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Oxygen and Peroxide Bleaching of Wheat Straw Soda AQ-Pulp From Shouguan Paper Mill

1. Raw Materials

We got from Shouguan Paper Mill about 10 kgs of air dried pulp from the actual production, filtrate from the bleach line and a sample of well water used in the mill.

1.1 Raw Material Analysis

See Table I.

The metal content, in particular calcium, magnesium and iron of pulp sample was extremely high. Pulps prepared from wheat straw supplied by Shouguan Mill but prepared in our laboratory, had only about 1/3 of the metal content. The well water contains some calcium and magnesium as well but it is more or less free from heavy metals.

The ash content of the pulp is high as well. Most of this is SiO_2. This indicates that the raw material was heavily soiled. After additional washing, the Kappa number of the pulp was 19 which is much higher than what can be achieved in standard wheat straw pulping. Soda anthrachinon cooking of the Shouguan raw material in Raleigh as well as in Hamburg resulted in Kappa numbers in the area of 13.

2. Pulp Bleaching

The pulp was first subjected to an acid wash and then we started OP bleaching trials, but we had to realize that the pulp was not bleachable to an acceptable brightness level just in one stage. We were able to obtain a final brightness of 72 % ISO charging more than 15 % peroxide. This of course is not acceptable for a commercial operation and so we decided to conduct a fairly mild oxygen delignification to Kappa number 13 which may be the normal lignin after standard soda AQ cooking of wheat straw. Different alkali charges in oxygen delignification were applied. 1.5 % NaOH was required to yield a Kappa number of 13 in 16 minutes reaction time at 90° C. This was followed by an acid wash and an OP stage charging 5 % H_2O_2. Results are given in table 1. The Kappa number after the starting oxygen delignification was 12.9 and pulp viscosity was 861 ml/g. Conditions applied in OP bleaching were quite drastic. The Kappa number dropped to 2.5. Magnesium sulphate and Heptol were not able to stabilize the peroxide which was more or less completely consumed. The resulting brightness was 67 % ISO which does not meet the minimum requirements for wood-free writing and printing papers.

Instead of OP bleaching we applied a pure P stage charging 5 % peroxide, as well. We tested different combinations of stabilizers and charged different amounts of Heptol. OP bleaching was conducted at 90° C and 3 h reaction time. In some trials the acid wash in between the two bleaching stages was replaced by a removal of heavy metals using EDTA. Results are listed in table 2. The results show that magnesiumsulfate in P stages is more efficient than Heptol is. For heavy metal removal an acid wash is more effective than a Q stage. But in general all bleaching results are very poor and do not accomplish the requirements.

In additional trials we applied different conditions for heavy metal removal from pulp. The starting material was the oxygen delignified pulp, Kappa number 12.9. Acid washing was done at two different starting pH levels: 2.5 and 2.1. Treatment time was 30 min at 70° C and 5 % consistency. Table 3 shows the corresponding results. Heavy metal removal by an acid wash is more effective than by a Q stage. In a Q stage calcium remains in the pulp to a higher extent. In all treatments iron is very stable, even when drastic conditions are applied. There are only marginal differences by varying the pH between 2.5 and 2.1.

Conditions applied in wheat straw bleaching applied so far were not able to yield an acceptable brightness level. Therefore we intensified once more the treatment conditions in acid washing as well as in OP and P bleaching (table 4). One treatment was conducted charging 5.5 % sulphuric acid which resulted in a pH of 2.5 and in two treatments the sulphuric acid charge was 7 % yielding a pH of 2.1. In these treatments the temperature was increased from 50 to 70° C. In the OP or P treatment after the A1 stage, temperature was 100° C at 4 h reaction time. After A2 treatment the final OP stage was conducted at 120° C and 1 h reaction time. Different stabilizers were charged. More drastic conditions yielded better results. An acid wash for heavy metal removal is necessary and the best stabilizing agent is magnesium sulphate and sodium silicate. When peroxide is applied instead of an OP stage, pulp brightness becomes poorer (table 5).

The results obtained were not satisfying. Therefore the conditions in oxygen bleaching were intensified to achieve a lower Kapper number and better final bleachability of the pulp. Table 6 shows that by increasing the sodium hydroxide charge, temperature and reaction time the resulting Kappa numbers are ranging from 6 - 9, depending on the alkali charge applied. Two of these predelignified pulps with Kappa number 6.6 and 9.1 were subjected to an acid wash followed by an OP stage at 120° C in one hour reaction time. In the OP stage, different stabilizers were used. Despite of the intensified predelignification, the final brightness of the pulp after OP bleaching was below 70 % ISO (table 6).

In a final set of experiments predelignification conditions in oxygen bleaching of the unbleached pulp were intensified once more. The akkali charge was increased to 3 % while maintaining other parameters applied in the previous set of experiments. The resulting Kappa number was 5.9. The oxygen stage was followed by various metal iron removing procedures (table 7). Sodium bisulfite was used together with DTPA to improve the removal in particular of iron ions. Another treatment used sodium bisulfite as well, followed by an acidification stage. Standard acid washing procedures were applied using different sulphuric acid charges. In these heavy metal removing stages temperature was increased to 90° C at 30 min treatment time.

All these pulps were subjected to OP bleaching applying constant conditions. The resulting pulp brightness varied from 73 to 77 % ISO. These results confirmed that acid washing at low pH is required before OP bleaching.

In the final set of experiments the conditions in acid washing were varied once more and the results indicate that the strongest conditions yield the best brightness response. The presence of magnesium sulfate in the OP stage is very important for the brightness response of the pulp. Additional stabilizers are not required but the application of Heptol or sodium silicate benefits pulp viscosity (table 7).

3. Conclusions

The pulp supplied by Shouguang Paper Mill had a very high Kappa number, high ash and heavy metal content. Probably the raw material is heavily soiled. This of course has a major impact on the bleachability of the pulp. It was not possible to get a satisfying bleaching response by application of an acid wash followed by just one OP stage. OP bleaching preceded by an acid wash starting from a Kappa number of around 13 yielded about 72 % ISO brightness. 77 % ISO can be achieved by an intensified oxygen delignification down to a Kappa number of around 6 followed by an acid wash and an OP stage. The addition of magnesium sulfate in such an OP stage is very important. Heptol as well as silicate improved brightness to a very limited extent, but pulp viscosity is increased.

It seems to be necessary to improve the cleaning facilities for the wheat straw in the mill. If one stage bleaching will be applied in the mill Kappa number, soil and metal content of the pulp has to be decreased. If this could be done successfully, a brightness of 75 % ISO could be obtained in one OP stage. But if certain variations in raw material quality and cooking conditions can not be omitted, a two stage bleaching is required starting with an oxygen delignification followed by an acid wash and a final OP stage. With these conditions even higher Kappa number pulps with a high dirt content can be bleached to a brightness level above 75 % ISO.

Table I

Analysis of Unbleached Pulp, Filtrate and Well Water Supplied by Shouguan Mill

Sample	Metals										
	Ca [ppm]	Mg [ppm]	Mn [ppm]	Fe [ppm]	Cu [ppm]	Cr [ppm]	Klason-lignin %	Acid soluble %	Ash %	SiO_2 %	DCM %
Pulp, Sample 1	10473	4418	86,0	1199	4,5	2,8	13,6	0,55	10,6	8,4	0,58
Pulp, Sample 2	10803	4516	87,0	1205	4,3	2,9	14,5	0,54	10,7	8,4	0,60
Filtrate	61,3	21,2	0,2	0,5	0,02	0,01	COD = 577,4 mg O_2/l				
Well water	62,4	21,0	-	-	-	0,01					

Table 1

O and O/A/OP Bleaching

	H_2SO_4 [%]	NaOH [%]	H_2O_2 [%]	$MgSO_4$ [%]	Heptol [%]	Kappa-No.	pH_I	pH_E	P-Consumpt. [%]	Brightness [% ISO]	Viscosity [ml/g]
Unbleached	-	-	-	-	-	19,0	-		-	22,2	820
50°C (120 min)			18,7				-		(98,3)		
50°C (180 min)			18,7				-		(98,9)		
O1	-	1,5	-	0,5	-	13,0	12,2	10,2	-	24,4	850
O2	-	2	-	0,5	-	11,6	12,4	10,5	-	26,8	868
O3 (800 g)	-	1,5	-	0,5	-	12,9	11,7	10,2	-	26,1	861
O3/A (70°C)	5,5	-	-	-	-	13,8	-	2,48	-	26,8	(889)
O3/A/OP1	-	3	5	0,5	0,5	2,6	11,2	9,8	99,1	67,7	769
O3/A/OP2	-	3	5	0,5		2,5	11,3	9,9	98,7	67,1	755

<u>Reaction conditions</u>

O-stage: 60 min, 90°C, 0,6 Mpa O_2-pressure

OP-stage: 120 min, temp- 120° C, pressure 0,6 Mpa

Acid wash (A): 30 min., 5 % consistency, 70° C.

Table 2

In the trials PO to P8 an acid wash was conducted, whereas in trials P9 to P 15 this treatment was replaced by a Q stage.

	NaOH [%]	H_2O_2 [%]	$MgSO_4$ [%]	Heptol [%]	pH_I	pH_E	P-consumpt. [%]	Brigthness [% ISO]	Viscosity [ml/g]
O/A/P and O/Q/P Bleaching Sequences									
P O	3	5	0,5	-	11,3	10,3	87,2	58,3	811
P 1	3	5	0,5	0,05	11,3	10,3	86,6	56,9	821
P 2	3	5	0,5	0,1	11,3	10,3	88,8	58,6	832
P 3	3	5	0,5	0,3	11,2	10,25	85,5	58,3	820
P 4	3	5	0,5	0,5	11,3	10,3	85,7	57,5	833
P 5	3	5	-	0,05	11,3	10,4	100	43,0	
P 6	3	5	-	0,1	11,3	10,4	99,8	41,8	
P 7	3	5	-	0,3	11,3	10,4	99,7	47,6	
P 8	3	5	-	0,5	11,3	10,4	99,7	48,2	
O/EDTA/P Bleaching Sequences									
P 9	3	5	0,5	-	11,4	10,4	98,1	54,5	
P 10	3	5	0,5	0,05	11,4	10,5	99,0	54,9	
P 11	3	5	0,5	0,1	11,4	10,4	99,9	52,7	
P 12	3	5	0,5	0,3	11,4	10,3	97,6	53,8	
P 13	3	5	0,5	0,5	11,4	10,3	96,7	55,7	
P 14	3	5	-	0,1	11,5	10,7	99,7	51	
P 15		5	-	-	11,4	11,0	99,9	49,2	
EDTA wash (50°C)	-	-	-	-	5,6 - 6,1	-	-	25,4	

P-stage: 3 h, 98° C

Table 3

Removal of Heavy Metals by an Acid Wash or Q-Stage

Sample	Ca [ppm]	Mg [ppm]	Mn [ppm]	Fe [ppm]	Cu [ppm]	Cr [ppm]	PH value	Kappa No.
Acid wash	18	539	13	1128	2,0	2,0	2,5	12,9
Acid wash	17	554	13	1150	2,4	1,9	2,5	12,9
Acid wash	14	405	11	1159	2,4	1,8	2,1	12,9
Acid wash	12	416	11	1151	2,4	1,8	2,1	12,9
EDTA	1295	306	39	1168	2,1	1,8		
EDTA	1307	308	38	1084	2,0	1,6		

Table 4

Wheat Straw Pulp 0/A1/OP and 0/A2/OP Bleaching

	H_2SO_4 [%]	NaOH [%]	H_2O_2 [%]	$MgSO_4$ [%]	Heptol 2706 [%]	Na_2SiO_3 [%]	pH_i	pH_E	P-cons. [%]	Brightness [% ISO]	Visc. ml/g	Kappa no.	Temp. [°C]	Time h	Yield [%]
03/A1	5,5	-	-	-	-	-	-	2,48	-	26,8	(889)	(13,8)	100	4	95,5
03/A1/OP3	-	3	5	0,5	0,1	-	11,3	10,1	99,4	64,3	-		100	4	95,8
03/A1/OP4	-	3	5	0,5	-	5	11,2	10,5	99,3	68,0	849		100	4	95,0
03/OP5	-	3	5	0,5	-	5	11,3	11,1	100,0	51,7	-		100	4	97,0
03/A1/P6	-	3	5	0,5	-	5	11,2	10,7	99,7	62,9	848		100	4	94,8
03/A2	7	-	-	-	-	-	-	2,1	-		-				94,7
03/A2/OP7	-	3	5	0,5	0,1		11,2	10,1	97,7	69,3	810		120	1	93,8
03/A2/OP8	-	3	5	0,5	-	5	11,2	10,4	97,8	71,9	789		120	1	96,3
03/A2/OP9	-	3	7	0,5	-	5	11,0	10,3	97,9	71,8	745		120	1	93,5
03/A2/OP10	-	3	5	1	-	5	11,2	10,1	96,6	67,4			120	1	
03/A2/OP11	-	3	5	0,5	0,1	-	11,3	10,1	97,9	63,6			120	1	

Pressure: 0,6 MPA

Acid wash: 5 % consistency, 30 min, A1 50°C, A2 70° C

Table 5

Wheat Straw Pulp O/A1/P and O/A2/P Bleaching

	NaOH [%]	H_2O_2 [%]	$MgSO_4$ [%]	Heptol [%]	Na_2SiO_3 [%]	pH_I	pH_A	P-cons. [%]	Brightness [% ISO]	Visc.	Kappa no.	Temp. [°C]	Time [h]
O/A1/P16	3	5	0,5	-	5	11,2	10,6	81,5	60,2	not		98	2
O/A2/P19	3	5	0,5	-	5	11,2	10,6	81,3	61,7	de-		98	2
O/A2/P20	3	5	0,5	0,1	-	11,3	10,4	79,7	58,9	ter-		98	2
O/A1/P17	3	5	0,5	-	5	11,2	10,5	84,8	63,2	mi-		98	4
O/A1/P18	3	5	0,5	0,1	-	11,3	10,2	91,7	60,2	ned		98	4

Table 6

Intensified Oxygen Delignification Followed by OP-Bleaching

Bleaching Sequence	H_2SO_4 [%]	NaOH [%]	H_2O_2 [%]	$MgSO_4$ [%]	Heptol [%]	Na_2SiO_3	pH_i	pH_E	P-cons. [%]	Brightness [% ISO]	Visc. ml/g	Kappa no.	Temp. [°C]	Time [min]	Yield [%]
04	-	1,5	-	0,5	-	-	12,2	9,85	-	28,7	862	9,1	110	90	97
05	-	2,0	-	0,5	-	-	12,5	10,2	-	31,0	874	8,0	110	90	95
06	-	2,5	-	0,5	-	-	12,7	10,4	-	31,9	880	6,6	110	90	94,8
07	-	2,0	-	0,5	-	-	12,5	10,5	-	25,4	869	9,4	110	90	95,6
04/A	7,5	-	-	-	-	-	-	2,1	-	-	not		70	30	
06/A	7,5	-	-	-	-	-	-	2,1	-	-	de-		70	30	
04/A/OP12	-	3	5	0,5	0,1	-	11,2	10,2	97,5	68.6	ter-		120	60	
04/A/OP13	-	3	5	0,5	-	5	11,2	10,6	98,2	68,6	mi-		120	60	
06/A/OP14	-	3	5	0,5	0,1	-	11,3	10,5	97,7	68,4	ned		120	60	
06/A/OP15	-	3	5	0,5	-	5	11,2	10,7	97,6	69,6			120	60	

Oxygen stage: pressure 0,3 MPA O_2 except 07: pressure 0,3 MPA compressed air

OP-stage: pressure 0,6 MPA O_2

Acid wash: 5 % consistency

Table 7

Wheat Straw Pulp O8, O8/A, O8/A/OP

Intensified Oxygen Delignification Followed by Different Heavy Metal Removal Steps Followed by a Final OP Stage

Bleaching Sequence	$NaHSO_3$ [%]	H_2SO_4 [%]	NaOH [%]	H_2O_2 [%]	$MgSO_4$ [%]	Heptol [%]	Na_2SiO_3	pH_I	pH_E	P-cons. [%]	Brightness [% ISO]	Visc. ml/g	Kappa no.	Temp. [°C]	Time [min]	Yield [%]
08	-	-	3	-	0,5	-	-	12,8	10,7	-	35,5	827	5,9	110	90	95,0
08/A1 (DTPA)	4,875	3,0	-	-	-	-	-	-	5,95	-	41,4	863		90	30	96,2
08/A2	4,875	10,5	-	-	-	-	-	-	1,8	-	45,4	840		90	30	93,3
08/A3	-	7,5	-	-	-	-	-	-	1,9	-	40,6	840		90	30	92,9
08/A4	-	10,0	-	-	-	-	-	-	1,7	-	40,4	808		90	30	93,0
08/A1/OP16	-	-	3	5	0,5	-	5	11,4	10,8	98,4	72,9	661		120	60	97,3
08/A2/OP17	-	-	3	5	0,5	-	5	11,2	10,6	97,2	77,3	642		120	60	93,5
08/A3/OP18	-	-	3	5	0,5	-	5	11,2	10,6	97,6	77,4	652		120	60	94,3
08/A4/OP19	-	-	3	5	0,5	-	5	11,2	10,6	97,0	76,8	677		120	60	92,0
08/A5	-	7,5	-	-	-	-	-	-	1,9	-	40,3	892		70	30	95,5
08/A3/OP20	-	-	3	5	0,5	0,1	-	11,2	10,2	96,8	77,1	686		120	60	95,0
08/A3/OP21	-	-	3	5	0,5	-	-	11,2	10,2	96,5	76,7	658		120	60	94,3
08/A5/OP22	-	-	3	5	0,5	-	5	11,1	10,4	96,2	74,4	704		120	60	93,5
08/A5/OP23	-	-	3	5	0,5	0,1	-	11,2	10,5	97,2	75,7	702		120	60	93,3