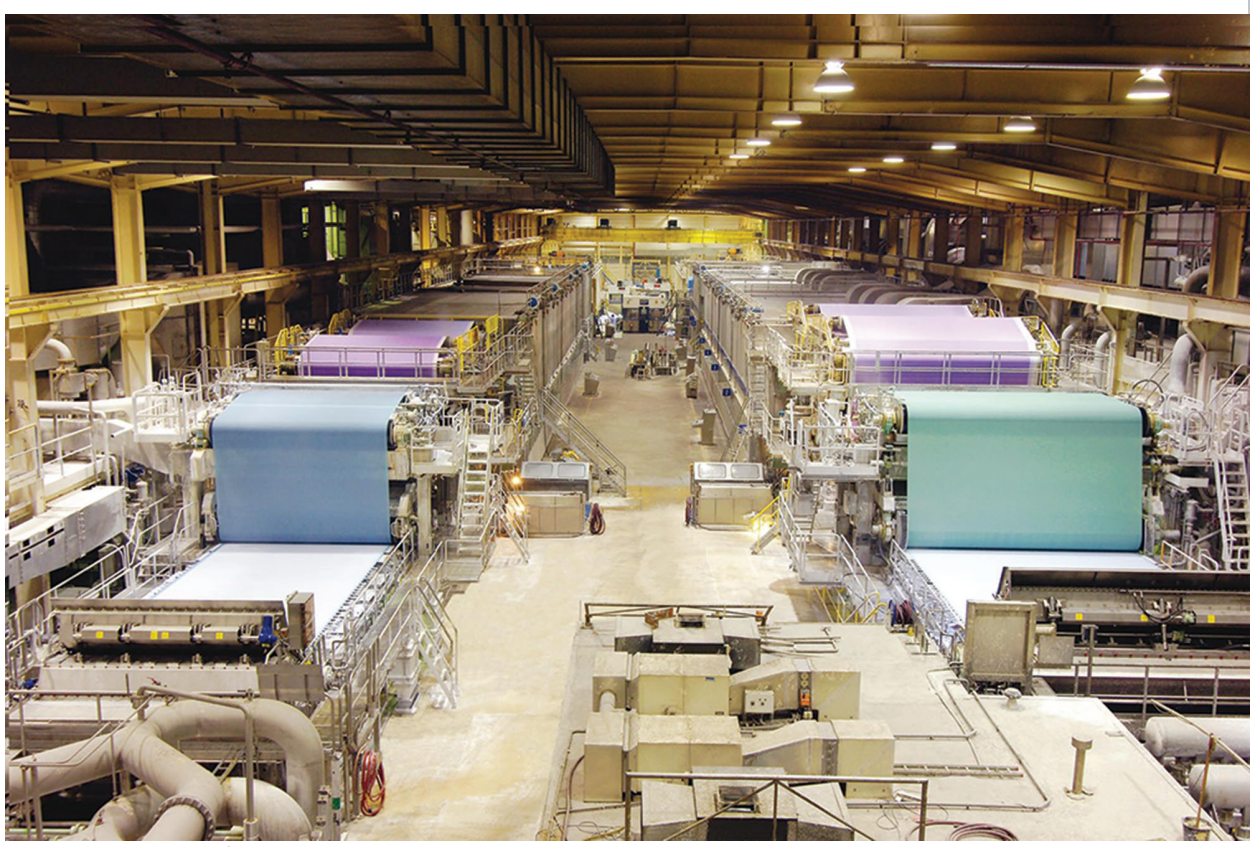
Improved Paper Mill Waste Water Treatment Process by Use of an Online TOC Analyser

Crown Van Gelder N.V. is an independent, modern and versatile paper manufacturer. The paper mill is located on the North Sea Canal close to Amsterdam/ Velsen in the Netherlands. CVG produces specialties for graphical and industrial applications in the woodfree uncoated and single-coated paper sector. The annual production capacity of the two sophisticated paper machines approaches 220,000 tons of paper on reels.



CVG paper mill production facility with paper machines

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Paper mills are known for their substantial use of production water. At CVG most of it is reused in the process partly treated by their two-stage waste water treatment plant: First through a physical-chemical purification and then by biological purification in two biofilters. In March 2012 a new online TOC analyser was installed. This LAR QuickTOC continuously monitors the Total Organic Carbon (TOC) concentration of the inlet water stream to the biofilters. Composite samples where collected and analysed in their laboratory by the Chemical Oxygen Demand (COD) analysis method, proving that the online TOC method correlates very well to the COD method.

The degradation of solved organic substances, mainly partially degraded starch, is done by a layer of microbial organisms that grow on the hollow filling of the biofilters. The "healthy biological growth" of the bacteria's in the biofilters can be optimised by a well balanced nutrient dosing rate. The performance and efficiency of the biofilters then improves significant. Now, having the continuously TOC/COD input, CVG operators can match and fine tune the nutrient dosing rate even when the discharged organic load and flow of the waste water changes. Moreover, peak loads can be avoided by pumping the highly contaminated waster into a holding and buffer tank (so called: peak shaving). The installation of this new TOC analyser helped CVG's to control their discharged waste water purity up to a quality level higher than that required by the discharge permit. Only then they return their purified water to the North Sea Canal.

The Online TOC-analysis of paper mill waste water: a challenge or a pitfall?

Paper mill waste water is known for its problematic composition and characteristics. The percentage of biobased materials is relatively low. As a consequence the purification of it is tough. Basically the waste water contains minuscule fibres, fillers, whiteners, carbonates, starch, pigments, glue's, additives, etc. These species are present as particulates (suspended solids) as well as in a dissolved state.

Generally online analysers and paper mill waste water don't go well together. The waste water has the annoying tendency to foul and plug/block the wetted parts e.g. sample tubes, sample pump, solenoids, vessels, reactor etc. The time investment that is needed to clean and replace the relative small analyser parts is just too long. It is therefore very understandable that the paper mill maintenance and service engineers shy away from using on-line analysers. However, among many types and makes of TOC analyser there is one TOC analyser with an exceptional innovative design. In this showcase we describe the successful installation and use of the QuickTOC, manufactured by LAR Process Analysers AG, Berlin.

Biofilters with carriers of biomass

QuickTOC, an innovative and exceptional design / Selection of the online TOC by Crown Van Gelder

Crown Van Gelder started with a TOC analyser market study. They really wanted its installation and long term operation to be successful. Its performances should be outstanding. The selection criteria they where demanding e.g. accurate measuring results, reliable operation, fast response, low use of reagents, multi stream capabilities, rugged, low maintenance and of coarse a reasonable investment. To be on the safe side CVG engineers wanted to:

- visit a reference installation
- have test samples analysed
- carry out a two month trial on site.

The analyser showing the most potential in offering solutions would be the QuickTOC from LAR Process Analysers AG.

QuickTOC

How it works:

The LAR TOC analysers' measuring principle is based on the non-catalytic thermal oxidation technique and relies on the ultra high combustion temperature in order to oxidise any carbon present in the water sample. Its innovative design is unique and successfully operates in numerous waste water applications. There is no sample pre-treatment or dilution technique needed. Only three components are in contact with the sample: The sample (pump) tube, a quarts glass overflow vessel and a rugged injection needle. Samples are directly injected into the reactor. It offers a full oxidation up to 50,000 mg/litre C, irrespective of the state of the organics (dissolved or particulate) is injected and regardless of the organic content of the sample. After every sample injection and measurement cycle, the injection needle is cleaned and flushed with DI or distilled water in order to avoid memory effects.

The applied 1,200°C thermal oxidation is superior to any other online oxidation method as it guarantees the complete degradation of all carbon compounds without the necessity of catalysts. It uses an exceptional design using a XY robot system which controls the position of the injection needle. It is positioned either in the sample overflow vessel while drawing a fresh sample into the needle, in the injection port of the reactor while injecting the sample into the reactor, in the waste vessel during rinsing or in the calibration vessel while taking a calibration standard solution. This novel design eliminates the need for components that are often subject to maintenance such as pinch valves, rotating multi-port valves, pumps and more. Furthermore, this analyser is available in a multi stream configuration with up to 6 streams.

Pre-testing with real samples

ODS proposed to perform a durability test with real CVG samples. As the results of it were required in a relatively short period of time the procedure was speeded up. A 10 litre tank containing CVG's waste water was acidified to pH 2, carbonates were removed by purging the sample with carrier gas. The analyser was configured as a TC mode which offers the shortest cycle time. By use of an extra pump the sample was circulating from the tank through the analyser sample vessel back into the tank.

During a period of three weeks a relatively large amount of sample, ten times more than usual, was injected into the reactor of the TOC analyser. Every week the reactor was visually inspected. It was proved that - even after injected more than ten thousand samples - the reactor was completely unblocked. Based on these results it was expected that the reactor maintenance would be needed only once per 6 to 12 months. Even then, the eventually formed residue in the reactor outlet can be removed during the analyser operation. It is a routine job which only takes about 10 minutes.

On-site trial:

Soon the QuickTOC analyser was put online. Waste water was pumped and transferred through a 1½" fast sample loop. Close to the analyser it flows at high velocity through the FlowSampler which is based on the so called anti-isokinetic principle. Via a 45-degree pipe connection the sample extraction tube is brought into the centre of the fast sample loop, pointing downstream. As a result of the high velocity in the fast sample loop, big and high mass particles will pass by. However, smaller particles, especially the saturated organic particles such as fibres and fillers, will be sucked into the sample tube and transferred to the TOC analyser. It works straightforward and its operation is maintenance free. The analyser was calibrated successfully. The Personnel were trained. All were ready to go.

Easy to use and easy to maintain

TOC/COD correlation study

For waste water processing and control it is important to know the amount of oxygen that is needed to oxidise it. It can be measured by use of the laboratory COD dichromate method. However, this COD method uses hazardous chemicals and it takes about two hours to perform a complete COD measurement. More and more, it is replaced by the somewhat faster and easier COD cuvette test. However, both COD methods are time consuming and not suitable for online use.

On the other hand the QuickTOC analyser responds fast and is therefore very suitable for waste water process control. The withdraw is that the TOC method actually is a carbon counting method instead of an oxygen demand method. Given that a good reproducible COD/TOC correlation could be found, the TOC method would be very suitable.

Therefore, CVG started a correlation study. Composite samples were taken and COD analyses were performed in the laboratory. After a period of about a month the outcome of the COD laboratory analyses were compared to the measured TOC values. A reproducible COD/TOC correlation factor was found.

Moreover, when measuring the waste water flow as well, the discharge load can easily be calculated by use of the following formula: Load (kg –O2/minute) = flow (litres/minute) times COD (mg/litre –O2 . 106). Then, the waste water's COD value and the discharge load is continuously available to be used for real time process control. This all is most useful for CVG to optimally operate their waste water treatment plant.

In those cases where the waste water composition keeps steady and where the COD/TOC correlation factor is reproducible, the TOC method is very suitable. Moreover, the LAR QuickTOCultra offers the capability to enter the COD/TOC correlation factor and its output is directly presented in mg/litre oxygen demand (COD). In other cases, with a varying sample composition, we recommend the QuickCODultra which determines the Total Oxygen Demand (TOD).

Holding Buffer Tank

Sample transfer and blow back:

Actually, the QuickTOC analyser proved itself to be reliable, accurate and it performed very well. It hardly needs any attention. Also the performance of the FlowSampler was fine and maintenance free. However, there was one point of particular interest. During the transfer of the sample from the sampling point to the analyser inlet, the sample tube fouled by deposition of a slimy matter. It caused plugging of the sample tube. Being an exceptional case it needed an extra solution. Hence, ODS designed, built and installed a simple blow back unit. It operated as follows: Once per 50 measurement cycles a solenoid valve is activated for only a few seconds and as a consequence pressurised air flows in reverse through the sample tube. By that, all contaminates and debris is flushed back into the fast sample loop. This blow back unit proved to be very effective. From then on, the routine maintenance and attention for the analyser was reduced to a minimum.

Summary

Experience is the best teacher:

The LAR TOC analyser proved to be very reliable and a very valid process tool. Decades of refinement have resulted in the QuickTOCultra: An advanced TOC analyser that measures TOC at 1,200 °C, higher than any other analyser, resulting in a "TRUE TOC" measurement that incorporates the volatile, particulate and difficult to oxidise organics that can be lost with other measuring methods.

It provides Crown van Gelder with the needed information of TOC content and, through correlation, the chemical oxygen demand. When a high peak load is monitored the operators can consider to pump this highly contaminated charge/ batch into the buffer tank and postpone its gradually discharge to the biofilters to a later time. By doing so, the intake load of the biofilters is averaged. Secondly, dosing of nutrient agents can be controlled in a smoother way. This all benefits to the health of the biofilters bacteria assuring a higher degree of treatment efficiency and, of course, to the purity of the effluent water which is to be discharged into the North Sea Canal.

About the Author

Piet Broertjes (1951) Environmental project engineer at ODS Sampling & Analytical Systems, Barendrecht, the Netherlands, with over 25 years of experience in designing and implementing online TOC analyser systems to monitor cooling water, waste water and process water