Real-time process analyser for in-process monitoring of **green liquor in the recausticising process**

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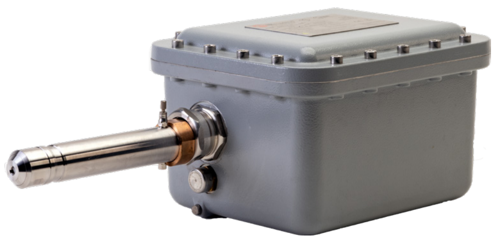
Abstract

There is a need in the pulp industry to accurately monitor chemical constituents of green liquor for improved process efficiency, pulp quality and recovery boiler operation. Current technologies struggle to accurately monitor these constituents in real time. The installation of the IRmadilloDiamond into a pulp mill successfully demonstrates how the FTIR-based process analyser can provide real-time, on-line analysis of green liquor inorganic chemicals, thereby making it a powerful monitoring solution for pulp mills.



IRmadilloDiamond

Introduction

The Kraft process is the dominant method of pulp manufacture globally. The process of converting wood into wood pulp involves treating wood chips with steam, sodium sulphide (Na_2S) and caustic soda (NaOH) at elevated temperature and pressure. This produces pulp and, as a by-product, inorganic chemicals that can be recovered back to Na_2S and NaOH through a recausticising process.

Recausticising is the process of converting green liquor (Na_2CO_3 + Na_2S) into white liquor (Na_2S + NaOH) that is returned to the digester to be reused in the cooking process.

The presence of Na_2S and NaOH in the cooking liquor protects the pulp fibres from degradation during the cooking process. The control of the chemical composition of the cooking liquor is critical for production of the strong pulp fibres. Analysis of the green liquor provides critical information for that control. Today, this is typically monitored off-line using titration methods but this is too infrequent to allow meaningful process optimisation decisions. The ability to measure green liquor composition in real time using FTIR brings new possibilities for mill optimisation.

Key Words

- Kraft process
- Recausticising process
- Pulp and paper industry
- Green liquor
- Sodium carbonate (Na_2CO_3)
- Sodium sulphide (Na_2S)
- Sodium hydroxide / caustic soda (NaOH)
- Liquor alkalinity

Features & Benefits

- Mid-infrared/FTIR spectral analysis
- Vibration tolerant
- Long-term stability
- Low maintenance
- Compact design
- Real-time, multi-component analysis
- Easy to use

In addition to control of chemical composition, effective recycling of cooking chemicals is essential for paper mills to remain financially viable. Real-time process analytics can improve the efficiency of this process. Current instruments available for monitoring specific elements of the manufacturing process, such as near-infrared spectroscopy (NIR), may struggle because:

- They require sample conditioning
- They are not compatible with suspended solids/bubbles
- They are not compatible with fluctuating temperatures
- They cannot differentiate between similar molecules

The Keit IRmadilloDiamond has been specifically designed for harsh, unforgiving, and caustic environments, and is ideally suited for monitoring pulp and paper manufacture – enabling real-time control and improved efficiency and therefore saving the mill money.

Experimental

The IRmadilloDiamond was installed in a pulp mill and calibrated on-line to allow indicative measurements of the key species of interest and consequently to allow improved control and optimisation of the liquor recausticising process.

A 30-min background scan was taken prior to installation. The IRmadilloDiamond was then installed in the process (100–105°C, 3–4 barg and pH 14) using a welded flange interfacing with a 2” pipe. Spectral data was collected continuously (scan average 120 s) over a period of one month.

The IRmadilloDiamond was calibrated using timestamped, off-line reference values (4 off-line samples every other day) that corresponded to on-line spectral data using the frequency region 800–1800 cm^{-1}.

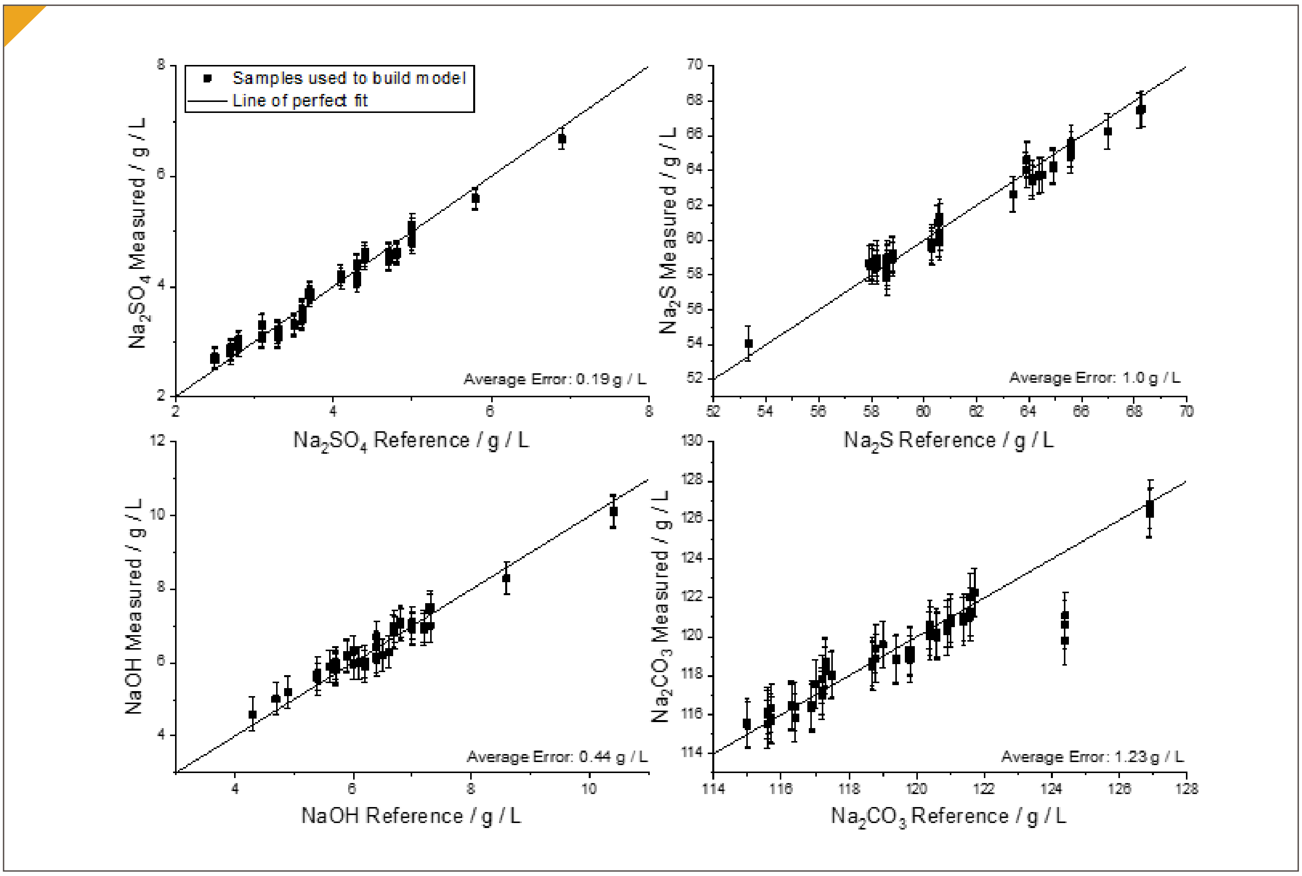


Figure 1: Reference vs. measured plots of absolute chemical concentrations from data collected over one month.

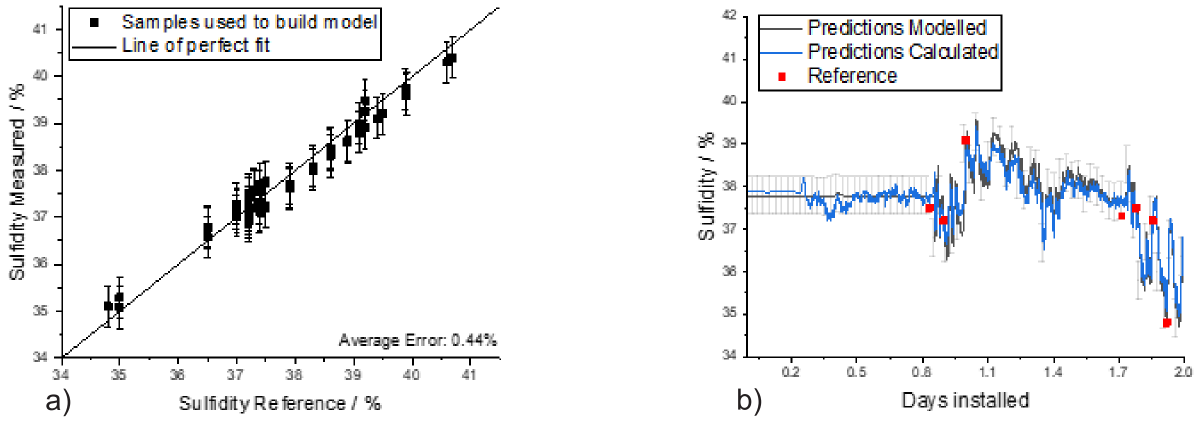


Figure 2: a) On left, plot of measured vs. off-line reference values of sulfidity **b)** On right, plot of sulfidity monitored over two weeks, demonstrating that commonly used calculated values (such as EA, AA, TTA and Sulfidity) can be easily calculated in the DCS based on the chemical compositions provided by the IRmadillo.

The IRmadilloDiamond was used to analyse:

- Na_2SO_4
- NaOH
- Na_2S
- $NaCO_3$
- Reduction Efficiency (RE)
- Effective Alkali (EA)
- Active Alkali (AA)
- Total Titratable Alkali (TTA)
- Sulfidity (% = Na_2S / (Na_2S + 80% (NaOH + Na_2CO_3)))

Chemometric models for absolute chemical concentrations were built using support vector regression (SVR) methodology (see Figure 1).

Chemometric models for calculated properties - RE, EA, AA, TTA and sulfidity - were also initially built using support vector regression (SVR) methodology from reference data (see Figure 2a for one example).

Predictions of RE, EA, AA, TTA and sulfidity were then calculated from direct chemical concentrations and compared to predictions from chemometrics models (see Figure 2b).

Results and discussion

SVR modelling was used due to the non-linear correlation between the components to be measured and the spectral response.

Figure 1 shows the measured value from the IRmadilloDiamond on the y-axis and the reference value on the x-axis for all key chemical compounds in green liquor. The results clearly show that the relationship between the measured and reference values is extremely linear; the IRmadilloDiamond is demonstrating excellent performance in all cases.

The average error (which is used as a limit of detection – LoD – for low concentration ranges) across the corresponding concentration range is 0.19 g / L for Na_2SO_4, 1.0 g / L for Na_2S, 0.44 g / L for NaOH and 1.23 g / L for Na_2CO_3.

Figure 2a shows the measured value vs. off-line reference value of sulfidity, a calculated key property of green liquor. However, Figure 2b clearly shows that when used to monitor the green liquor line (black trend) it was not as accurate as calculating sulfidity from raw chemical concentrations. This demonstrates that for calculated properties (such as EA, AA, TTA and RE) it would be more accurate to calculate these in the DCS itself from the raw concentrations of the individual chemicals.

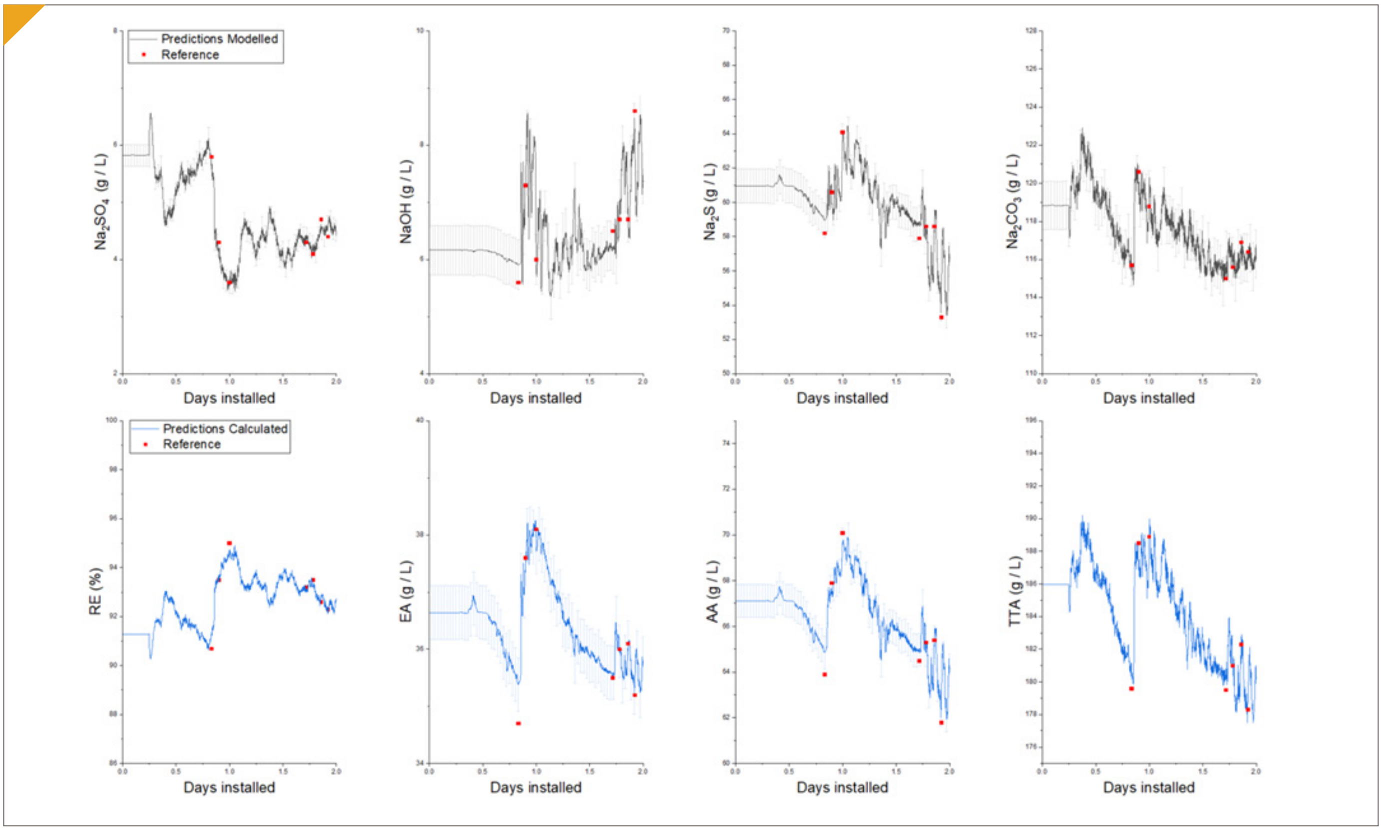


Figure 3: Predictions (modelled and calculated) of reaction constituents throughout the recausticising process, monitored by the IRmadilloDiamond across two weeks in a paper mill.

Figure 3 shows traces from the IRmadilloDiamond of all key green liquor constituents over time, installed in a paper mill over a two-week period.

The blue trends show the predictions of calculated properties based on raw chemical concentrations, and the black trends show predictions based on chemometric models built using off-line reference values of absolute chemical concentrations. Intervals of plateau on these plots show the periods of time when the line was flushed with weak liquor.

The four chemometric models are currently being used for indicative trending and predictions of the green liquor line and will be augmented for improved robustness and accuracy as more off-line data is collected.

Conclusions

The IRmadilloDiamond has shown to be an effective process analyser for green liquor monitoring in the recausticising process.

The Keit IRmadilloDiamond is specifically designed for harsh, unforgiving, and caustic environments, and is ideally suited for monitoring pulp and paper manufacture.

The on-line, real-time measurements can be used to finely control the chemical composition of the green liquor as well as improve overall efficiency of the recausticising process.

Keep in mind

Innovation in design means the IRmadillo analyser can be used on-line throughout the Kraft process — from wood processing through to additive control on the final product.

- Green liquor stream
- White liquor stream
- Weak black liquor stream
- Concentrated black liquor stream
- Unbleached pulp liquor stream

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