Investigation into the effect of using Oxidized White Liquor (Thiosulphate) in the E stage of the bleach plant on the chloride and potassium concentrations in the recovery circuit of the mill.

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The mill is experiencing corrosion in the super heater section of the recovery boiler due to high concentrations (1 Wt% black liquor solids) of chlorides (CI) and potassium (K) found in the recovery circuit. A high concentration of these substances in the black liquor fired to the boiler lowers the first melting point temperature of carryover in the recovery furnace. This can cause acceleration in the fouling rate of the boiler as well as the potential to increase the corrosion rate. The mill does not have a specific method to control chlorides and potassium levels. A purge of the Electrostatic Precipitator catch was carried out at various times to control the sulphur balance. This material has a higher concentration of potassium and chlorides as compared to black liquor. Chlorides and Potassium are purged from the liquor cycle through loses in the recovery circuit due to liquor spills and evaporator wash downs, and through the brown stock washers. As the mill reduces these losses, there will be a further increase in the concentration of these chemicals and another purge method will need to be found. This paper will investigate the use of Oxidized White Liquor, where the Na_2S has been oxidized to thiosulphate "OWL(T)", in the Eo stage as a means of effectively purging chlorides and potassium from the recovery cycle. A Win GEMS analysis was carried out on a generic mill to calculate the impact on a mill using OWL(T). The data showed that replacing the Eo stage caustic with OWL(T) can reduce the mill's operating costs and effectively remove chlorides and potassium from the liquor cycle.

INTRODUCTION

Background

The liquor cycle of the mill is an almost completely closed loop. The 4 main inputs of chemicals are the incoming wood, the make up caustic to the causticizing plant, the saltcake added to the recovery furnace for sulphur balance, and the fresh makeup water. Chlorides enter the cycle with the make up caustic and together with potassium in the incoming wood. Purges from the cycle include the out going washed pulp, the Electro Static Precipitator (ESP) catch that may be purged and any liquor losses that are not recovered. Since the aim of pulp washing is to remove and recover as much of the black liquor and chemicals as possible, there is little loss of chlorides and potassium from the cycle (1)(2).

As black liquor is burned in the recovery furnace a certain amount of the smaller droplets will be swept up into the upper regions of the furnace by the movement of flue gases (this is termed carry over), and a portion of the inorganic chemicals vaporise. The highest amounts of carry over particles are found in the upper furnace and superheaters. As the temperature of the flue gas decreases the vapours condense into microscopic

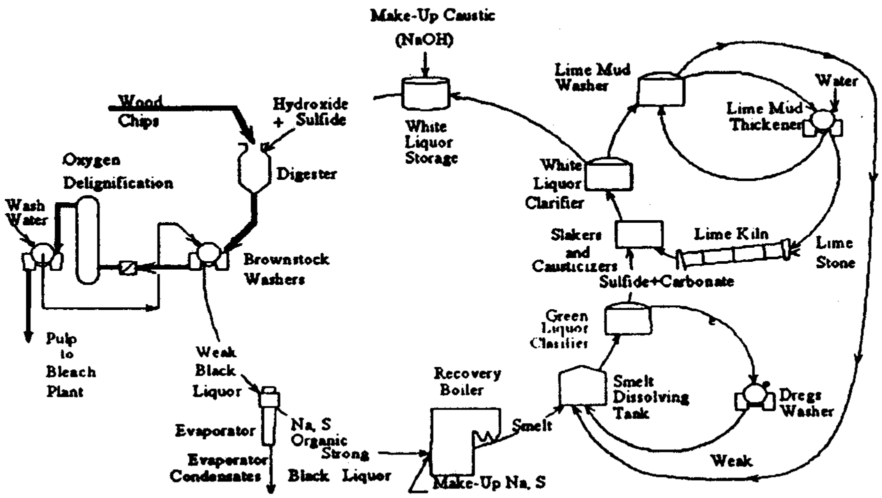

Fig. 1 : Kraft Process Cycles

particles called fume. This fume is removed in the electrostatic precipitator and returned to the black liquor. The fume composition is primarily Na_2SO_4(>80%), Na_2CO_3 (5-15%), KSO_4 and NaCl. Chlorides and potassium can increase the rate of corrosion of the superheater and lower the first melting point temperature of carryover, (see figure 1.2) which can accelerate the fouling rate of the boiler (5). The mill purges some ESP catch to control chloride and potassium concentrations in the liquor cycle. The purging of ash from the recovery boiler electrostatic precipitator is an established method of purging chloride and potassium (3).

Chlorine has a lower vaporization temperature than potassium and sodium and hence has a higher concentration (relative to Na and K) in the fume as compared to its concentration in black liquor. The change in the chloride concentration between the black liquor and the ESP catch is characterized by the "Chloride Enrichment Factor" which is defined as Cl/(Na+K) in the ESP catch divided by Cl/(Na+K) in the virgin black liquor (molar basis). This value ranges from 1.5 to about 2.5. Similarly, there is a potassium enrichment factor "KEF", K/(Na+K). This value typically range between 1.2 and 2.0 reflecting the lower volatility of potassium (2).

The R3H Process for the manufacture of Chlorine Dioxide (ClO2) generates excess saltcake by the following reactions (8):

$$NaClO_3 + HCl + 1/2H_2SO_4 \rightarrow ClO_2 + 1/2Cl_2 + 1/2\ Na_2SO_4 + H_2O$$

This saltcake can be added to the strong black liquor prior to firing to the recovery furnace. The saltcake is reduced in the recovery boiler to Na_2S and then hydrolysed in the smelt tank to form NaSH and NaOH. One mole of caustic is produced from one mole of saltcake. However, the excess saltcake will raise the sulfidity of the white liquor. In order to balance the high sulfidity, caustic will need to be added, generating an excess of white liquor. This excess white liquor can then be oxidized to Thiosulphate. Much work has been carried out on the suitability of oxidized white liquor as a caustic source for E stage bleaching (4). It was found that in order to use this excess white liquor in the bleach plant all of the Na_2S would need to be oxidized to prevent a negative impact on bleach plant performance (6).

The primary compounds in white liquor are NaOH and NaSH. NaSH is produced when Na_2S in the smelt from the recovery boiler is mixed with water

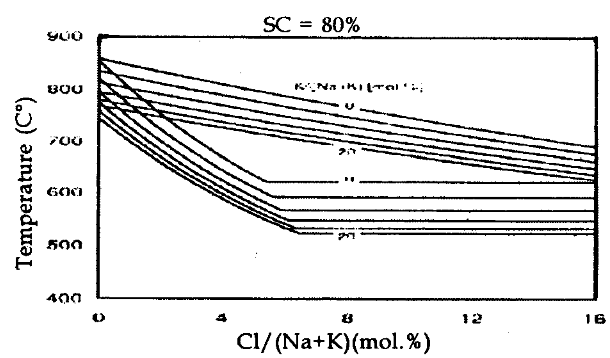

Fig. 2 : Calculated diagram showing the effect of chlorine and potassium on the sticky temperature (T_{15}) and flow temperature (T_{10}) of salt mixtures containing sulphate and carbonate (7)

in the smelt-dissolving tank.

The chemical equation is :

$$Na_2S + H_2O \rightarrow NaSH + NaOH$$

When white liquor is oxidized to thiosulphate, OWL(T), the following equation applies:

$$2NaSH + 2O_2\ \ Na_2S_2O_3 + H_2O$$

Where as when white liquor is oxidized to sulphate the reaction is :

$NaSH + NaOH + 2O_2\ Na_2SO4 + H_2O$

As can be seen, the NaOh is preserved when oxidising to thiosulphate, but lost when oxidising to sulphate.

Now the excess white liquor can be oxidized and used to displace some, or all of the caustic added to the E stage of the bleach plant. The amount of caustic that can be displaced is a function of the amount of available saltcake that can be used. The saving is caustic purchases comes from the fact that less caustic needs to be added to the causticizing plant to control sulfidity than needs to be added to the bleach plant. Since all effluent from the E stage is sewered, the chlorides and the potassium in the OWL(T) are purged from the liquor circuit (4).

Methodology

An initial mill audit will be done. The data that will be monitored is attached as appendix A. This will form the base case of the mill. A WinGEMS analysis will then be done on the data to calculate the effects of using OWL(T) on chloride and potassium concentrations in the liquor and the amount of make - up caustic that is expected to be saved.

The effect on the chloride and potassium concentration will be plotted as the mill simulation is manipulated to include a white liquor oxidation stage. This will show the lowering of the concentrations of these chemicals as they are removed from the circuit. The consumption of caustic will be monitored in order to prove the savings that have been suggested.

Hypotheses

The expected impact on the mill simulation will include the following :

1. Lower Chloride and potassium levels in the recovery circuit. This will mean less fouling in the upper heat transfer areas of the boiler and lower corrosion rate of the boiler tubes.

2. Lower consumption of purchased caustic that would normally be used in the E stage.

3. By effectively purging the liquor circuit, the mill can now start to close the liquor cycle by reducing liquor loses without the build up of unwanted chemicals.

RESULTS AND DISCUSSION

The initial plant audit showed the following:

The plant current capacity is about 570 000 tonnes of pulp a year. This is made up of hardwood and softwood pulp. The ratios of wood are roughly 115 906 tonnes/month of Hardwood and 37525 tonnes/month Softwood. Only the hardwood is bleached through a two-stage O2 delignification plant and then on to the Bleach Plant : Do Eo D E D. The final bleach brightness is 91 ISO. The overall pulp yield is about 48%.

There are 14 Digesters (2 lines of 7), 10 of these are for hardwood and 4 for softwood. There is only one white recaustizing plant (so a set sulphidity of 35% is maintained), supplying both the hard and softwood digesters. The cook times and temperatures are manipulated for softwood digestion.

All the brown Stock and cooking liquors are recovered together, before being fired to the 2 recovery boilers.

The evaporator plant is currently running at close to it's maximum design capacity. The evaporators take the liquor from 17% to 72% after the concentrator for firing. The system limits are the hydraulic capacity of the evaporators and the storage tank sizes.

The 2 recovery boilers are capable of firing 2300 tonnes/day and 1250 tonnes/day of black liquor solids, but are not being operated at full capacity. There is no purge of ESP catch; the only loss of chlorine from the system is HCl gas that is vented with the combustion gases from the recovery furnace. The sulphidity of the white liquor system remains quite steady. There was one occasion 6 month ago, when some ESP catch was sewered for sulphidity control. All the ESP catch is sent to the weak liquor storage tanks; this Black liquor heating value has an average value of 13.5 MJ/Kg, with about 63% inorganic calculated as Na_2SO4. As can be seen in the spreadsheet, the boilers produce from 65 - 79 Kg/s steam in Unit 1 and 28-38 Kg/s steam in Unit 2.

The Recaustizing area is running at about 80% Causticizing Efficiency. A full analysis of the white liquor properties is presented in the appendix. The mill does buy in Soda ash for Sodium control. The caustic comes from the mill's own Caustic membrane cell plant, the NaCl is bought in from Namibia. The production is about 65t/day NaOH. This is used in the bleach plant, the demineralisation water plant and sometimes in the make-up of White liquor. The excess HCL from the plant is sold. The Salt Cake make- up is 58 tonnes/ day and this comes off the R3 ClO2 Generator. There is less than 0.1% Cl in the salt cake.

ClO_2 Generation on the plant is mainly through the R3 process, but there is the flexibility to run R3H and R8 methods in the same plant. There is excess capacity in the plant and it does not run all the time or at full production. The current production is as follows:

28 Mt/day ClO_2

This comes from 38l/s of 8.2g/l ClO2 solution from the plant. About 0.32 l/s of 98% H_2SO_4 is used.

The mill has 3 power boilers, one is bark/coal/

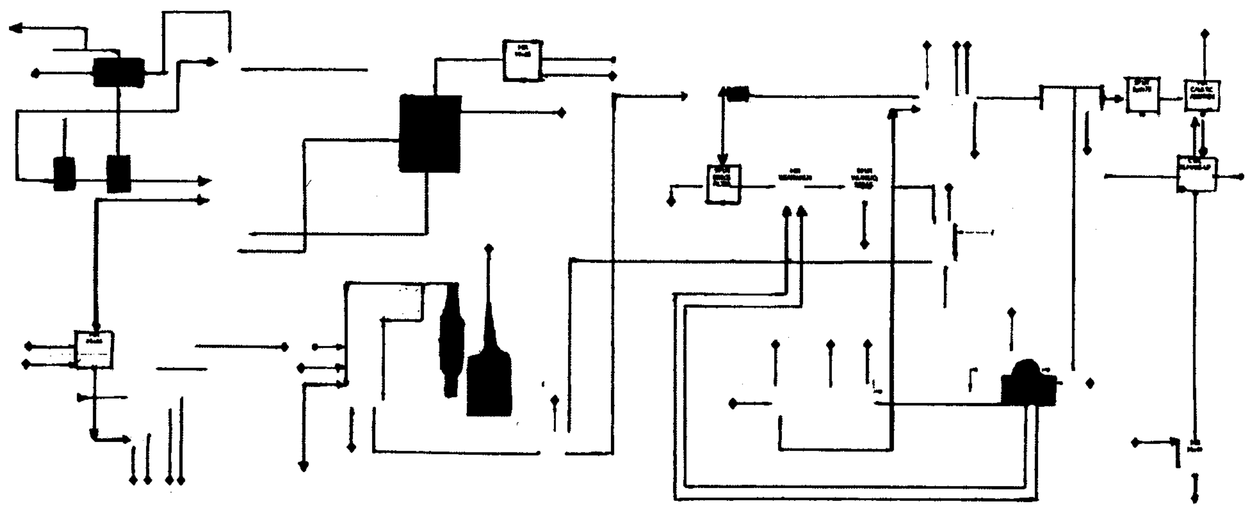

Fig. 3 : Full WinGEMS Simulation Model

methanol fired, while the other 2 are coal fired. Each is capable of producing 23,5 kg/s of 8.2 MPa Steam at 480°C. All Steam that is produced on the mill goes through the power turbines.

All this information was correlated and incorporated in the WinGEMS model below.

Base Case Simulation

The only CL and Potassium that entered the circuit came in form the wood.

The chloride and potassium levels for the incoming wood was set a 500ppm Cl and 800ppm K.

The black liquor losses were set at 4%.

The following areas of the simulation allowed for small loses of Cl and K:

Dregs removed from the dregs washer, Grits removed from the slaker, Minor loses with the pulp flowing from the brown stock washers.

Running the simulation with the above data showed that the Cl and K equilibrium levels in the white liquor ran at 5,45g/l and 8,72/l respectively. These values were then set as the base level for the

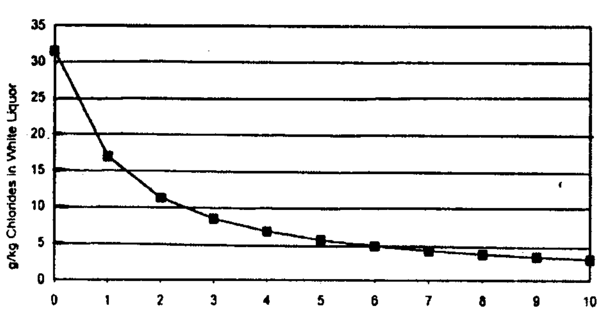

Fig. 4 : Chloride concentration in White Liquor vs. Black Liquor loses

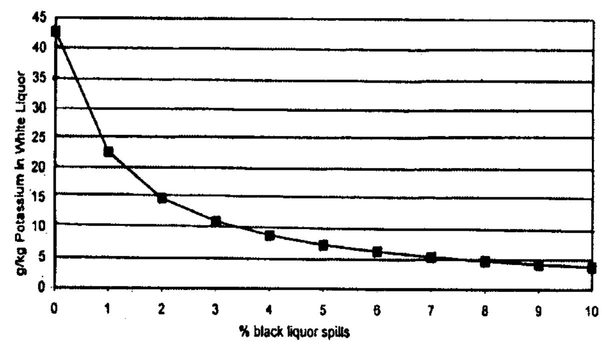

Fig. 5 : Potassium concentration in White Liquor vs. Black Liquor Loses.

simulation.

The simulation was then run, changing just the amount of black liquor lost from the system as spills, going from 10% liquor loses to 0% (as in a closed mill).

As can be seen from these graphs, as the mill goes towards closed process, the concentrations of chlorides and potassium rise rapidly to concentrations that cannot be tolerated in the recovery furnace. This simulation shows that the mill cannot embark on a closure program, until an effective purge has been found.

The next set of simulations run shows the effect of varying chloride concentrations from the incoming wood to the process. These series of simulations were run using the base case conditions.

The final set of simulations run were set up with a white liquor oxidizer, sending the excess white liquor to the E stage of the bleach plant. The caustic requirement for the E stage was set as 1,5% on

Table 1 : WinGEMS Analysis: Overall Analysis

		Actual
Wood/Pulp		
Furnish	Swd/Hwd/etc	Hwd/Swd
Species		Eucalyptus Pine
B.S Pulp Production	admtpd	1500
B.S. Yield	%	52
Wood Requirement	odmtpd	
Shrinkage through bleach plant	%	
Bleached Pulp Production	admtpd	
Bleached Yield	%	48
Chloride	ppm	
Potassium	ppm	
White Liquor Properties		
Active Alkali	g/l as NaOH	
	or g/l as Na2O	102
Effective Alkali	g/l as NaOH	
	or g/l as Na2O	84
Sulphidity	%	35
Total Titratable Alkali	g/l as NaOH	
	or g/l as Na2O	119
Na_2SO_4 as chemical	g/l as Na_2SO_4	3.63
Na_2CO_3 as chemical	g/l as Na_2CO_3	
$Na_2S_2O_3$ as chemical	g/l $Na_2S_2O_3$	
Chloride	g/l as Cl	
Potassium	g/l as K	
Black Liquor Properties		
Measured Na_2S as chemical	g/l Na_2S	
Solids concentration Na_2S measured	%	70
Liquor heating value	Kj/Kg	13.5
Carbon	Wt% of BLS	35.5
Hydrogen	Wt% of BLS	3.5,
Oxygen	Wt% of BLS	34.4
Sodium	Wt% of BLS	19.5
Sulfur	Wt% of BLS	5
Chloride	Wt% of BLS	0.5
Potassium	Wt% of BLS	1.5
Recovery Flue Gas		
H_2S	ppmv (dry)	1.86
SO_2	ppmv (dry)	60.3
CO	ppmv (dry)	
H_2	ppmv (dry)	
Particulate	g/DSCM	100mg/m3
Saltcake Makeup		
From ClO_2 Generator	Mt/day	80
Purchased	Mt/day	
ClO_2 Generator Saltcake Properties		
Sodium	Wt %	
Sulphur	Wt %	
Oxygen	Wt %	
Chloride	Wt %	
Other	Wt %	
Caustic Makeup Properties		
Addition Rate (100% basis)	Mt/d	65
NaOH concentration	%	
Chloride	ppm as Cl	

		Actual		
Digester Operation				
E.A. on Wood as NaOH	%			
Liquor to Wood Ratio				
Liquor flow to Digester	lpm			
Brownstock				
No. of Washers				
Washer type				
Wash water flow	lpm			
Displacement Ratio (overall) or Efficiency Factor				
Carryover as Na_2SO_4	Kg/admt	130		
Evaporator				
WBL flow	lps	180		
WBL solids	%	17%		
SBL flow	lps	40		
SBL solids	%	72%		
Steam Flow	kg/s	7		
Steam Economy				
Recovery Boiler(s)				
Type	DCE/ICE	ICE	ICE	
Virgin Solids to Boilers	mt/day	2300	1250	
Solids Concentration (before recycle)	%	72%	72	
Excess Air	%	1.25%	1.25	
FD Air Temperature	°C	170	180	
Reduction Efficiency	%	90%	90	
Smelt Temperature	°C			
Economizer Flue Gas Temperature	°C	171	178.7	
Recycle from ESP Etc.	Mt/hr			
Blowdown Steam	Mt/hr			
Sootblowing Steam	kg/s	2.0		
Feedwater Temp	°C	114		
High Pressure	bar	8.5	8.5	
Temperature	°C	480	480	
Steam Production	kg/s	70	30	
Recaust				
Lime Kiln Product	Mt/d	360777		
CaO in Product	%	82%		
Causticizing Efficiency	%	78%		
Thermal Efficiency	Gj/Kg CaO			
Fuel Type				
Chlorine Dioxide Generator				
Type		R 3		
Production	Mt/d	28		
Byproduct		Na2SO4		
H_2SO_4	Kg/KgClO_2			
Na_2SO_4	Kg/KgClO_2		80.0 Mt/d	
Power Boiler (s)		1	2	3
Fuel Type		Bark/coal	coal	coal
Steam Production	kg/s	23.5	23.5	23.5
Steam Pressure	Bar	8.2	8.2	8.2
Steam Temperature	°C	480	480	480
Efficiency	%			
Turbine (s)		1	2	3
Steam Feed	kg/s	42	66	
Inlet Steam Pressure	Bar	8.2	8.2	

Bleach Plant Operation

Brownstock production	admt/d	1,000
Brownstock consistency	%	12
Bleach Production	admt/d	940

Bleaching Sequence Example		O	D_0	Eop	D_1
Inlet Kappa		25	15		
Outlet Kappa		15		2.5	
Dose of Primary Chemical (as Chemical)	Kg/Mt	25	14.3	15	5
Dose of Secondary Chemical (as Chemical)	Kg/Mt			5	
Dose of Tertiary Chemical (as Chemical)	Kg/Mt			5	
Kappa Factor			0.25		
Temperature	°C	100	70	80	80
Inlet Pressure	Bar (g)	6	0	2.0	0
Outlet Pressure	Bar (g)	5		0	
Time at Pressure	Minutes	60		15	
End pH		10	4	10	4
Time at Atmospheric	Minutes	0	60	60	120
Brightness	% ISO			62	88
Reverted Brightness	% ISO				86
Final Viscosity					
Consumption		O	D_0	Eop	D_1
Primary Chemical (as Chemical)	Kg/day	25	14	15	5
Secondary Chemical (as Chemical)				5	
Tertiary Chemical (as Chemical)				5	

Wash Water		O	D_0	Eop	D_1
Flow 1	lpm	7,000	3,500		7,000
Source 1		Condensate	D_1	White	White
Flow 2			3500		
Source 2			White		
Seal Tank flow 1	lpm	7,000	7,000	7,000	3,500
Flow 1 sent to		BS Decker	Acid Sewer	Alkali Sewer	Eop Shower
Seal Tank flow 2	lpm				3500
Flow 2 sent to					D_0 Shower
Washer Discharge Consistency		12%	12%	12%	12%

Effluent

		Acid Stage	Alkali Stage	Combined Bleach Effluent	Total Mill
Flow	lpm	7,000	7,000	14,000	20,000
	m^3/day	10,080	10,080	20,160	28,800
AOX	Kg/mt	0.5	0.4	0.90	1.00
	Kg/day	500	400	900	1,000
Colour	Kg/mt	23.0	68.0	91.0	100
	Kg/day	23,000	68,000	91,000	100,000
BOD	Mt/mt	6.50	4.80	11.30	25
	Kg/day	6,500	4,800	11,300	25,000
COD	Mt/mt	22.0	53.0	75.0	100
	Kg/day	22,000	53,000	75,000	100,000

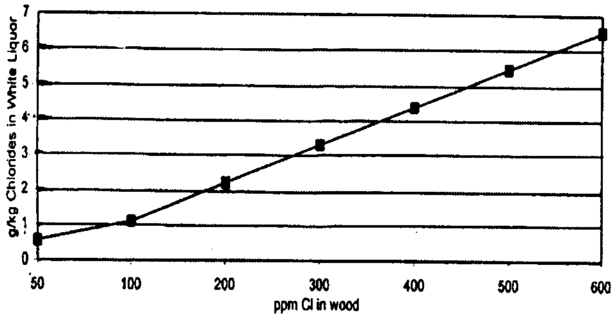

Fig. 6 : Chloride concentration in White Liquor vs. Chloride concentration in wood

pulp. This worked out to require a white liquor bleed steam of 175l/min.

The black liquor were then manipulated from 10% to 0%, and the concentrations of the Cl and K were

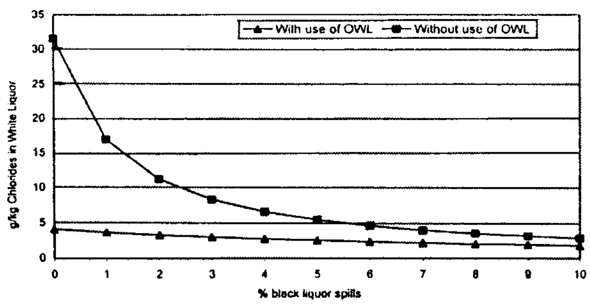

Fig. 7 : Chloride concentration in White Liquor vs. Black Liquor loses With and Without the use of OWL(T)

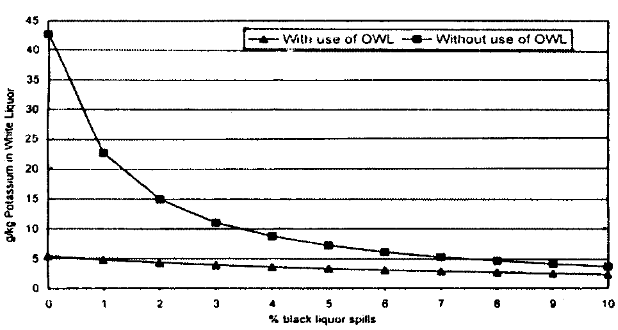

Fig. 8 : Potassium concentration in White Liquor vs. Black Liquor loses With and Without the use of OWL(T)

noted.

Discussion

The results show that the purging of white liquor is a very effective way of removing chlorides and potassium from the recovery circuit. In order to generate the excess white liquor, the saltcake make up goes from 26.9 mt/day to 39.5mt/day. This is still well within the production of the ClO_2 generator, but is still dependant on the production rate of ClO_2 for the bleach plant.

The mill will need to purge chlorides and potassium from the recovery circuit if they wish to proceed with a mill closure program. The concentration of these chemicals rises exponentially with the percent of mill closure. The use of Oxidized White Liquor (T) drops the chloride levels from 31.5g/kg white liquor to 4.1g/kg white liquor at 0% black liquor loses, and potassium from 42.71g/kg white liquor to 5.46/kg white liquor, both these levels are well below the predicted levels in the base case. This will raise the first melting point temperature of the carry-over from the base case of 650°C to 700°C when WLO(T) is used and there are no black liquor loses.

CONCLUSION

The WinGEMS analysis proves that there is a definite benefit is using OWL(T) in the bleach plant to purge chlorides and potassium from the recovery circuit.

The purging of chlorides and potassium will allow the mill to close their liquor losses, and reduce the fouling rate of the recovery furnaces.

In order to fully quantify the above findings, it is recommended that a full plant scale investigation and trial be carried out on this process.

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