The Modern White Liquor Plant

Executive Summary

The pulping industry has a long history and has over time been affected by different trends that have increased the complexity of the process solutions in the mills. This has given mills a multitude of conditions and requirements to adapt to, and has also created mill specific solutions. This paper discusses and evaluates the trend of a resource efficient and clean world and its impact on white liquor plants over the world.

Within this trend we see further closure of the mills, which can lead to an increased need to purify recovery boiler ash as well as an increased focus on cleaning of green liquor. The benefit of high dregs removal through filtration is, however, countered by other trends, e.g. greater focus on power consumption and total process cost. This paper includes an evaluation of process impact when using green liquor filtration and clarification technologies, respectively. Also, strategies to mitigate the impact of different strategies of lime cycle management are discussed.

The paper also evaluates the possibilities to reduce the carbon footprint through substitution of oil with renewable resources such as wood residues and bark. Since bark has the added benefit of typically being a waste stream, the evaluation has focused on bark as an alternative fuel. Potential pitfalls are discussed with focus on overall lime cycle chemistry and management of non-process elements (NPE).

Introduction

Over time, the pulp mill industry has been affected by many different trends. The trend that has probably had the biggest impact – although varying over time – is concern for the environment. In the early days of the industry, fresh cooking liquors were used once and then discharged. This was followed by the installation of recovery processes which evolved significantly and today provide both a means of using the same liquor over and over as well as the energy the mill needs.

In later years, the changes have been smaller and more gradual. Increased closure of the bleach plants during the 1980s created a need for purging additional NPE from the plant. Thus, development efforts focused on enhancing the separation efficiency of the green liquor cleaning unit, and different filter technologies were developed. Another effect was increased chloride levels in the liquor. This, combined with recovery boilers being designed for higher pressure levels, has made ash treatment systems standard in most new mills. Some of this development, with technologies that were optimal based on the requirements at that time, is currently re-evaluated based on partially modified demands.

The intention of this paper is to evaluate and, to some degree, quantify the impact on overall chemistry and the cost of increased NPE load within the white liquor plant. Note that all results are based on theoretical calculations, not empirical tests, and should therefore be regarded as a tool for prediction rather than absolute truth.

Theoretical mill balance calculations

The work is based on theoretical mill balance calculations for NPE where a reference mill is used. It has been assumed that no changes in the process outside the white liquor plant are made, nor inside the plant with the exception for clearly defined variations. Results from variations in the process solutions and raw material quality have been compared to a base case (referred to as case 0).

The mill balance has been made in cooperation with RISE Bioeconomy (former Innventia). It has been done using standard WinGEMS blocks, adapted to include calculations based on general know-how about enrichment, solubility factors, etc.

The reference model is based on a typical South American mill built during the last decade. It has continuous cooking, oxygen delignification, ECF bleaching, high pressure recovery boiler and ash leaching. The main water source in the recausticizing plant is condensate from the evaporation plant and fuel for the lime kiln is fuel oil.

A number of cases (variation in process solution, raw material quality and content of NPE) have been simulated. The input data for these simulations and results are presented below.

Note that a simplified method for calculating the split between dregs in clear liquor and dregs in the exiting dregs stream respectively has been used. This means that the exact composition of the dregs entrained by the clear liquor may differ to some extent from the calculated composition, however the impact is assumed to be negligible.

Basis for mill balance – Cases

Cases 1-8 focus on the impact of different levels of clarity in the purified green liquor. From a process point of view, the cleaner the green liquor is, the easier the NPE management becomes; however, the increased cost of energy counters this benefit in terms of operational cost, and the process impact of higher levels of suspended solids has therefore been evaluated. Cases 1-4 focus on maintaining the active CaO level in the lime cycle by allowing a bigger purge, whereas cases 5-8 allow the active CaO to decrease, by keeping the amount of lime purged (including dead load) constant. In cases 1-4, the operational cost

will increase due to an increase of makeup and purge; in cases 5-8 the cost will increase based on the requirement for more fuel.

Cases 9-15 consider different purge strategies (case 0 is used as part of the evaluation):

- Case 0: lime mud is purged from the lime mud filter
- Case 9: lime mud is purged from the dregs filter
- Case 10 – 15: lime mud is purged via the lime kiln ESP; assumptions about enrichment of P, S and Na (if applicable) and the resulting effect on purge volumes have been made

Finally, cases 16-20 study the effect of replacing fuel oil with bark (no gasification). Two different bark qualities have been used in the evaluation, and in case 20 a makeup lime containing less NPE was used to see the impact of makeup quality on the process.

Below is a table describing the different cases in more detail.

| Case | Suspended solids in clear GL | | | | | Fuel | | | Makeup lime | | Active CaO | | Purge | | | | | | | | |
	5 mg/l	20 mg/l	40 mg/l	100 mg/l	200 mg/l	Oil	Bark 1	Bark 2	MU 1	MU 2	89%	Calc	LM 1	LM 2	Dregs	$E_p=1$	$E_p=1.5$	$E_p=1.75$	$E_p=2$	$E_p=1, E_S=4.6$	$E_p=1, E_{Na}=1.76$
0		G				G			G		G			Y*							
1	G					G			G		G			Y							
2			G			G			G		G			Y							
3				G		G			G		G			Y							
4					G	G			G		G			Y							
5	G					G			G			Y	G*								
6			G			G			G			Y	G*								
7				G		G			G			Y	G*								
8					G	G			G			Y	G*								
9		G				G			G		G				Y						
10		G				G			G		G					Y					
11		G				G			G		G						Y				
12		G				G			G		G							Y			
13		G				G			G		G								Y		
14		G				G			G		G									Y	
15		G				G			G		G										Y
16		G					G		G		G			Y							
17		G						G	G		G			Y**							
18		G						G	G			Y	G*								
19		G					G		G			Y	G**								
20		G						G		G	G			Y							

Table 1. The differences in input for cases 0-20. Green fields indicate that the parameter is an input to the calculation. Yellow fields are the result. The chart only includes parameters deemed to be of interest for the understanding of the evaluation.

Table information is explained on the next page…

Elucidation of Table 1 information:

Bark 1, Bark 2, MU 1, MU 2	See "Basis for mill balance – Raw material" (next page) for further details about NPE content and origin of the data used.
*	Amount of lime mud required to be purged for case 0. This amount has been used as input for LM 1 in cases 5-8 and 18.
**	Amount of lime mud required to be purged for case 17. This amount has been used as input for LM 1 in case 19.
LM 1	Lime cycle quality maintained by purge from the lime mud filter. Dry solids 78%. Amount fixed to the same amount as the amount calculated for case 0.
LM 2	Lime cycle quality maintained by purge from the lime mud filter. Dry solids 78%. Total amount of solids (including liquid) calculated.
Dregs	Lime cycle quality maintained by purge from the dregs filter. Dry solids 45%. Total amount of solids (including liquid) calculated.
Lime kiln ESP	Lime cycle quality maintained by purge of the lime kiln ESP dust. Total amount of solids calculated. Some cases with an assumed enrichment of P, S and Na have also been calculated to see the theoretical impact.

- The P enrichment numbers have been chosen as levels that are reasonable based on data collected by Valmet. See "Enrichment factors in kiln ESP dust" (next page) for further details.
- The numbers for S and Na have been chosen based on [1]. The actual numbers have been chosen as the largest calculated enrichment, excluding values that have been deemed questionable. This was done to evaluate maximum reasonable loss of chemicals due to enrichment. The difference was so small that it was deemed negligible.

Basis for mill balance – Raw material

	Al	Si	Na	Mg	K	Ca	P	Mn	Cl	Ba
Wood, mg/kg OD	19	8	98	156	798	798	55	34	461	10
Bark 1, mg/kg DS	1300	8700	700	1900	2900	16,600	300	530	1500	
Bark 2, mg/kg DS	50	730	30	450	1900	10,700	440	700	240	
Makeup lime 1, mg/kg (% as oxide)	800 (Al_2O_3 0.15%)	6500 (SiO_2 1.4%)		2400 (MgO 0.4%)			860 (P_2O_5 0.21%)	350 (Mn_2O_3 0.04%)		
Makeup lime 2, mg/kg (% as oxide)	700 (Al_2O_3 0.12%)	1100 (SiO_2 0.23%)		3800 (MgO 0.6%)			100 (P_2O_5 0.023%)	100 (Mn_2O_3 0.012%)		

Table 2. Assumed NPE (of relevance) in raw material.

Explanation of how the qualities above have been chosen:

Wood – a type of South American Eucalyptus

Bark 1 – NPE levels are an average of 7 samples that have been collected from a total of three different South American mills.

Bark 2 – Birch, reference values taken from [3]

Makeup lime 1 – a type available in South America

Makeup lime 2 – a type with very good purity

Basis for mill balance – Enrichment factors in kiln ESP dust

The composition of solids in different positions of the lime kiln has been measured at many mills. The evaluated samples have been extracted from 27 different mills from all over the world over the past 25 years. In this context, the results have been used to evaluate typical enrichment of elements in kiln ESP dust. Note that this is a macro-based evaluation without any plant specific analysis.

Enrichment has been calculated by comparing the element content (as oxide) relative to the CaO content in the ESP dust with the element content relative to the CaO content in a comparative sample (in this case lime mud):

$$E_x = \frac{\left(\frac{m_X}{m_{CaO}}\right)_{Dust}}{\left(\frac{m_X}{m_{CaO}}\right)_{Comparative}}$$

Where:

E_x = Enrichment of element X
m_x = Wt.% content of element X as oxide in a sample
m_{CaO} = Wt.% content of Calcium as CaO in a sample

Since enrichment of P in ESP dust is considered to be fairly common and a contributing factor to choosing to handle lime cycle management through the purge of ESP dust, it was decided to evaluate the impact of E_P on purge volumes. To determine reasonable levels for evaluation, E_P was plotted.

The numbers for E_P varied from 1 to 3.5 (see Graph 1), and for the mill balance calculation, it was decided to use the numbers 1.5, 1.75 and 2 respectively.
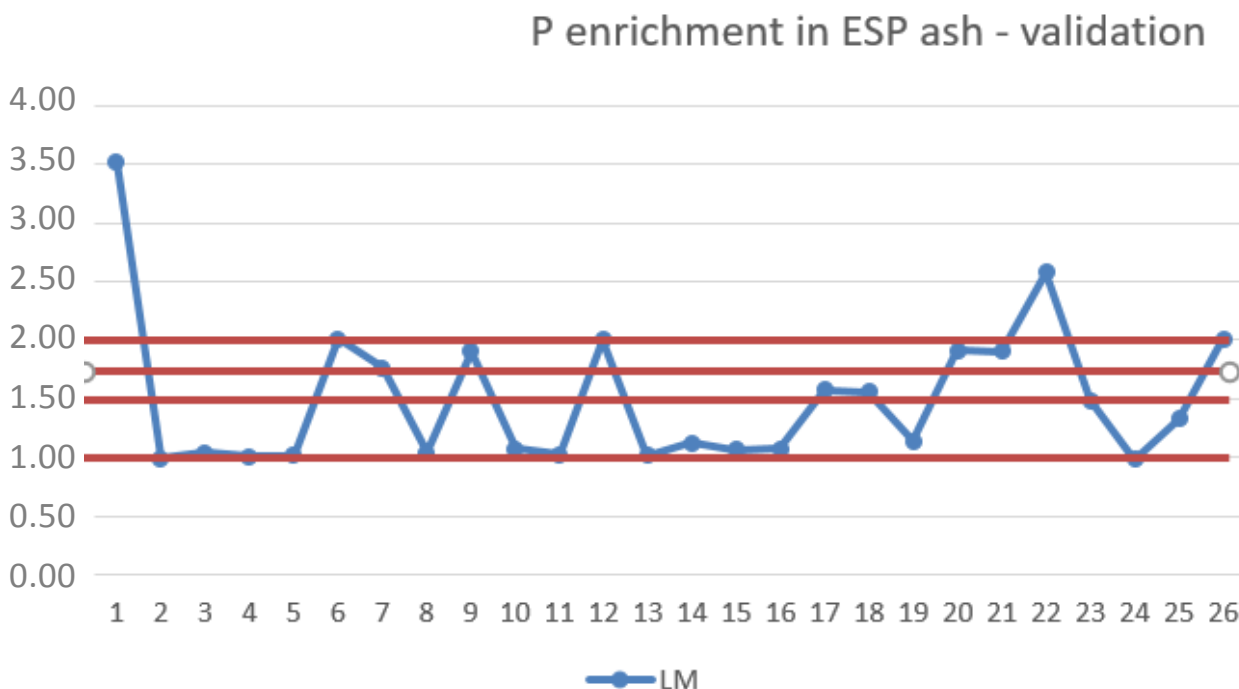

Graph 1. P enrichment in kiln ESP dust. Out of 26 samples, 24 are above 1 (92%), 11 are above 1.5 (42%), 8 are above 1.75 (31%) and 4 are above 2.0 (15%).

Impact of variations in green liquor clarity

The first process variation concerns green liquor dregs removal. It is well known that an increase in NPE to the slaker results in increased dead load in the lime cycle. This can be dealt with in two ways. One way is to increase the purge from the lime cycle and maintain the active CaO level (case 0-4), another is to maintain a certain level of purge and allow active CaO to be reduced (case 0 and 5-8), thereby affecting the fuel consumption.

Conclusions

Calculations have been made for clarities ranging from 5 mg/l to 200 mg/l and studying the lime cycle. Both the calculated increase of purge (cases 0-4, see Graph 2 next page) and calculated reduction of active CaO (cases 0 and 5-8, see Graph 3 next page) are linear, meaning that a mill that reduces the suspended solids levels in green liquor in a stepwise manner would see a similar stepwise change in either the required amount of purge or achieved active CaO. The actual slope would most probably differ a great deal between mills so no quantification of relevance can be made.

LM from LM filter (100%dry) vs SS in GL
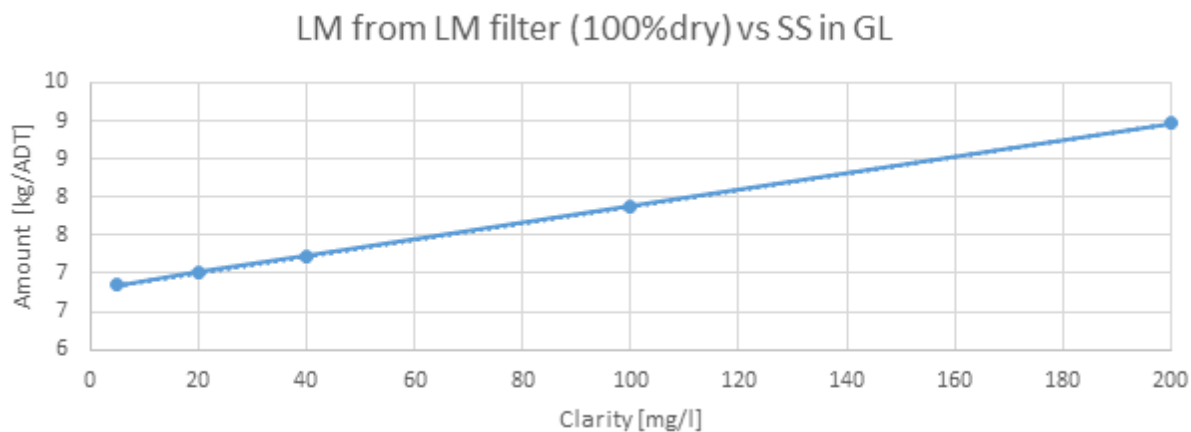
Graph 2. Amount of lime mud required to be purged at different green liquor clarity, if active CaO is maintained constant.

Active CaO vs SS in GL
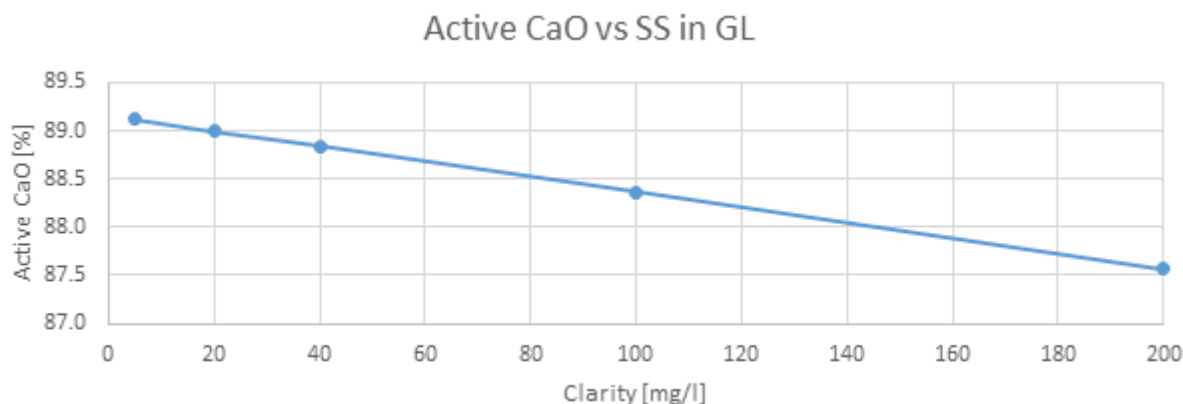
Graph 3. Active CaO at different green liquor clarity, if the amount of lime mud (as 100% dry solids) is maintained constant.

Changes in the green liquor clarity had only a very small effect on the white liquor quality. The exception was an increase in Si in the cases where active CaO was maintained (see Graph 4). The reason for this is the quality of the makeup lime. Since these cases included larger purges, they were more sensitive to the fact that the assumed makeup lime had high levels of Si. If an alternative with higher levels of suspended solids in green liquor is chosen and lime cycle management is handled by purging more lime mud, then the quality of the makeup should be monitored to limit any ill effects outside the white liquor plant.

Si [mg/l]
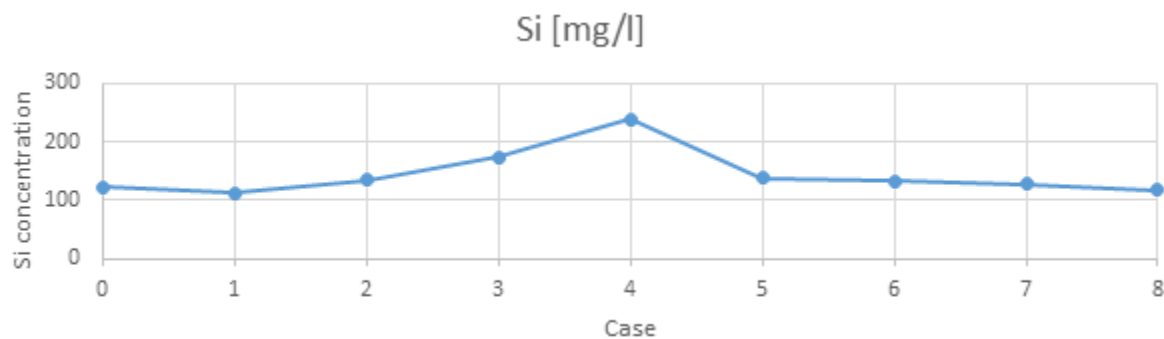
Graph 4. Si concentration in white liquor for cases 0-8.

It can be noted that from a process perspective, there are clear benefits to having good dregs separation (limited purge, good fuel economy, risk of overbearing of NPE to white liquor if makeup quality is poor, etc.). However, the increased cost in energy for filters compared to traditional clarifiers makes it worthwhile to compare the gain in process against an increase in overall operating cost.

Impact of different purging strategies

A second aspect to the environmental concern is the overall tighter requirements on solids emission –in terms of both quality and quantity. In this work, we have focused on the quantitative aspect only. This can be evaluated from different perspectives and one such perspective is the choice of where to purge from the lime cycle (cases 0, 9 and 10).

Common discharge points are via the green liquor dregs discharge (typically as filter precoat), the lime mud filter (continuous or discontinuous discharges) and the lime kiln ESP dust (continuous or discontinuous discharges). In addition, some non-controllable purge takes place with the grits rejection from the slaker. Some mills have found ways of disposing of this for a small income, e.g. using kiln ESP dust as fertilizer, but for most mills this is a cost both for transport and landfill.

Conclusions on choice of purge stream

Our calculations show no impact on the amount of makeup required, nor on the white liquor quality regardless of where the purge is made, if there is no enrichment or depletion of elements in the discharge stream. We have only limited information about actual cost of transport and landfill, in addition there may be a difference in cost of landfill depending on the quality of the media which has not been accounted for, and finally there is a large variation in unitary cost of fuel. The numbers below must therefore only be viewed as an indication.

If we assume that the cost of landfill is the same regardless of media, the difference in operating cost will stem from the difference in dry solids content and the cost of fuel for drying the ESP dust only. An indication of relative cost is shown below (Table 3). Note that in addition to the uncertainty in unitary cost, the actual amounts differ in between mills, depending on process solutions, raw material etc. and the numbers should therefore be seen as an indication only.

Purge location	Amount	Relative cost of disposal	Fuel cost	Total relative cost
Dregs discharge	15 kg/ADT (@DS 45%)*	+120%	0	+75%
Lime mud filter	9 kg/ADT (@DS 78%)	+30%	0	Ref
Kiln ESP dust	7 kg/ADT (@DS 100%)	Ref (0.07 US $/ADT)	Ref (0.25 US $/ADT)	+250%

*In order to use comparative numbers, this amount excludes the dregs that will in reality be part of the discharged lime mud.

Table 3. Relative cost for purging strategy. Cost of transport and landfill, regardless of media or dryness, is based on 10 US $/ton of material, fuel cost is based on 0.91 US $/Nm³ of natural gas, with a heat value of 35.8 MJ/Nm³ and assuming DS 78% on lime mud to the kiln.

It can be concluded that for this case, the cost of discharge as kiln ESP dust is considerably costlier than the alternatives. It should however be pointed out that there is a large variation in the cost basis.

Conclusions on impact of enrichment in purge stream

In addition to the above, enrichment of elements in kiln ESP dust has been discussed and could have an impact on the required amount of kiln ESP dust that must be purged, which in turn would affect the result of the conclusion above. Based on [1], enrichment of S and Na respectively was used in separate calculations (cases 14-15), however no major differences compared to case 0 could be seen and therefore no further evaluation of these will be made. For P, based on enrichment 1.5, 1.75 and 2 respectively, (cases 10-13) there was a reduction of the amount of purge required and the impact on purge strategy where there is a confirmed enrichment is therefore worth considering.

Since P (along with Si) has the largest impact on active CaO, an enrichment of P in the purge stream reduces the amount of lime to purge. In the case of this reference mill, P was the major contributor to the dead load and Si was only present to a fairly small degree, which led to a substantial reduction of the purge requirement in the case of P enrichment. The reduction was not linear (see Graph 5) but the trend shows that the higher the enrichment, the smaller the amount required to purge. The calculations were based on a maximum E_P of 2, but as pointed out before, the collected data set included only four points out of 26 that had higher numbers.
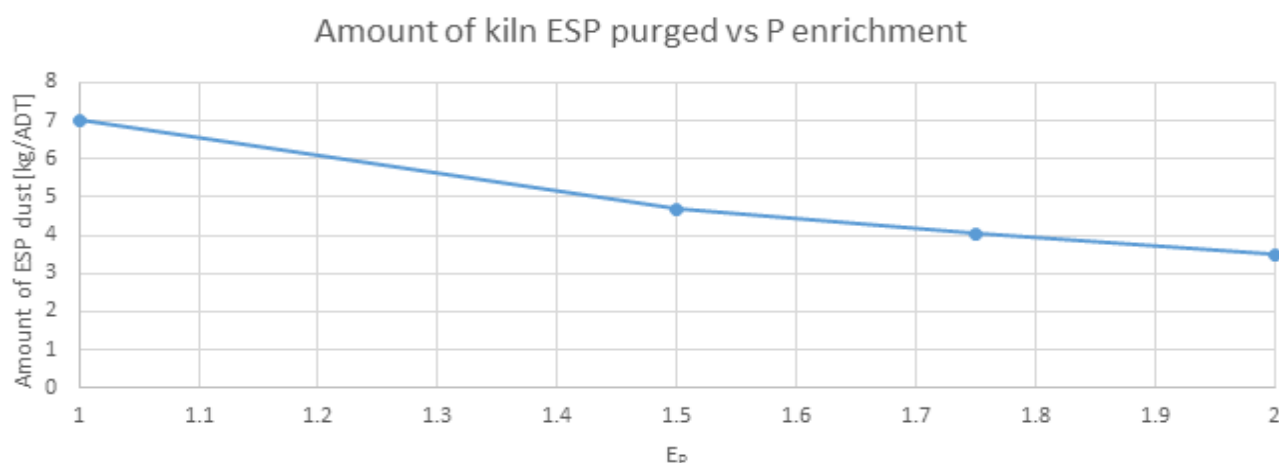
Graph 5. The potential reduction of amount to purge as kiln ESP dust, assuming an enrichment of P of up to 2. Comparing two mills identical to our reference mill, where one has no enrichment and the other has an enrichment of 2, the reduction is approximately 50%.

An interesting effect concerning general Si levels in the plant appeared when studying P enrichment. The Si level in the overall plant (see examples in Graph 6) was reduced although no change was made to the quality of the raw material, nor in the process solution, with the exception for reducing lime cycle purge,
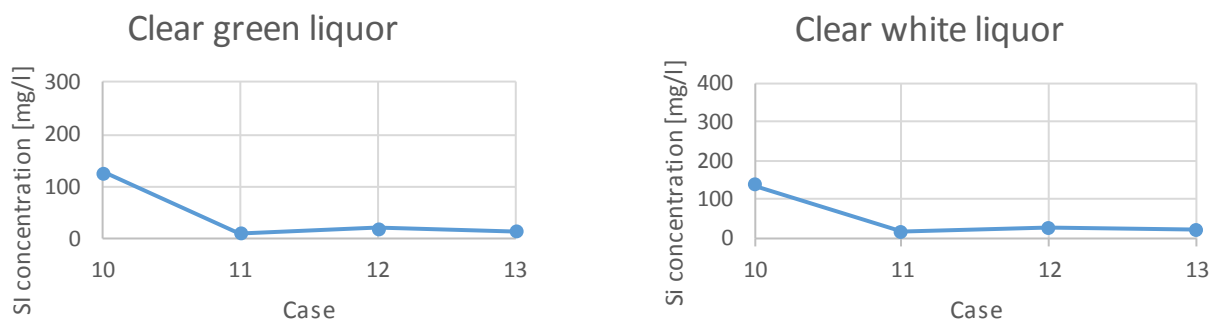
Graph 6. The Si level in green and white liquor respectively for cases 10-13. Case 10 is in the same range as the base case but the reduced amount of makeup used in cases 11-13 reduces the level in the overall system. The Si level in burnt lime is low in all these cases.

typically considered as a remedy to high Si levels rather than the contrary. Just as for a previous case, the reason was the quality of the assumed makeup lime. As mentioned, the makeup lime was high in Si but it was also low in P, thus causing the amount of Si taken into the system to be reduced as the amount of makeup (due to reduction in purge) was reduced.

The conclusion is that any mill requiring large amounts of purge from the lime cycle, regardless of the reason, should closely monitor the quality of the makeup lime to limit any ill effects outside the white liquor plant.

Impact of replacing fossil fuel with biofuel in the lime kiln

Finally, some mills are working actively on reducing the carbon footprint of the mill and one way to do this is by replacing the fossil fuel to the kiln with biofuel. Solutions implemented in actual mills are the use of powdered or gasified wood or bark. This paper does not account for challenges in safety or control strategies; the sole aspect for study is the NPE content which is a problem mainly when using bark.

The effect of replacing fossil fuel with bark was studied to identify, and to some degree quantify, the consequences of targeting a better environmental profile by this means. The calculations (cases 0 and 16-20) were based on bark powder replacing fuel oil. The bark powder heat value used in the calculation was 19.0 MJ/kg as LHV. Two different bark qualities were used in the evaluation (for details, refer to "Basis for mill balance – Raw material" mentioned previously). Bark 1 represents a South American bark. Bark 2 represents a European type birch bark.

Conclusions

The main conclusion confirms that the quality of both bark and makeup lime are very important. Comparing the different cases, we see that:

1. By replacing oil with birch bark 2,
    a. the lime cycle purge requirement increased from 2% to 6% when maintaining the same level of active CaO.
    b. OR the active CaO was reduced from 89% down to 80%.
2. By replacing oil with bark 1, the results were considerably worse. The purge requirements increased to more than 30% of the lime cycle. For active CaO, the reduction was so large that it was not deemed feasible (active CaO of 70% while purging more than in the case of oil).

In the calculations for bark 2, an additional calculation was made when replacing the makeup lime with one being cleaner as far as Al, Si, P and Mn was concerned. By doing this, purge requirement could be reduced from 6% to 3% which is within a reasonable operational level.

Transition metals – Lime cycle accumulation and transfer to white liquor

Looking at the effect on white liquor, there are elevations of some elements. One important issue is the fate of transition metals and their possible influence on other process stages. Such hypothetical situation will be studied using Mn as an example.

Mn, whose main source in a kraft pulp mill is wood raw material, is effectively removed from the liquor cycle via green liquor sludge as solid MnS and/or $Mn(OH)_2$ during normal operation. Its solubility in green liquor seems to be lower than in white liquor, meaning that as long as the sludge removal works properly, no accumulation of Mn in the lime cycle is expected. The same is valid for other transition metals.

The situation, however, changes if Mn is introduced into the lime cycle in another fashion, e.g. via lime kiln fuel. Mn may then accumulate in lime mud as MnS which will be transformed to various, relatively inert, Mn oxides during recalcination in the kiln. Some Mn will be transferred to white liquor, and although its solubility in white liquor is believed to be rather low, ~0.4 mmol/L (~22 mg/L) [2], some mills have recently reported higher concentrations. Still, even a white liquor Mn concentration below the solubility limit may be problematic. If such liquor is oxidized and used as an alkali source in delignification and bleaching, Mn, as well as the other transition metals, may cause decomposition of oxygen-based bleaching chemicals and radical formation, upon which the pulp quality may be compromised [1]. Monitoring the transition metal content in white liquor when a biofuel, such as bark, is used in the lime kiln is therefore strongly recommended.

Increased levels of other elements in white liquor

In addition to transition metals, the theoretical calculations showed that the concentration of some other elements increased when biofuel was used in the lime kiln. These elements were Cl, Si and Al. In an actual mill, the Cl level would probably have been handled by increasing the treatment of ash from the recovery boiler ESP, but this was not accounted for in our evaluation. The increased Si level in the white liquor resulted in an elevation in the weak black liquor as well, but the levels are lower than critical in the evaporation plant. The Al on the other hand reached concentrations that could be detrimental to the evaporation train in terms of scaling, but only in the cases where bark 1 was being used. It should be noted that the level of Al in this bark was very high.

Summary

Summarizing the findings, it is possible to a certain extent to design systems with larger intake of NPE, but it comes at a cost. Green liquor purification using a clarifier with reasonable results (100 mg/l) rather than a filter with very good results (5 mg/l) in this case reduced active CaO with less than 1 %-unit, to compare with the use of biofuel where the reduction (in the case of reasonable quality of bark) was 9 %-units. Adding poor green liquor clarity to the use of biofuel would probably give an additive effect since the loss in active CaO due to NPE from the biofuel would in no way be affected by the green liquor clarity.

Overall, the quality of raw material is an important factor but it was seen that the lime makeup quality in particular, became crucial in cases where a larger makeup was required. The quality influenced the white liquor plant, but also the rest of the mill since part of the NPE was transferred to the white liquor.

Purge strategy was evaluated on a basic level; however, a complete evaluation would have to include more information specific to a given mill. Based on the assumptions made in this paper, purging via the lime mud filter would be most cost effective whereas purging via the kiln ESP the least cost effective. The main reason for this was the fuel cost. If a more specific evaluation were to be made, the preliminary work could include an alternative assuming a certain enrichment of P.

Finally, the use of biofuel is of great interest as a means of improving the environmental profile, but great care should be taken in ensuring that the NPE content (mainly in the biomass, but also in the lime makeup) is within reason. The evaluation was based solely on the use of bark due to its added benefit of typically being a waste stream, and it can be noted that wood does not have nearly the same level of NPE and will cause much less concern.

References

[1]   Bialik M, Jensen A, Ahlroth M, "New challenges regarding no process elements in the liquor and lime cycle", Tappi J. 14(7), 421-42 (2015)

[2]   Ulmgren P, "Processfrämmande grundämnen i vitlutsberedningen del 1", SCAN FORSK-Rapport 512 (1988)

[3]   Werkelin J. "Ash-forming elements and their chemical forms in woody biomass fuels", 2008

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