduction of 3-4 units was obtained at 100°C for 30 min (Esteves et al. 2021). This together with the present study shows that the residual alkali level has only a minor effect on lignin re-precipitation.

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Oxygen delignification

The hypothesis at the onset of the study was that low residual alkali will cause re-precipitation of lignin in the washing stage and this in turn will affect the subsequent oxygen delignification stage. The results after oxygen delignification when washing after cooking was performed on delignified chips is summarized in Table 8. The kappa number after oxygen delignification ranged from 11 to 13. The end-pH was 11.5.

Table 8
Results from oxygen delignification of pulps washed as delignified chips after cooking. Duplicate trials.

Residual alkali	Washing	Kappa no. unbleach.	NaOH %	Kappa no. oxygen	End-pH	NaOH % / Δkappa	Degree of delignification	Δkappa
Low	normal	29.1	2.91	13.0	11.6	0.180	55.5%	16.1
	short H2O	28.3	2.77	12.1	11.3	0.171	57.3%	16.2
Medium	normal	26.2	2.41	11.9	11.4	0.168	54.6%	14.3
	short NaOH	26.4	2.45	11.7	11.6	0.167	55.7%	14.7
	short H2O	28.3	2.77	11.3	11.4	0.163	60.1%	17.0
High	normal	27.7	2.67	11.5	11.6	0.164	58.5%	16.2
	short H2O	27.2	2.59	12.2	11.5	0.172	55.1%	15.0

The degree of delignification achieved varied from 55 to 60%. However, as seen from Table 8 and Figure 5, neither the level of the residual alkali in cooking nor the washing procedure affected the outcome of the oxygen delignification on a statistically significant level. There is no trend, depending on residual alkali in cooking nor on how the washing was performed. The differences are within experimental error. This is in accordance with the previous study by Colodette et al. (2002) in which the residual alkali level had only a slight effect on oxygen delignification, despite the large difference in high and low residual alkali in their study, 10 vs. 0.1 g NaOH/l.

Oxygen delignification was also performed on pulp washed as pulp fibres after cooking. Results from oxygen delignification of pulps washed at room temperature with either water or alkali are summarized in Table 9. No trend is seen on the performance of the oxygen delignification stage depending on the residual alkali in cooking or on how the washing was performed. The differences are within experimental error.

Table 9
Results from oxygen delignification of pulps washed at room temperature. Duplicate trials.

Residual alkali	Washing	Kappa no. Unbl.	NaOH %	Kappa no. oxygen	End-pH	NaOH % / Δ kappa	Degree of delignification	Δ kappa
Low	H ₂ O	33.3	3.40	13.1	12.0	0.17	60.7	20.2
	0.1 M NaOH	32.1	3.20	12.7	12.0	0.17	60.4	19.4
Medium	H ₂ O	28.2	2.60	11.9	11.0	0.16	57.8	16.3
	0.1 M NaOH	27.6	2.49	12.3	11.3	0.16	55.4	15.3
High	H ₂ O	27.8	2.53	12.0	11.4	0.16	56.8	15.8
	0.1 M NaOH	27.0	2.40	11.4	11.1	0.15	57.8	15.6

The results from washing oxygen delignified pulps at 60°C with either water or alkali are summarized in Table 10. Results from washing of pulps cooked at higher ionic strength are also shown. When cooking was performed without addition of sodium carbonate, the level of residual alkali appears to affect the degree of delignification in the oxygen stage. The higher the residual alkali level, the higher the degree of delignification in the oxygen stage. However, a higher residual alkali level was obtained by a higher charge of effective alkali and since the sulfidity was kept constant, a higher effective alkali charge led to a higher hydrosulfide ion concentration and thereby also a higher sodium ion concentration (see Table 1 for details). So, whether the effect on bleachability depended on an increased hydroxide ion, hydrosulfide ion or sodium ion concentration cannot be distinguished from these experiments. However, when oxygen delignification was performed on pulps produced with sodium carbonate addition to the cooking liquor, the degree of delignification in the oxygen stage was higher compared to bleaching pulps from cooks

without sodium carbonate addition. For the pulps from cooks at higher ionic strength, no apparent effect of the residual alkali level on the degree of delignification in the oxygen stage was observed.

Table 10

Results from oxygen delignification of pulps washed at 60°C. Higher sodium ion concentration at each residual alkali level is by addition of Na₂CO₃ to the cooking liquor. Single trial.

Res. alkali	[Na ⁺]	Washing	Kappa no. Unbl.	NaOH %	Kappa no. oxygen	End-pH	NaOH % / Δkappa	Degree of delign.	Δkappa
Low	1.32	H ₂ O	25.2	2.2	12.1	11.6	0.17	51.9	13.1
		0.1 M NaOH	24.5	2.1	12.4	11.7	0.16	49.3	12.1
	1.83	H ₂ O	27	2.6	11.6	11.3	0.17	57.0	15.4
		0.1 M NaOH	26.7	2.5	10.9	11.1	0.16	59.2	15.8
Medium	1.56	H ₂ O	27.7	2.7	12.8	11.7	0.17	53.9	14.9
		0.1 M NaOH	27.2	2.6	12.2	11.2	0.18	55.1	15.0
	2.06	H ₂ O	29.0	2.7	11.7	10.9	0.16	59.6	17.3
		0.1 M NaOH	28.5	2.6	11.8	11.0	0.16	58.8	16.7
High	1.78	H ₂ O	26.3	2.4	11.2	11.2	0.18	57.4	15.1
		0.1 M NaOH	26.0	2.2	11.3	11.3	0.17	56.5	14.7
	2.28	H ₂ O	29.2	2.8	11.9	10.8	0.16	59.4	17.3
		0.1 M NaOH	28.6	2.7	12.0	10.8	0.16	58.1	16.6

In Fig. 6, the results are presented as the degree of delignification in the oxygen stage as a function of the sodium ion concentration in the cook. The degree of delignification in the oxygen stage seems to increase with the ionic strength in the cook. When pulps produced with addition of sodium carbonate to the cooking liquor were oxygen delignified, the degree of delignification was higher compared to without sodium carbonate addition and plateaued at approx. 59% degree of delignification. The effect of ionic strength in cooking on the degree of delignification in the oxygen stage has previously been observed by Sjöström (1999).

The results can be interpreted as an effect of lignin solubility; higher ionic strength decreases the lignin solubility (Dang et al. 2016; Mattson et al. 2017). This is clearly seen by the higher kappa number of pulps

cooked at higher ionic strength. The ionic strength affects the Donnan equilibrium and thereby the concentration of hydroxide and hydrosulfide ions in the fibre wall; at higher ionic strength the concentration is higher at the reaction site. So, delignification reactions may proceed even more efficiently as more of the active ions are at the reaction site in the fibre wall. However, although the hydrosulfide ions keep on cleaving bonds in the lignin molecules, the hydroxide ions cannot solubilize them at high ionic strength until their molar mass is lower.

The higher the ionic strength, the lower the molar mass needs to be for the lignin to become/remain soluble. In the cooking stage, the residual lignin in the pulp has been degraded by the active cooking chemicals to assumedly same extent independent of ionic strength, but at higher ionic strength the limit for dissolution is at lower molar mass. This is schematically illustrated in Fig. 7. Consequently, the pulp entering the oxygen stage after a cook at high ionic strength has more lignin with lower molar mass. In the oxygen stage, low molar mass lignin will need less oxidation than high molar mass lignin to be solubilized and this is a plausible explanation for the improved degree of delignification with increased ionic strength in the cooking stage.

It should be kept in mind that the sodium hydroxide charge was varied in the oxygen stage, which also affects the degree of delignification. However, the correlation is not as good as for the sodium ion concentration in the cook so it is likely that at least partly the ionic strength in the cook can explain bleachability in the oxygen stage.

The alkalinity in the cook, resulting in different residual alkali, affects viscosity and the chemical composition of the pulp, as seen in Table 11. The viscosity was negatively affected by increased residual alkali. As expected, the xylan content decreased with increased residual alkali since xylan will stay in solution at higher alkali concentrations and not re-precipitate onto the fibres. A higher sodium ion concentration in the cook reduces the xylan solubility resulting in a slightly higher xylan content. The glucomannan content on the other hand was slightly decreased when the cook was performed at higher sodium ion concentration. This can be explained by the suppressed Donnan effect at higher ionic strength, which leads to increased hydroxide ion concentration in the fibre wall liquor and probably to more pronounced peeling.

Table 11

Chemical composition and viscosity of oxygen delignified pulps washed at 60°C as pulp after cooking.

Res. alkali	[Na ⁺]	Washing	Viscosity, ml/g	Relative composition in pulp, %			
				Xylan	Glucomannan	Cellulose	Lignin
Low	1.32	H ₂ O	1090	8.0	8.2	79.3	4.5
		0.1 M NaOH	1068	8.0	8.2	79.2	4.6
	1.83	H ₂ O	1025	8.2	7.7	79.5	4.6
		0.1 M NaOH	1028	8.2	7.6	79.5	4.7
Medium	1.56	H ₂ O	1048	8.0	8.3	79.0	4.8
		0.1 M NaOH	1031	7.8	8.3	79.3	4.6
	2.06	H ₂ O	1044	8.0	8.0	78.4	5.6
		0.1 M NaOH	1000	8.6	8.0	78.4	5.0
High	1.78	H ₂ O	1016	7.1	8.6	79.9	4.4
		0.1 M NaOH	1009	7.1	8.5	79.8	4.5
	2.28	H ₂ O	1017	7.7	8.2	78.7	5.4
		0.1 M NaOH	1006	7.8	8.2	78.6	5.4

Conclusions

The hypothesis at the onset of the study was that a too low residual alkali level will cause re-precipitation of lignin in the washing stage, which would affect the subsequent oxygen delignification stage. Washing after kraft cooking was performed on delignified chips as well as pulp fibres and by using water or alkali as washing liquor. The results show that only very small amounts of lignin re-precipitate during washing, evaluated as lignin removed by alkali, and the residual alkali level had no effect on the amount of re-precipitated lignin. Washing with 0.1 M alkali removed on average more lignin compared to washing with water, the amount corresponding to one kappa number unit. The amount was small, but the difference was consistent. Whether delignified chips or pulp was washed, at room temperature or at 60°C, the difference was observed.

No effect of residual alkali level was observed on the performance of the oxygen delignification stage. However, it appears that the ionic strength during cooking has an impact on the oxygen stage. A higher ionic strength during cooking seemed to increase the degree of delignification obtained in the oxygen stage. The solubility is negatively affected by an increased ionic strength, and it is proposed that lignin with lower molar mass remaining in the pulp after cooking with high ionic strength will more easily be

removed in the oxygen stage. This points to the importance of taking into account the conditions in the cooking stage when optimising the degree of delignification in the oxygen stage.

The residual alkali level affected the lignin concentration in the lumen after cooking. At the low residual alkali level, the lignin concentration in the lumen liquor was equal to the free liquor and as the residual alkali level increased, the lignin concentration in the lumen increased, while the lignin concentration in the free black liquor remained on the same level at all residual alkali levels. After a washing stage, the lignin concentration was highest in the lumen liquor. The concentration was similar at all residual alkali levels.

Declarations

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Figures

Figure 1

Normal lab wash and the procedure to fractionate free and entrapped liquor.

Figure 2

Short wash after cooking and procedure to fractionate free and entrapped liquor.

Figure 3

Experimental set-up for washing trials on pulp fibres.

Figure 4

Schematic presentation of distribution of lignin in pulp and liquor fractions after cooking and washing.

Figure 5

a) Degree of delignification and b) kappa number reduction in oxygen delignification of pulps washed as delignified chips after cooking. Results based on two trials at each residual alkali level.

Figure 6

Degree of delignification in the oxygen bleaching stage vs the sodium ion concentration in the cook. For Hi[Na⁺] cooks, sodium carbonate was added to the cooking liquor. H₂O and NaOH denotes washing with either water or alkali after cooking.

Figure 7

Schematic illustration of the amount of lignin dissolved and remaining insoluble in cooking and oxygen delignification stages.