Online SAC₂₅₄ Measurement Yields Operational Savings in the Paper Production Ozone System

Introduction

Paper mills often have a large amount of waste water contaminated with high organic loads in the form of Chemical Oxygen Demand (COD). To tackle these elevated pollutant loads in waste water, operators can enhance conventional biological treatment with the use of ozone.

Biological treatment with ozone

Two-stage biological treatment often can not adequately tackle a higher COD load, as lignin and lignin derivatives form a low-activity residual COD that is difficult to break down chemically. And, while the complete breakdown of the low-activity COD using ozone is possible in principle, it is costly.

However, ozone treatment as a complementary, third treatment stage can be used for further COD elimination. A low ozone dose that increases bioavailability – or the BOD_5/COD ratio – is cost-effective. The substances produced are broken down using a subsequent aerobic

Parameters for controlling an ozone system

Increasing the BOD₅/COD ratio is a prerequisite for further residual COD elimination. Online measurement of these two parameters would be optimal for controlling the ozone system. However, because these parameters are not measured reliably online, a suitable indicator parameter is needed.

The correlation depicted in *Figure 1* shows that Spectral Absorption Coefficient (SAC) – an independent total parameter representing dissolved organic substances in water – can be correlated to BOD or COD. (See Hach Application Solution Note AS-SAC6 titled "SAC as a Predictor: the Relationship and Correlation of Oxygen Demand Parameters and SAC" for more detailed info). Operators should note that the correlations and parameters appropriate for process control depend on the type of waste water. For this reason, a dedicated strategy must be prepared for each specific waste water stream. low load process (e.g. bio-filtration). In this way a COD reduction of 25 to 90 % can be achieved.

Ozone acts in various ways on paper waste water. The reduction in COD and the increase in the BOD₅/COD ratio are of primary importance. However, the coloration of the waste water also is a factor. The brown coloration is largely caused by lignin derivatives with C=C double bonds that are attacked and destroyed by ozone. If the process returns treated waste water to manufacturing, removal of the coloration is an important issue.

The action of the ozone on the treated waste water depends on a number of factors, primarily the load (COD), feed flow rate, and dwell time in the ozone reactor. Operators can control treatment performance in relation to the feed load using the specific ozone dose – the ratio between the ozone dose and the COD of the feed water.



Figure 1 – This correlation between the BOD₅/COD ratio and Spectral Absorption Coefficient (SAC) exhibits a high correlation coefficient of 0.82.



Using SAC to control the ozone dose

Investigators examined how quickly and precisely a previously defined target for the SAC or BOD₅/COD ratio is reached when the composition of the waste water changes. The flow rate remains constant at 600 L/h (*Figure 2*).

The waste water has a load with an equivalent SAC of 400 m⁻¹. Within two hours the ozone reduces SAC to a target of approximately 150 m⁻¹. The ozone system is loaded alternately with pure waste water and mixtures of waste water and fresh water. The time required to achieve the target SAC of approximately 150 m⁻¹ is no more than two hours.

A newly defined target for SAC of approximately 200 m⁻¹ is achieved in a period of less than two hours.

A separate trial investigated how the irregular addition of fresh water to the waste water affects the target to be achieved (*Figure 3*). In this trial the feed quality changes continuously by the irregular addition of fresh water once the target was reached. Once the disturbance is over, the target is reached again in approximately one hour.



Figure 2 – An ozone control system designed to achieve a defined BOD_5/COD ratio or a defined SAC value



Figure 3 – The ozone regulation system with continuously changing feed quality

Table 1 shows the estimated operating costs of a paper mill ozone system with and without regulation of the ozone dose applied.

The data in *Table 1* come from a trial during which a COD value of 135 mg/L was to be established in the outlet from the ozone system (*Figure 4*). The COD in the feed was 223 mg/L. To achieve the target, a dose of 135 mg O_3/L is required. Once the target is reached, the COD in the feed is reduced to 183 mg/L by dilution. To achieve the new target, an ozone dose of 80 mg O_3/L is required.

Result – The reduction in the COD concentration from 223 mg/L to 183 mg/L in the feed water is not measured by an unregulated ozone system. The system continues to produce 13.50 kg O₃/h for an assumed flow rate of 100 m³/h. The energy costs in this case are 22.23/h or 2.22/m³ of water. The regulated ozone system produces only 8.00 kg O₃/h for the reduced waste water concentration. The energy costs are reduced to 13.17/h or 0.13/m³ of water.

Savings – Extrapolated over a year, costs of \$195,000 would be incurred for uncontrolled ozone treatment. If the feed concentration is different for 50 % of the operating time, \$39,130 in operating costs can be saved by using control. This amount corresponds to a saving of approximately 20% per year.

		Without	With
		regulation of the O₃dose to be used	
COD waste water O ₃ feed	mg/l	223	183
COD treated waste water	mg/	137	137
Water flow rate	m³/h	100	100
Ozone dose	g/m³	135	80
Ozone concentration (gas)	g/m³	150	150
Necessary ozone mass	kg/h	13.50	8.00
Operating costs			
Spec. energy demand	kWh/kg O ₃	10.00	
Energy demand	kWh/h	135.00	80.00
Spec. energy costs	\$/kWh	0.08	
Energy costs per h	\$/h	10.53	6.24
Oxygen demand	m³/h		
Spec. oxygen demand	\$/Nm ³	0.13	
Oxygen costs per h	\$/h		
Total energy costs	\$/h	22.23	13.17
	\$/m ³	0.22	0.13

Table 1 – Estimated operating costs for an ozone system



Figure 4 – Trial with changing feed concentration

Product Application

While an ozone system can support biological treatment in meeting waste water discharge requirements, operation of the ozone system can be significantly more efficient – and yield operational savings for paper mills of all sizes – with real-time process control.

And while the correlation between SAC and BOD₅/COD ratio must be determined individually for each system, the SAC measurement has shown to be an effective control parameter for an ozone system.

The Hach UVAS® sc Sensor yields delay-free measurement of the dissolved organic substances in the waste water. With self-cleaning design for low maintenance and reagentless operation, it helps further minimize the cost of ozone system operation. This application solution note is one of several Hach documents describing wastewater process control based on continuous SAC measurement. For more detail, refer to:

"Continuous SAC₂₅₄ Determination of Organic Pollutants Supports Management of Municipal Collection Systems," Hach Application Solution AS-SAC1

"Continuous SAC₂₅₄ Determination of Organic Pollutants Is Key in Real-time Wastewater Treatment Control," Hach Application Solution AS-SAC2

"Continuous SAC₂₅₄ and TOC Measurement of Airport Runoff Streamlines Separation of Polluted and Unpolluted Water," Hach Application Solution AS-SAC3

"SAC₂₅₄ Sensor Provides Reagent-free, Sampling-free Monitoring of Organic Materials in Drinking Water Treatment," Hach Application Solution AS-SAC5

"SAC₂₅₄ as an Oxygen Demand Predictor: the Relationship and Correlation of Oxygen Demand Parameters and SAC," Hach Application Solution AS-SAC6



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