



FITNIR ONLINE – CHLORINE DIOXIDE GENERATOR APPLICATION

FITNIR's fully automated online analyzer reliably measures complete liquor compositions to help pulp mills decrease process variability for improved efficiency and profitability. Fast, frequent and accurate measurements drive process control strategies for optimization. FITNIR Online is capable of sampling from multiple sources and testing numerous components simultaneously, providing true measurements of sodium chlorate and sulfuric acid in generator solutions to achieve the most efficient mode of operation. With its proven application for the chlorine dioxide generator, FITNIR is the next generation of process analyzers for pulp mills.

Innovative Solution to Traditional Measurement Challenges

THE NEED FOR ACCURATE & TIMELY DATA

The production of chlorine dioxide (ClO₂) is a major contributor of the overall bleaching cost of a Kraft mill. In an effort to reduce this cost, methods of increasing ClO₂ generator efficiency are needed. A major factor adversely affecting generator efficiency is poor process stability and high variability due to the lack of adequate process measurements for generator acid and chlorate concentrations, as well as integrated process control strategies including level control.

ClO₂ is generated by combining sodium chlorate (NaClO₃) and sulfuric acid (H₂SO₄) and reacted with methanol to form gaseous chlorine dioxide, with methanol as the limiting reagent. The measurements of ClO₂ strength and the acid and chlorate concentrations are done by manual titration. The typical concentration of ClO₂ strength is 10 – 12 g/L while the acid and chlorate strengths are approximately 400g/L and 200g/L, respectively (R8).

As such, ClO₂ generator stability and efficiency are highly dependent on tight control of the chlorate (ClO₃) and acid (H₂SO₄) concentrations in the generator liquor. Unfortunately, these variables are seldom, if ever, under closed-loop control.

INNOVATIVE SOLUTION

Online measurements of Kraft pulping liquors have historically been a hurdle for the pulp processing industry. Traditional measurement techniques (i.e., conductivity, density, temperature and differential pressure) have only had moderate success due to scaling and fouling of their probes, along with lacking chemical specificity that only infers key chemical properties. Until recently, the industry has accepted laboratory titrations

as its method of choice for complete liquor composition analysis. For ClO₂ generator applications, standard titration suffers from solids interference during pipetting, a long reaction time requirement for ClO₃, and endpoint detection. All of these lead to testing errors for acid and chlorate.

FITNIR Online is a fully automated process analyzer capable of sampling from multiple sources and testing numerous components simultaneously. FITNIR Online's ClO₂ generator application is the only online process analyzer that can provide true generator liquor acid and chlorate concentrations, as well as solids content.

MEASUREMENT PRINCIPLES

Near infrared (NIR) spectrometry, which roughly spans the frequency range 14000 cm⁻¹ to 4000 cm⁻¹ (700 nm to 2500 nm), comprises of overtones and combinations of fundamental vibrations of -CH, -NH, -OH, and -SH. Molecules and anions have unique spectral features that can be used for quantification as the absorption bands are proportional to concentration. By scanning the entire spectral region, simultaneous measurements of multiple chemical properties can be determined. NIR spectrometry has seen wide-spread use due to its lower water absorption bands. Consequently, NIR can operate through glass, can be transmitted via low hydroxyl fibre optic cables, and generally requires

Table I: ClO₂ generator measurement efficiency

CLO ₂ GENERATOR LIQUOR	MEASUREMENT RANGE	ACCURACY (1 sigma value)
Chlorate (NaClO ₃)	0 - 490 g/L	± 2.5 g/L
Acid (H ₂ SO ₄)	0 - 425 g/L	± 1.0 g/L
Solids (%)	0 - 40%	± 0.8%

KEY FEATURES

- > Fully automated for frequent testing
- > Patented application with large pathlength flowcell
- > High repeatability, accuracy, and reliability
- > Automated flushing of sample lines and cell with water to prevent scaling
- > Sample scanning and measurements take only minutes
- > Data transfer to mill's PLC and DCS via Modbus and OPC
- > Automated process and diagnostic alarms ensure reliable operations
- > Remote analysis via fibre-optic cable
- > Little or no need for recalibration resulting in nearly 100% uptime
- > No chemical requirements

minimal sample preparation. Moreover, NIR is more amenable for use with large pathlength cells up to 20 mm thus, eliminating plugging.

PROPERTIES MEASURED

As shown in Table I below, FITNIR Online's ClO₂ generator application measures a comprehensive set of properties associated with the ClO₂ generator liquor. Acid and chlorate information is required for compositional control of the generator, while the solids indicate saltcake filtering efficiency.

CLO₂ GENERATOR OPTIMIZATION & CONTROL

The primary advantage of applying FITNIR Online for ClO₂ generation is its ability to provide reliable and accurate online measurements of chlorate and acid strength in generator solutions. Control strategies based on reliable FITNIR data have resulted in significant reductions in acid and chlorate strength variations. Table II summarizes the results achieved through optimization. Typically, 45% to 50% reduction in variation can be achieved.

Once variations in the key parameters have been reduced, control applications running the generator closer to the whiteout region significantly improves

Table II: Improvements in ClO₂ generator operations

SVP-LITE	MANUAL	AUTOMATIC FT-NIR
Chlorate Variability (Std. Dev.)	39 g/L	18 g/L
Acid	27 g/L	14 g/L
Efficiency	93.8%	97.4%
Annual Savings	\$0	\$800,000

reaction efficiencies. Annual savings in the range of \$500,000 to over \$1M can be realized, depending on generator production capacity.

CLO₂ GENERATOR ANALYZER INSTALLATION & RESULTS

Installation: Figure I shows a schematic diagram of an SVP ClO₂ generator integrated with FITNIR Online, sampling from a line feeding the saltcake filter. Measurement sequencing is controlled by a user-defined table on the DCS. Typical measurement frequency is every 10 to 15 minutes. Boosted demineralized water is used to flush the flow cell as well as backflushing the sample lines, thus ensuring reliable performance.

KEY BENEFITS

- > **\$0.5M - \$1.2M savings/year**
- > **6 – 12 months ROI**
- > **Improves ClO₂ generator control and efficiency**
- > **Reduces process variability by 45 - 50%**
- > **Reduces occurrences of puffs**
- > **Improves safety for operators and testers**
- > **Requires fewer lab tests**

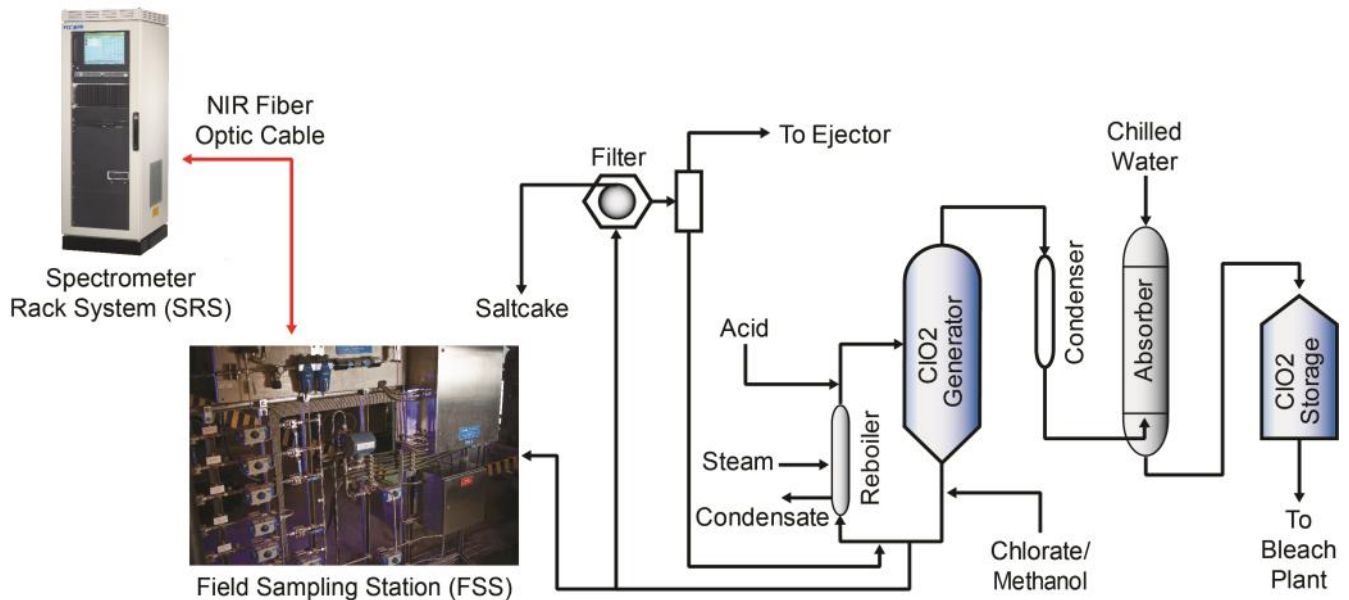


Figure I: Schematic diagram showing ClO₂ generator integrated with FITNIR Online. Measurement point is at the discharge of the saltcake filter pump and the spectrometer system is located in the MCC room connected to the cell via fibre optic cable.

Results: Figures 2 and 3 compare the results for chlorate and acid against manual titrations performed in a technical lab for an SVP-HP process. Excellent

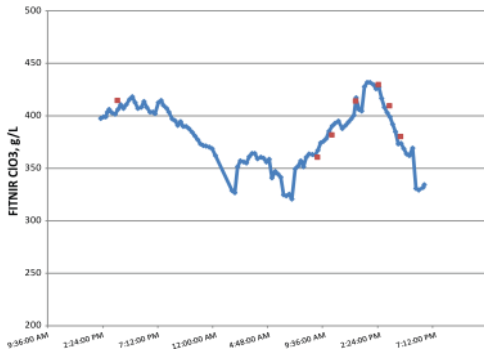


Figure 2: FITNIR chlorate strength validation

correlation is observed for both constituents. The swings in the concentrations are associated with manual operations and poor level

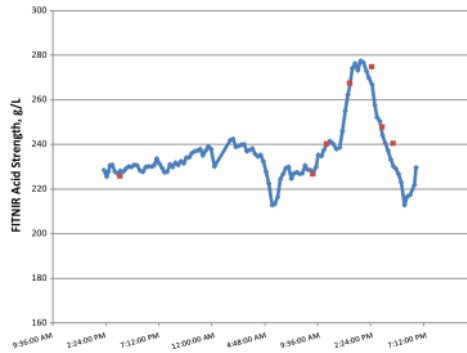


Figure 3: FITNIR acid strength validation

control. The integration of compositional control using FITNIR Online for ClO₂ generators results in a significant reduction in variability (Figure 4).

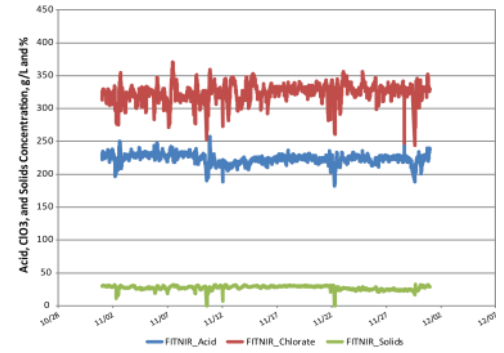


Figure 4: FITNIR generator acid, chlorate and solids trend for 30 days. Generator is an SVP-HP process running with compositional control.

PLATFORM TECHNOLOGY

FITNIR Online for ClO₂ generation samples liquor from the generator recirculation loop using a remote field sampling station connected to the central analyzer/spectrometer, located in an MCC or DCS room. Being a true platform technology, the system can easily be expanded to measure other process streams outside of the ClO₂ generator such as the digester, recovery boiler/dissolving tank, recaust and others by simply connecting additional field sampling stations to the spectrometer by fiber optic cables. One centralized spectrometer can

monitor up to eight field sampling stations. Each field sampling station can typically accommodate up to six samples. This platform capability unique to FITNIR's analyzers minimizes analyzer hardware and maintenance, as configurations can be done centrally at a single station.

ROBUST EQUIPMENT

The sample interface between the process and the spectrometer is a rugged flow cell with a large optical pathlength. The window material has high hardness and excellent chemical resistance for acid

and caustic environments as well as a large temperature range. All piping and valving utilize standard mill store parts, with wetted parts being titanium. Demineralized water is used to regularly flush the sample lines, ensuring reliable operations without plugging. Water references are performed every hour to eliminate measurement drift. Many mills have been running with the same calibration for as long as 10 years without the need for recalibration. The result: excellent reliability and superior uptime.

FITNIR SUPPORT

At FITNIR, we understand your business. Our expertise in both the lab and in the field goes into every aspect of our product development. Our innovations, process knowledge and dedication are focused on supporting your business success.

FITNIR offers a wide range of customer support services, including project coordination, application engineering (including kickoff meeting, system configuration calibration and validation), system verification and testing, application documentation, training and after-sales support.

Contact FITNIR Analyzers Inc. to find out how we can partner with you to optimize your chlorine dioxide generator operations.

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