Benefits of implementing IRmadillo FTIR analyzer in Kraft chemical recovery processes

Introduction

IRmadillo FTIR analyzer has demonstrated the ability to measure many important chemical species in Kraft mill liquors in real time, including:

Sulfate	**Sulfide**	**Carbonate**
Hydroxide	**Dissolved lignin**	**Total dissolved solids**
Tall oil soap content	**Thiosulphate**	**Oxalate**
Residual alkali		

These measurements allow important parameters such as **reduction efficiency** (RE), **total titratable alkali** (TTA), **effective alkali** (EA), **causticizing efficiency** (CE) and **sulfidity** to be calculated and monitored in real time, thereby allowing optimization of the recovery and recausticizing areas in a Kraft pulp mill.

In many mills, these measurements are provided by taking manual samples from the process and carrying out offline analysis such as titration. Because they are slow, infrequent and often unreliable these results are not well suited to process control and optimization.

The control and optimization opportunities enabled by these real-time measurements from IRmadillo are discussed in turn below.

Green Liquor

Green liquor (GL) is created in the smelt dissolving tank as water (weak wash) is added to the smelt produced by the recovery boiler. The critical control measurement at this point is GL density. Overly concentrated green liquor results in slow smelt dissolution, this may result in the accumulation of molten smelt in the dissolving tank. This can cause violent smelt-water interactions, increasing the risk of **explosions** in the dissolving tank. In addition, excessive density also promotes the formation of pirssonite scale in the green liquor handling system. On the other hand, if density is too low, the alkali concentration of white liquor being charged to the digesters may be too low and this will lead to yield and/or production capacity losses as well as excess water needing to be removed in the evaporators. Density is controlled through the addition of weak wash. Typically, operators either take regular samples to check the density and then adjust the wash flow accordingly, or density may be measured online by a variety of methods such as a standpipe, refractometers or nuclear gauges which can be used as the measured variable in a PID loop which manipulates wash flow.

The next most important parameters (from a composition point of view) at this point in the process are RE and TTA.

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Reduction efficiency (the conversion of sulfate to sulfide in the boiler) should be maintained as high as possible because low values indicate incomplete conversion of sulfide. Low reduction efficiency has the effect of increasing sulfate 'deadload' in the circuit which has the effect of reducing black liquor heating value in the recovery boiler and hence results in reduced HP steam generation. This in turn means that more primary fuel (e.g. gas) is needed to generate HP steam for the mill. The increase in sulfate in the black liquor may also require increased brownstock washing of the pulp to remove it from the pulp fibers and this also leads to additional water being sent to the evaporators and therefore increased steam consumption.

RE can either be measured in the raw green liquor or, if the composition and flow rate of wash liquor is known, back-calculated from clarified GL measurement. With the availability of RE as an online measurement, the recovery boiler can be operated in such a way to keep RE at its target.

An IRmadillo can also be used to calculate TTA (i.e. the sum of carbonate, hydroxide and sulfide concentrations) in the green liquor. In general, TTA should also be maintained as high as possible in GL, subject to a maximum value dictated by the 'Goodwin' equilibrium curve. Achieving target TTA leads to the following benefits:

1. High TTA reduces the amount of water in the recovery cycle. This helps reduce steam consumption in the evaporators (reducing the fuel required to produce the steam), reduces pumping requirements and may also debottleneck production if the evaporators are limiting production. It will also lead to reduced steam consumption used to heat the white liquor up to the required digester charge temperature.

2. Reducing TTA variability allows improved control of reaction stoichiometry in the lime slaker. Stabilizing TTA concentration in the green liquor is a key factor in improving causticizing efficiency, which in turn reduces carbonate deadload and the danger of over-liming and evaporator fouling (see below).

An IRmadillo may be installed in the raw green liquor (GL) stream as it exits the smelt dissolving tank, or – if available – on a recirculation line on the dissolving tank itself. See figure 1 for an example of such an installation. The analyzer can be calibrated to measure the important species at this point (sulfate, sulfide, carbonate and hydroxide). It may also be possible to build a calibration for green liquor density – in which case it could act as a back-up to the existing density measurement - but this has not been proven.

At this stage in the process there is a substantial risk of probe fouling or scaling due to build-up of pirssonite deposits. It has been shown that scale deposits on the IRmadillo probe tip can be removed by periodically cleaning with hydrochloric acid (manually); however, a more efficient method is to use an *IR-Jet* pressure washing accessory supplied by Keit which has been shown in the field to successfully keep the probe clean in high-scaling liquors.

Most mills periodically swap the green liquor and weak wash lines to help reduce the build-up of scale; this may mean that two IRmadillo analyzers will be needed on RGL to provide a continuous reading.

It should be noted that the presence of raw green liquor dregs will have no effect on the IRmadillo's ability to measure GL composition – this is because IRmadillo only measures liquid composition and is unaffected by the presence of suspended solids in the liquid phase.

An IRmadillo may also be installed after the GL clarifier (in which dregs are removed) – perhaps close to the slaker inlet. It could then be used to measure TTA and use the value as the measured value in a PID controller to maintain TTA by adjusting the flow of a weak wash 'trim' flow. Another advantage of this location is that the TTA value could be used as a 'feedforward' input to a control scheme on the causticizer, to more accurately dose lime to the slaker.

The potential economic benefits from installing IRmadillo in green liquor include the following:

- By enabling an increase in average reduction efficiency through continuous measurement of RE, sulfate deadload can be reduced – which means less water circulating around the process and therefore less energy required for evaporation (and hence less steam required from the boilers). Estimated benefit: **$250,000 per annum** per percent increase in RE (for a 2200 Te/day mill). If evaporators or recovery boilers are limiting production, this reduction in deadload may allow additional mill capacity (with the potential for very significant economic benefits).
- By measuring CGL composition in real time, the weak wash trim flow may be controlled in order to achieve a target TTA value and reduce its variability. This will allow the causticizing reaction to be operated closer to optimum (according to the 'Goodwin curve') which in turn will increase the WL effective alkali and reduce energy consumption in the evaporators. A 1 g/l increase in average TTA is estimated to generate savings of around **$60,000 per annum** for a 2200 Te/day mill through reduction in LP steam consumption and increase in HP steam production from the boiler.
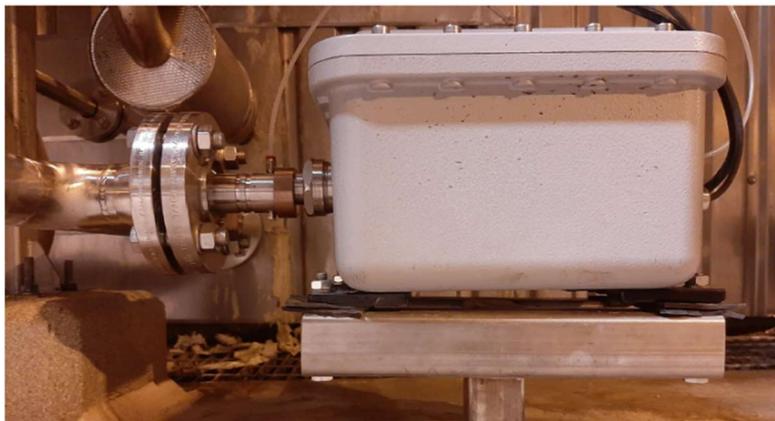

Figure 1: IRmadillo installed in green liquor pipework

White Liquor

Recausticizing is the process of converting green liquor into white liquor. By slaking with lime (calcium oxide), sodium carbonate is converted into sodium hydroxide. The causticizing reaction is initiated in the slaker and reaches equilibrium in the downstream causticizer vessels. White liquor is clarified or filtered to remove lime mud particles and then stored ready to be fed to the digesters. The main objective is to maximize the conversion of carbonate to hydroxide and produce a uniform quality of white liquor. By maximizing WL effective alkali strength, the desired 'alkali-to-wood' ratio can be achieved in the digester with minimum water which then has to be subsequently removed in the evaporators.

A key measure of the reaction is 'causticizing efficiency'. Expressed as a percentage, it is defined as:

$$\frac{NaOH_w - NaOH_g}{NaOH_w - NaOH_g + Na2CO3_w} \times 100$$

Where subscripts *w* and *g* represent the concentration of caustic and sodium carbonate in the white and green liquor respectively. For a given liquor alkalinity (TTA), there is an optimum CE value (as defined by the Goodwin Curve) and the mill will – ideally - attempt to operate as close to that value as possible, given the limitations of the existing instrumentation. If CE is too low, the '**carbonate deadload**' is high, meaning that excess water is traveling around the recovery process. This has the same negative effects on mill operation as mentioned for sulfate deadload above – energy consumption and potential bottlenecking. On the other hand, If CE is too high, it can lead to lime mud particle precipitation and blockage of filters and clarifiers, known as 'overliming' and significant operating difficulties. Elevated carbonate concentrations in the black liquor can also lead to increased fouling of evaporator surfaces due to scale formation which require 'boil outs' and hence reduced production capacity.

Typically, the causticizing process is monitored by taking samples of raw and clarified white liquor and measuring the carbonate, hydroxide, sulfate and sulfide content via titration. These results provide an indication of causticizing efficiency (CE) and are then used to adjust the causticizer operation (typically by adjusting the lime addition rate). The progress of the causticizing reaction is often monitored by differential temperature measurement between the slaker inlet and outlets. Because the reaction continues in the causticizing vessels, this delta T measurement does not give a complete picture and hence the need for manual samples.

Installing IRmadillo into this section of the process will allow the operators to continuously monitor the **causticizing efficiency** reaction and make adjustments to keep the CE at its desired value. This will reduce steam consumption and the risk of carbonate scaling in the evaporators, avoid over-liming events and reduce energy consumption in the lime kiln. It will also lead to reduced white liquor EA (effective alkali) variability which can thereby increase digester yield and reduce kappa variability. **Make-up chemical consumption** will likely also reduce due to fewer spills and losses as less water travels around the recovery circuit.

Suggested locations for IRmadillo analyzer in WL are:

- on the outlet of the first stage causticizer to monitor the causticizing efficiency
- on the feed to the digester from the WL tank, giving an online measurement of EA which will enable more consistent loading of the digester (i.e. better control of the 'alkali-to-wood' ratio)

With real-time measurements of CE in the outlet of the causticizer and good control of green liquor TTA value, an automatic control scheme may be implemented in the DCS which would calculate the target CE based on the Goodwin curve and TTA value to ensure optimum CE is achieved, which in turn would have the effect of minimizing carbonate deadload and maximizing EA. The main 'handle' for this scheme would be the lime-to-green liquor ratio with TTA, slaker delta T and CE as the key measurements.

The key financial benefits of tighter TTA and CE control and EA measurement include:
- reduction in evaporator steam consumption through a reduction in carbonate deadload
- reduction in steam consumption used to heat white liquor charged to the digester
- reduction in evaporator fouling

- improve digester yield and reduce kappa variability. Anecdotally, Keit has been told that stabilizing WL EA could allow average kappa value to be increased by 2, which would be worth approximately $**200,000/year** in a typical Kraft mill

Weak black liquor

After the brownstock washing step, weak black liquor (WBL) from the digesters is collected in the weak black liquor storage tank before being fed to the evaporators and thence to the recovery boiler. Tall oil soap is often recovered as a valuable byproduct at this stage by gravity separation (skimming) from the WBL. The important measurements to consider at this point are **residual effective alkali (REA)** and **tall oil soap concentration** in the WBL after skimming. An IRmadillo can measure both these parameters and the importance of these are considered in turn below.

Tall oil soap should be removed from black liquor for two reasons: it is economically valuable and, if the recovery boiler is a production bottleneck, it takes up 'space' in the boiler which could otherwise be used to burn black liquor solids and hence increase digester throughput. Therefore, an online measurement of residual tall oil soap can allow the soap skimming operation to be operated in such a way as to maximize soap removal and generate a good payback - this will vary depending on local economics e.g. value of tall oil soap but can be in the order of several **$100,000 per annum**. If the recovery boiler is limiting production, then the benefits can be very significant indeed, because by sending less soap to the boiler, more black liquor solids can be processed and additional pulp produced.

Measurement of REA in black liquor can allow the mill to optimize the alkali-to-wood ratio in the digesters (one measurement point would be needed in the outlet of each digester). It is important that REA is kept above a minimum value to avoid lignin precipitation in the evaporators. Excess REA above this minimum means that unnecessary WL – and hence water - is charged to the digesters which in turn requires additional steam to remove in the evaporators and a corresponding reduction in HP steam production from the recovery boilers – which costs money. Hence it makes sense to measure the residual alkali in the digester outlet and use this information to adjust the digester charge ratios to keep it as low as possible (but above the limit of precipitation).

Other Measurements

In addition to the measurements mentioned above, an IRmadillo can be used to provide other real-time composition results:

- Chloride – this could be measured anywhere in the circuit. If chloride levels are too high, this can lead to excessive fouling of the recovery boiler heat transfer surfaces due to black liquor reaching its sticking point. It can also lead to corrosion problems. By having real time information about this component, the mill can optimize purging strategies and avoid operational difficulties.
- Thiosulfate. This is also present in green liquor and is not routinely measured by most mills. However, it is also a contributor to "deadload" as it is not an active chemical used in pulping but nonetheless takes up space in the liquors – and therefore additional water to be removed in the evaporators. Measuring thiosulfate allows identification of further opportunities for deadload reduction.

- Chlorate and sulfuric acid in chlorine dioxide generators. This can allow the reactor feeds to be controlled so that expensive raw material consumption is reduced, and hazardous 'decomposition' events are avoided.

Summary

IRmadillo FTIR analyzers can be used in Kraft mills to measure the composition of green, white and black liquors. This in turn allows measurement and better control of reduction efficiency, TTA, CE and EA which can realize significant savings. Although all mills are different (i.e. economics, constraints and operating objectives), indicative benefits for a 2000 o.d. Ton/day mill from this approach are as follows:

Parameter	Improvement (average)	Benefits per year (approx)
Reduction Efficiency (RE)	2% increase	**$100,000**
Causticizing Efficiency (CE)	2% increase	**$100,000**
Total Titratable Alkali (TTA)	2 g/l increase	**$130,000**
Residual Effective Alkali (REA)	2 g/l decrease	**$450,000**
Tall oil soap yield	20% increase	**$300,000** (depending on value of tall oil soap)

References

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[2] Grace, M and Tran, H: TAPPI JOURNAL July 2009