On-line measurement of Hydrogen Sulphide in Wastewaters

Sewer corrosion, bad odours and toxicity. Sulphides are a major headache for many sewer operators. The on-line and in-situ measurement of sulphides is an important tool for controlling the negative impacts of this group of substances. This paper presents a spectrometric method for the real time monitoring of the concentration of hydrogen sulphide the in liquid phase. The performance of this method has already been demonstrated at several sites, showing that especially the combination of UV/Vis spectrometry with pH measurements allows fast and accurate sulphide monitoring.

Sulphides in Wastewater

Sulphides are a highly problematic group of substances in sewer systems. Sulphides, comprising hydrogen sulphide (H_2S), bisulfide (HS^-) and sulphide (S_2^-), are formed when organic materials are degraded by bacteria under anoxic conditions (anaerobic digestion). Such conditions commonly occur when waste water is transported in pressure mains, where anaerobic conditions can rapidly develop as no re-aeration takes place or when big distances appear in sewer systems leading to long transportation times. Even at low temperatures, significant H_2S levels are produced at typical transport times and COD concentrations.

The presence of sulphides in the wastewater has unpleasant consequences; First of all, sulphide can be biologically degraded, leading to the formation of sulphuric acid. This acid is known to be a main responsible for corrosion in sewer systems and pipes (*figure 1*). It attacks both concrete and metal, corrosion rates of several millimetres per year being no exception. Further adverse properties of hydrogen sulphide are its very strong and foul odour, even concentrations of 5 ppb can be perceived by humans. Besides this, it is also a highly toxic gas, with first ill effects induced at 10 - 20 ppm levels, and risk of fatalities at 300 - 500 ppm. This has lead to numerous incidents involving sewer maintenance workers already.

Figure 1: Example of sewer corrosion due to sulphuric acid formation from hydrogen sulphide.

Controlling Sulphide Formation

Sewer operators that are aware of problematic sulphide levels in their networks can reduce the concentrations by active control. The formation of sulphide can be prevented by elimination of the anoxic conditions, for example by aeration or oxygenation of the water. Another possibility is the dosing of an alternative substrate for the sulphide forming bacteria into the wastewater that is preferentially digested under anaerobic conditions by the bacteria responsible for hydrogen sulphide formation. The most commonly used alternative substrate is nitrate. Further methods known to reduce the concentration of sulphide and/or to reduce the population of the sulphide forming bacteria are the dosing of iron salts and adjustment of pH.

Measuring and Monitoring

In order to practice an effective sulphide control strategy, an on-line indication of the sulphide concentration is required. Until recently, this was possible only by measurement of H_2S in the headspace of the water. This is a very indirect indication of the sulphide concentration in the wastewater, and a reliable quantitative measurement requires strictly controlled environmental conditions. Alternatively, collection of grab samples and laboratory analysis are used, but this is not suitable for on-line process control. An in-situ monitoring of the dissolved sulphide, in the water itself, is the first step in any successful strategy for reducing or preventing odour and corrosion problems and essential to optimise the control of the aeration or dosing strategies, taking into consideration both economical and procedural criteria.

The key to on-line and in-situ monitoring of sulphide is the pH driven equilibrium that exists between the three different species: H_2S, HS^- and S_2^-. In typical wastewater, only the hydrogen sulphide and the bisulphide ions are present. When the pH is known, it is possible to calculate the total concentration, hereinafter referred to as Hydrogen Sulphide, from the concentration of either species. The strong and distinct UV-absorption of the bisulphide ion opens up a simple and robust way to its measurement directly in liquid phase: UV-spectrometry.

The s::can spectro::lyser™, a fully submersible, on-line, spectrometer probe is ideally suited for this type of application. It can measure the UV/Vis absorption spectrum and from this information it can determine a range of parameters, including nitrate, nitrite, total and dissolved organics, total solids, colour, as well as specific chemicals or product compositions. Now, hydrogen sulphide can be added to this list of parameters. The strong and distinct signal of the bisulphide ion provides the primary input for this new parameter. In wastewaters of stable pH or pH above 8, the optical measurement provides reliable hydrogen sulphide readings. The use of full-spectral information provided by the spectro::lyser™ allows not only a quantitative measurement, but also a measurement that is not affected by cross-sensitivities.

In case pH is changing or below 8, which is known from the majority of wastewaters, the addition of a simple pH sensor to the s::can™ Monitoring System allows the calculation of the total dissolved Hydrogen Sulphide concentration from the bisulphide ion concentration and the pH. *Figure 2* shows the setup of such a complete system.

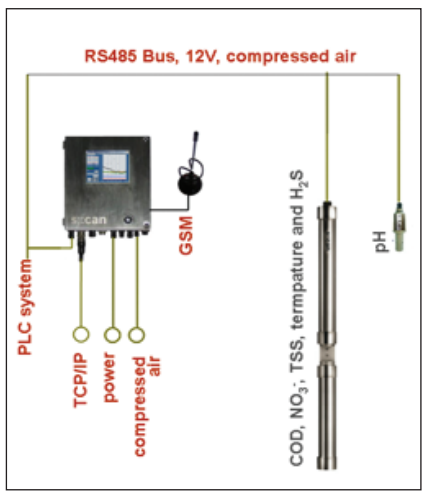

Figure 2: s::can™ Monitoring System providing readings for Hydrogen Sulphide, TSS, COD, NO_3^-, temperature and pH.

Opposed to other technologies, no cross sensitivity for the following ions exists: Sulphate, sulphite, chloride, bromide (up to sea water concentrations), hydrogen sulphate. Furthermore, the spectro::lyser™ offers a measurement of long term stability, with no need for regular maintenance or calibration. Stability of the measurement is ensured by the double beam design of the spectrometer and by a highly efficient automatic cleaning system using compressed air. If the formation of hydrogen sulphide is reduced by dosing nitrate salts the spectro::lyser™ can provide two parameters for an optimal process control: Nitrate and hydrogen sulphide.

Impressive Results in Sewer Monitoring.

The hydrogen sulphide measurement, with pH equilibrium correction, was applied at two field sites of the Gold Coast City Council (Australia). These sites were known to have different levels of hydrogen sulphide and different flow rates. An s::can spectro::lyser™ and a pH sensor were installed at both sites to log the UV/Vis spectrum and the pH of the sewage every 30 seconds. The first site was the inlet to the Elanora WWTP fed by a rising main of length 9.2 km carrying an average dry

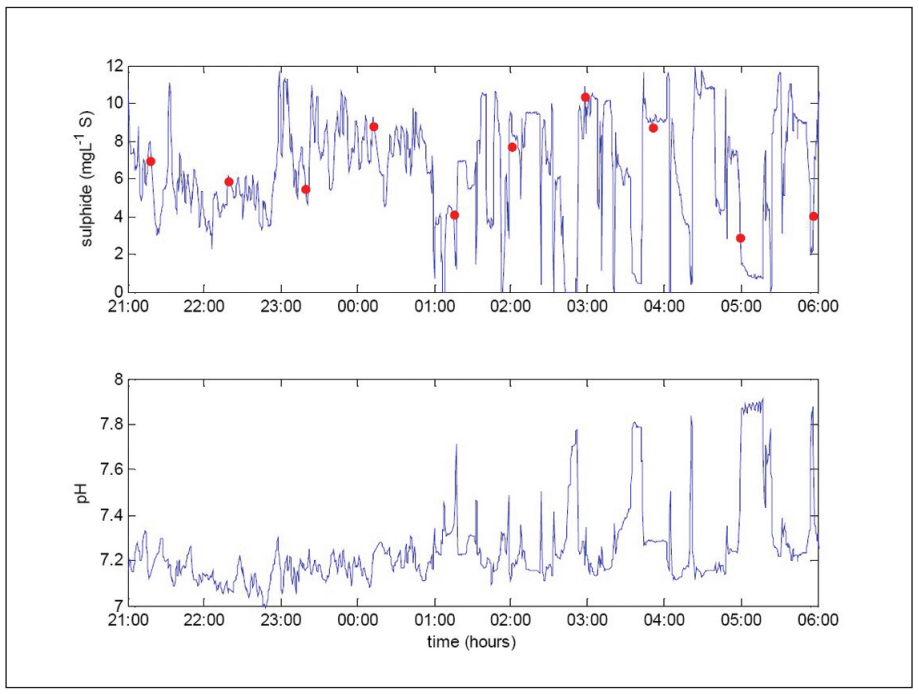

Figure 3: An example of a time series obtained with the on-line methodology, with laboratory validation samples overlaid. Highly variable sulphide and pH illustrate the importance of a high sampling frequency to accurately characterise the hydrogen sulphide concentration. • indicates reference analytical result.

weather flow of 16 ML/day. The retention time in the rising main is known from flow studies to be in the range of 3 - 4 hours. The s::can spectro::lyser™ was installed together with a pH sensor in a flow-through bypass. The second site was the inlet structure of the Coombabah WWTP, a plant being fed by rising mains that are much longer than at the first one. The total flow and hydrogen sulphide load at this site result from four different mains injecting into the inlet structure. Retention time in the different mains can be up to 4 hours. Here the s::can spectro::lyser™ and the pH sensor were mounted on a stainless steel bracket directly in the flow of the convergent channel. For verification of the on-line measurement results, a parallel manual sampling campaign was undertaken at each site.

The on-line results correlated very well with the off-line analytical testing, displaying accuracy better than ±1.2 mg/L with 95 % confidence over the tested range of 2 - 16 mg/L hydrogen sulphide and pH of 7.1 to 8.0. In the sewer, sulphide and pH levels were observed to fluctuate within minutes (*Figure 3*), which made the timing of sampling difficult. Hence on-line measurement of pH in the liquid phase with the in-situ pH sensor proved essential for the correct determination of the hydrogen sulphide concentration.

Summary

A new application for s::can™ Monitoring Systems using spectrometer probes and pH sensors has been introduced. Now it is possible to accurately and reliably measure Hydrogen Sulphide in waste water on-line and in-situ. This has shown that the variability in Hydrogen Sulphide levels is strong and rapid increases in concentration can occur, emphasising the need for an on-line measurement tool to facilitate efficient process control solutions.

(Lit*) .... Please ask for our literature and reference lists on CD!

AUTHOR DETAILS

Luke Sutherland-Stacey
Research Employee
DCM Process Control Ltd.
PO Box 113233
Newmarket
Auckland 1149, New Zealand
phone: + 64 9 520 3774
fax: + 64 9 520 3779
email: nzoffice@
dcmprocesscontrol.com
www.dcmprocesscontrol.com

Dr. Joep van den Broeke
Senior Scientist
s::can Messtechnik GmbH
Brigittagasse 22-24
1200 Vienna - Austria
phone: +43 1 2197393 - 0
fax: +43 1 2197393 - 12
email: office@s-can.at
www.s-can.at

Siemens Industry Solution: Water Treatment Saves Operating Cost in the Paper and Pulp Industry

Rising water prices and stricter regulations on the quality of waste water call for new solutions for companies needing water for their production. With the integration of the product range of US market leader USFilter, the **Siemens Industrial Solutions and Services (I&S) Group** now provides optimized solutions for the paper and pulp industry. At the heart of the process, the waste water produced is treated immediately for recirculation into the production subprocess. Products and systems provided by I&S' "Water Technologies" division enable full integration of individual processes into the production chain, covering fresh water treatment, secondary treatment and sludge treatment. This integration minimizes fresh water consumption and reduces or avoids the quantities of waste water produced. It also reduces the burden on the environment and saves cost.

Water is specifically used as a medium in almost all sections of the paper and pulp making process. Water is of decisive importance to the quality of pulp and paper. The process water used in each individual stage of papermaking is loaded with diverse substances and needs to be treated and purified before reuse or discharge.

The production of one ton of chemical pulp and paper requires up to 45 m^3 of fresh water. Simultaneously, each ton produces up to 40 m^3 of waste water. This means that an average pulp mill requires 63 million litres of fresh water per day.

In a typical paper and pulp mill, the cost of fresh water and discharging waste water accounts for up to ten per cent of production costs. New legislation with stricter regulations on discharge into rivers and sewage plants, added to rising fresh water rates, continues to drive up operating costs. Treating process water and closing water circuits helps to bring these costs down.

Siemens has developed water treatment and water circuit management solutions for each stage in pulp and papermaking. Each subprocess is equipped with the specific solution it requires, be it membrane filters, microflotation, anaerobic reactors, coarse filters or packed suspended bed reactors. Closing the water circuit in each stage of production rather than treating waste water collectively at a central plant, as was the case previously, has helped to reduce the amount of waste water produced while requiring significantly less fresh water.

Siemens Water Technologies provides a broad integrated range of products, systems and packages for water treatment in the paper and pulp industry: from fresh water treatment for production, water circuit solutions involving solids filters, biological and tertiary treatment through to sludge disposal and dewatering. In combination with integrated automation, entire pulp and paper mills, or individual subprocesses, can be further optimized in terms of business targets.

ATEX certified FLOWex is Flexible and Easily Operated

ORI GmbH (Germany) introduces the ORI FLOWex that is one-of-its-kind with the combination of high measuring accuracy and easy operation. ATEX certified, the flow meter is for the use in explosive areas, where it is essential to measure the water level or drainage in sewage water systems (II 2G EEx eib IIb T4). The compact and light housing is easy to install even in small manholes.

The combined sensor with an ultrasonic and pressure sensor is one of the smallest systems. The pressure sensor still works with high sensitivity and accuracy at low water levels. The ultrasonic sensor measures with the Puls-Doppler technology the velocity in different levels and determines automatically the average velocity.

The ORI FLOWex is equipped with an intrinsically RS 232 and Pulse Output. In combination with an automatic sampler volume- and flow proportional sampling can be done even in hazardous areas.

The data is logged in 2 MB data memory; this allows long autonomous measurement periods.ORI FLOWex is controllable and adjustable via PC or a mobile PDA . The read out and evaluation of the data and the settings of the parameters are carried out by the so-called "FileInspector", a very powerful software program also for the graphical and numeric illustration of the measured data.

Alert Stations for in-line Measurement

HOCER (France) carry out environmental studies in sea and river water. They design, manufacture and market highly sensitive inline systems for measuring chemical parameters in water & air. These alert stations allow you to measure on-line in river water, groundwater and source waters, some pollutants such as pesticides, hydrocarbons and industrial products up to 0.1 μg/l (ppb) corresponding to the European standards.

The independent alert stations can: Self-monitor the river water, Detect, Identify and quantize an accidental, chronic or volunteer pollution. Trigger an alarm on a mobile phone or on a computer, Optimize treatment processes, Check and control the quality of the produced water.

Our alert stations rely on the UV analysis through a 254nm UV spectrometer. The UV analysis allows you to continuously measure the organic matter (COD, BOD, Nitrates) and many other pollutants.

However some pollutants such as pesticides, hydrocarbons and some industrial pollutants need to be concentrated to be visible.

That is why we associate the spectrophotometer to a concentration module which is patented by HOCER. Thanks to that we can continuously measure these "micro pollutants" in the order of ppb levels. The UV spectrophotometer + the concentration module are wired to a PC computer in order to have a simple interface use. It's then possible to record the measurements and to communicate them easily (through a USB key, Intranet, Internet, GSM, and so on).