

Fourier transform near infrared process monitoring of multiple inorganic ions in aqueous solution

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Introduction

This paper presents the implementation of a multipoint process monitoring system for a three stream plant producing soda by the well established Solvay process. The Solvay process is briefly reviewed and the analysis requirements will be given. The calibration of the analyzers for the actual process samples is difficult and cannot be repeated easily. So one of the most important characteristics of the analyzers is that the calibration must be permanent even for replacement analyzers when servicing requires this. The implementation has been accomplished with a multipoint FO system using three analyzers for a total of 15 sampling points. There are four distinctly different analysis points in each process stream where the composition is unique. Some of these process points contain large amounts of solid particulates which must first be dissolved in a sample preparation step in order to determine the total amount of solids present as well.

The Solvay process

The Solvay process consists of the production of NaHCO_3 and NaCO_3 from NaCl and CaCO_3 . A concentrated aqueous solution of brine is reacted with NH_3 gas. Carbon dioxide liberated from CaCO_3 is bubbled through an ammonia salt solution to form $(\text{NH}_4)_2\text{CO}_3$ and NH_4HCO_3 . Ammonium carbonate and bicarbonate react with NaCl to form NaHCO_3 which precipitates out. The ammonia is recovered from NH_4Cl and CaO and CaCl_2 are by-products.

Process monitoring requirements

Process monitoring requirements are:

- Fill liquor which is the ammonia salt brine starting solution. Here we require to monitor the balance of NH_3^+ , Cl^- and CO_3^{-2} to insure adequate ammoniation and salt consumption.
- Hot liquor which is NH_3Cl solution after reaction of the CO_2 . Here we require to monitor the balance of NH_3^+ , Cl^- and CO_3^{-2} to control use of steam.
- Mixing liquor which is NH_3Cl with CaO in solid suspension. The monitoring of Ca^+ along with NH_3 and Cl is used to control the level of CaO .
- End liquor which is the final solution of CaCl_2 with dissolved Ca and CaO in solid suspension. The absence of NH_4^+ indicates full recovery of NH_3 .

Concentration ranges

The concentration ranges expected for each ion at the different process points are:
 NH_3^+ (in form of NH_4OH)

- fill liquor 60–100 g L⁻¹

■ hot liquor	50–100 g L ⁻¹
■ mix liquor	50–100 g L ⁻¹
■ end liquor	0–10 g L ⁻¹

CO₃⁻²

■ fill liquor	60–120 g L ⁻¹
■ hot liquor	50–100 g L ⁻¹
■ mix liquor	110–140 g L ⁻¹

Cl⁻ (in fill, hot and mix liquor NH₄Cl and end liquor CaCl₂)

■ fill liquor	140–170 g L ⁻¹
■ hot liquor	120–150 g L ⁻¹
■ mix liquor	110–140 g L ⁻¹
■ end liquor	80–100 g L ⁻¹

Ca⁺² (in the form of Ca(OH)₂ after dissolution of solids)

■ mix liquor	50–100 g L ⁻¹
■ end liquor	0–30 g L ⁻¹

Feasibility and calibration strategy

The inorganic ionic species in aqueous solution have no infrared (IR) bands. We therefore must monitor their effect on the spectrum of water in the near infrared (NIR). By laboratory test solutions we determined that we can distinguish NH₃⁺, Cl⁻ and CO₃⁻² ions. Temperature affects the water spectrum in a similar manner to the ions. We had to make a choice to either sample at constant temperature or include temperature in the calibration as an independent parameter.

The initial calibration effort centered around the analysis of laboratory solutions prepared with the aid of a consultant with experience in the Solvay process. This was found to be poorly representative of the actual process streams. Process samples were collected and analyzed in the lab by both NIR and titration. This was initially also unsuccessful. Finally, samples were analyzed directly on-line with the Fourier transform (FT) NIR analyzers and immediately analyzed by titration. This proved workable but did not provide a satisfactory range of concentrations. Eventually an unforeseen process upset provided a useful range of concentrations to round out the calibration.

Sampling

Each process monitoring point was provided with a bypass and sample conditioning hardware. The actual NIR analysis was done via a fiber coupled stainless steel transmission cell with sapphire windows from Galileo. Provision was made for cell flushing and cleaning as well as drying with compressed air and filling with sample or pure reference water. Frequent referencing with pure water provided reliable difference spectra of the process sample compared with water.

No specific sample conditioning apart from particulate filtering was required for the fill and hot liquor points. The mix and end liquor, with large amounts of solid particulate in suspension, required dissolution of the solid CaO in order to measure the equivalent Ca⁺.

What was installed and how well does it work

All analyzers and sampling points were supplied and installed, but because of the difficulty in dissolving the solid particulates, the monitoring points in the hot and end liquor were not

commissioned. One FT-NIR analyzer monitoring three hot liquor and three fill liquor process points have been commissioned and have been operational for nearly two years.

The analyzer tracks the stream deviations extremely well providing valuable process optimization information in a timely manner. There has been no down time since commissioning. The absence of calibration maintenance requirements has made the application feasible on a continued basis. There are essentially two problem areas with the installation; (i) there is an apparent corrosion problem with the stainless steel cells and (ii) some care is required to insure the purity of the reference water in order to avoid errors in analysis.

Conclusions

Process monitoring of inorganic ionic aqueous solutions is feasible. The Multipoint FO system is an economical solution. Calibration transfer from one FO channel to another has reduced calibration effort by three times. Absence of calibration drift is essential for success of the application because calibration maintenance is nearly impossible on a routine basis.