AA15 - Online FTIR Analysis for Improved Efficiency in Alumina Production

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Abstract

Online analysis of continuous and batch processes has seen a dramatic increase in recent years, with examples ranging from petrochemicals to pharmaceuticals, to industrial biotechnology and food & drink. The particularly challenging environment of alumina processing has meant that instrumentation needs specific features and characteristics to be truly suitable, features such as robustness, resistance to caustic conditions both in the analyte and the ambient environment, and reliability for long-term continuous use. Here we present the development of a novel FTIR spectrometer that achieves these requirements through the use of a static optics arrangement of mirrors, and a stable diamond-tipped light-pipe probe.

Firstly, we give a very brief explanation of spectroscopic analysis, and the difference between FTIR and other infrared methodologies. Next, we outline the novel arrangement of mirrors required to produce an interferogram without moving mirrors and compare the benefits and drawbacks of this approach with those of conventional designs.

We then share the results of laboratory analysis of synthetic Bayer liquors, with detection limits for aluminium hydroxide, sodium hydroxide, sodium carbonate and various sodium salts of organic acids. We then share the results of analysis on production samples – predominantly from spent liquor lines.

Lastly, we present work on in situ ultrasonic descaling solutions to avoid scale buildup and provide continuous cleaning of the probe – preventing the need for probe removal and manual cleaning.

Keywords: Online analysis, process improvement, FTIR spectroscopy, process analytical technology, real time analysis.

1. Introduction

Online process analytical technology (PAT) is an important area of development in a wide range of industrial processes [1, 2], and a key element of Industry 4.0 – the commonly accepted fourth industrial revolution we are currently experiencing. Traditional instrumentation (such as pH and temperature probes) is being complimented with more advanced techniques such as spectroscopy.

Spectroscopy can be defined as the interaction of light with matter, and the wavelength and energy of the light absorbed determines the underlying interaction studied. A full explanation of all the different spectroscopic techniques and wavelengths is beyond the scope of this article and is available elsewhere [3]. The majority of PAT implementations make use of vibrational spectroscopy – namely near-infrared (NIR), Raman and mid-infrared Fourier transform (FTIR) spectroscopies.

1.1 Near-Infrared Spectroscopy

NIR spectroscopy [4] is an absorbance technique where light in the wavelength range 0.8 – 2 µm is used to irradiate a sample and the light absorbed is proportional to combination and overtone bands of fundamental infrared vibrations. NIR instruments can be built on either dispersive (i.e. gratings and prisms) or Fourier transform (i.e. Michelson interferometers) principles. In either case the instrument is typically positioned far away from the sampling point, using a near infrared fibre to transmit the light from the source to the sample and back to the detector. To date most PAT spectrometers installs involve NIR instruments, because they have a track record of reliability in challenging environments. However, calibration and maintenance of NIR based approaches is "a complex process, requiring long-term database maintenance and calibration model update" [5]. Moreover, the lack of chemical information from NIR spectroscopy as a technique makes identifying and differentiating similar molecular structures with NIR a challenge at best, and impossible at worst.

1.2 Mid-Infrared FTIR Spectroscopy

FTIR spectroscopy [6] is also an absorbance technique, one which uses light between 2 and 20 µm, but it can offer substantially more information than NIR, as it investigates the fundamental vibrations of molecules rather than overtones and combination bands. This means that small changes in molecular structure can be identified and quantified [7], for example in the differentiation of proteins [8]. Conventional FTIR spectrometers use an arrangement of fixed and moving mirrors (based on the Michelson interferometer [9]), which means the instrument needs to be removed from any sources of vibration – common in industrial processes. While NIR spectrometers can use tried and tested fibres and probes to achieve this with relative ease, FTIR fibres are extremely fragile and have very low through-put of mid-infrared light – making their use in industrial settings very difficult to achieve.

1.3 Raman Spectroscopy

Raman spectroscopy [10] is a scattering and emission technique, where a laser is used to excite the sample to a virtual excited electronic state, which then relaxes back into the ground electronic state. Most molecules relax back into the same state they were initially in, emitting light of the same wavelength used for excitation (Raleigh scattering). A small proportion of molecules relax into a different vibrational state, emitting light that is shifted to a different wavelength (Raman scattering). There are examples of Raman spectroscopy being applied to the study of alumina processing with promising results [11], but in highly controlled environments at the laboratory scale. Raman instruments typically use fibre probes and near infrared lasers (either 785 or 1064 nm wavelengths). Raman spectroscopy often suffers from high fluorescence and requires complicated mathematical processing to remove these artefacts, which can reduce the reliability and robustness of analysis.

Here we present the use of a static optics FTIR spectrometer based on the Sagnac interferometer [12], with no moving parts or fibre optics. This gives the performance of a laboratory FTIR spectrometer but the robustness of a production NIR instrument – greatly increasing the information available for process control and opening the world of real time spectroscopy-based PAT to the alumina processing industry.

2. Instrument Design

We will briefly outline the optical design of conventional instruments and the novel design highlighted here to give context to the stability and performance of the static optics design.

The scale is shown to build up over time, rising from a spectral intensity of 0.7 absorbance units to a maximum of 0.34 over the allotted time (although it should be noted that the rate of growth suggested indefinite scaling without intervention). Over this time the intensity of the dissolved $Al(OH)_3$ and water peaks decreased – showing that the Gibbsite formation blocked the sensing of the liquid analyte of interest. The initial ultrasound pulse removed the substantial majority of the signal from scale almost immediately. Two further pulses removed the scale down to the baseline level of signal. This experiment was designed to represent a worst case scenario with sporadic ultrasonic cleaning, but a more practical periodic ultrasonic pulse of 5 s cleaning every 5 – 10 min of sensing would prevent the formation of any detectable level of scale on the probe itself, ensuring accurate measurements in real world applications.

5. Conclusions and Further Work

The authors conclude that the static optics FTIR spectrometer is sufficiently accurate for the monitoring of alumina processing in the Bayer process, with accurate measurement of $Al(OH)_3$, NaOH, Na_2CO_3 levels enabling real time closed loop control. Furthermore, it is possible to accurately monitor the levels of dissolved organic acid salts with the same instrument, with detection limits of 0.11 – 0.31 g/L depending on species. Lastly, the instrument can be coupled with externally mounted ultrasonic cleaning to ensure scale build up over time does not prevent long term measurement, regardless of the installation location.

The instrument is currently installed in one production site, with early stage discussions with other manufacturing plants world-wide. The authors hope to present more detailed online data from real world installations with potential discussion of return on investment and use case scenarios in due course. This will resolve open questions and concerns about the formation of particles in suspension such as sodium aluminosilicates. The design of the probe is resilient to interference from solids, as an attenuated reflectance probe (ATR) does not rely on traditional reflectance or transmission approaches, and only interacts with approximately 2 µm of liquid – meaning that solids do not interfere with the liquid analysis. It is expected that long term installations in multiple sites with varying impurity levels within the bauxite will resolve this question.

6. References

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