APN0889

Vibration-tolerant FTIR for in-process monitoring and control of recausticising in pulp production

Key Words

- Kraft process
- Recausticizing process
- Pulp production
- Green liquor
- Total titratable alkali (TTA)
- Sodium carbonate (Na_2CO_3)
- Sodium sufide (Na_2S)
- Sodium hydroxide (NaOH)
- Sodium sulfate (Na_2SO_4)
- Liquor alkalinity

Abstract

A static-optics FTIR instrument – the IRmadillo – has been used to measure and report total titratable alkali (TTA), sodium carbonate and sodium sulphide in real time in a green liquor stream to better control the recausticising process in a pulp mill. This installation has been running for longer than one year with no additional background scan being taken on the instrument.

Introduction

Recausticising green liquor into white liquor ready for reuse in wood digestion is one of the most important aspects of modern kraft-mill pulp production. But controlling the correct amount of lime is a challenge, especially when the only reference points are infrequent titration measurements as a reference to control against. If you under-lime the process, the white liquor will not be strong enough to effectively and efficiently digest the wood. If you over-lime, you will waste chemicals and energy as well as risk causing critical scaling events.

Total titratable alkali is a key input into controlling the lime slaker, commonly measured using autotitrators. The definition of TTA is normally:

$$TTA = [NaOH] + [Na_2CO_3] + [Na_2S]$$

Strictly speaking any other alkali such as Na_2SO_3 should also be included but is usually omitted for ease.

Autotitrators can measure the TTA, but they are slow, and require a sample to be removed from the green liquor line – a dangerous process. Auto-sampling autotitrators do exist, but require copious plumbing that can be expensive to maintain and difficult to install, and they are liable to scale up and block.

Here we present the use of a static-optics FTIR spectrometer – the IRmadillo – to measure TTA in real time upstream of the lime slaker in a pulp mill.

Instrument Installation and Calibration

The IRmadillo instrument was installed directly into the outlet of the smelt dissolving tank at a pulp mill using a welded flanged connection (see Figure 1). The pipe is periodically flushed to prevent scale formation.

Spectra were acquired continuously with a two-minute averaging time to optimise signal to noise ratio (SNR).

Calibration was performed using a range of partial least squares (PLS) and support vector regression (SVR) models using Eigenvector Research, Inc's (EVRI's) Solo chemometrics package. Reference data were provided by the mill using an autotitrator.

Results and discussion

The measurement of TTA, sodium carbonate (Na_2CO_3) and sodium sulphide (Na_2S) over time is shown in Figure 2. The instrument has been continuously measuring for a period of > 1 year, and data from November 2020 and November 2021 are shown on the graph to highlight the continued robustness and reliability of the system. Reference data as provided by autotitration are shown as red squares. (The line is periodically washed with weak green liquor, and this is shown as measurements substantially lower than the main measurements).

There is good agreement between the on-line IRmadillo measurement and the reference data, especially with the sodium sulphide measurement. The information provided by the IRmadillo allows differentiation between the contributions to TTA, potentially improving recausticising and dosing control. In this case it was found that the reference data provided from the autotitrator for sodium hydroxide (NaOH) was not suitable for building a calibration curve. Autotitrators record different plateaus of voltage vs concentration and make assumptions about cutoffs, and this may have propagated an error.

Features & Benefits of the IRmadillo

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

KEIT | INDUSTRIAL ANALYTICS
Measure | Trust | Improve

Figure 1: Photograph of the instrument installed at the outlet of the dissolving tank.

It is possible to calculate sodium hydroxide concentration by subtracting sodium sulphide and sodium carbonate concentrations from TTA. Those results are shown in Figure 3 – and show good agreement with the reference data.

Why does the measurement sometime not agree with the autotitrator?

Some of the measurement points do not agree with the reference data – as can be seen in both Figure 2 and Figure 3. There is always a continued data measurement that doesn't pass through a given reference point. This highlights the danger of autotitrators (and other laboratory/extractive techniques) compared to continuous in-line and on-line measurements. How can you ensure that the one individual measurement just made is accurate?

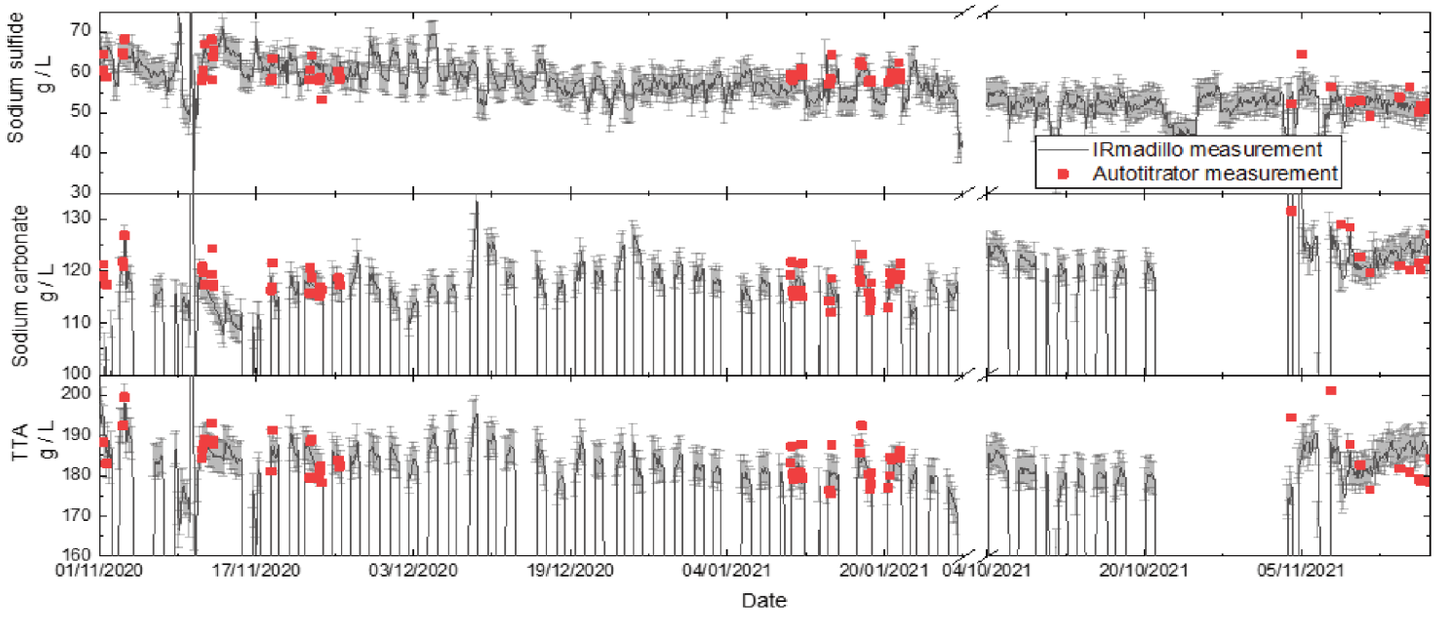

Figure 2: Results of IRmadillo on-line measurements of TTA, sodium carbonate and sodium sulphide over time

It is obvious from continuous data when a single measurement is wrong – it will be very different from the previous measurements, and can easily be discounted. But when only one measurement is taken every few hours it is much more difficult to understand whether it is true or not. During calibration of the IRmadillo, statistical tests were performed on the dataset to remove outliers which were statistically outside of reasonable limits (a 95 % confidence limit on Studentized residuals). This is particularly obvious on the measurements of the 5th November 2021 in Figure 2 – the TTA measurements are anomalously high. This highlights the dangers of relying on single extractive measurements like autotitrators: if a measurement is incorrect but the mill makes a change or process decision on it then there may be knock-on effects ranging from inefficiencies through to damage to the mill and the pulp product.

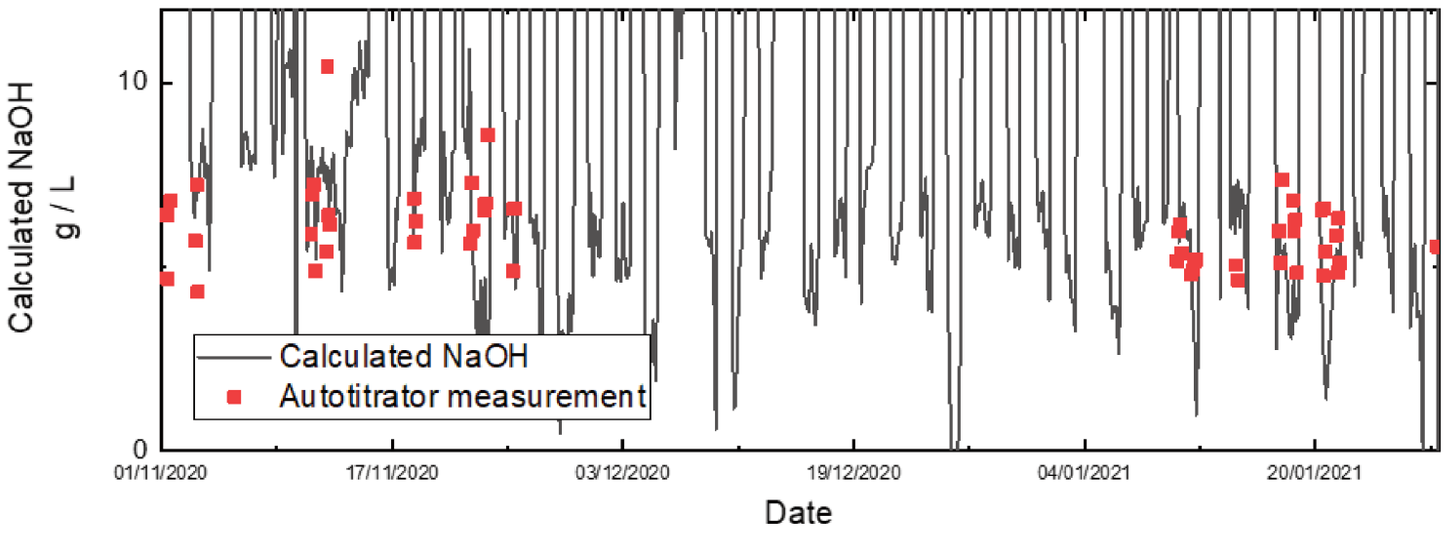

Figure 3: Results of IRmadillo NaOH calculated measurement over time

How can spectroscopy be more trustworthy than extractive sampling?

Spectroscopic calibrations are built upon off-line reference results, so additional scrutiny is applied to the reference data when building the calibration. That does sometimes mean removing outliers that fail statistical checks.

Once an instrument has been calibrated then every spectrum can have an automated check applied – such as Hotelling's T^2 and Q residual limits, which are standard statistical methods of confirming that a measurement is valid and has high confidence. The output of this test can be reported with any spectroscopic measurement to give the mill operators confidence in what the instrument is reporting.

What about scale?

Throughout the year this instrument has been installed, there has been only one major scaling incident. The instrument continued to operate during this time, but there was a delay in response for concentration changes as the chemistry was delayed moving through the porous scale.

These spectra of "scaled probe" were then used to build an indicator to alert the mill that scaling had occurred. The scale was easily removed using 1 M hydrochloric acid (HCl). This washing step took approximately 1 hr to perform.

Conclusions

This work shows that the IRmadillo can and has been calibrated to act as an *in situ* on-line TTA measurement analyser. Furthermore, the IRmadillo can report on the individual chemicals contributing to TTA, as well as other analytes – such as sodium sulphate (Na_2SO_4). This enables one instrument to act not only as a recausticising control device, but also an indicator of reduction efficiency.

Keep in mind

The IRmadillo is an FTIR instrument operating in the mid infrared wavelength range – not near infrared (NIR). The IRmadillo gives significantly more information than an NIR instrument. As a result, it has a much more stable calibration and needs a lot less sampling to build a robust calibration.

It may be tempting to compare NIR and FTIR as equivalent technologies, but they are fundamentally different with completely different physics and chemistry underwriting them!

Read more: www.keit.co.uk/IRmadillo-vs-NIR/

Contact us

+44 (0) 1235 431260

(Sales) enquiries@keit.co.uk

(Product Support) support@keit.co.uk

www.keit.co.uk

KEIT
INDUSTRIAL ANALYTICS
Measure | Trust | Improve

Keit Ltd. trading as Keit Industrial Analytics
4 Zephyr Building, Eighth Street, Harwell Campus, Didcot, Oxfordshire, OX11 0RL, United Kingdom

APN00889 (25 March 2024 12:13 pm)