Optimizing Dechlorination For Discharge Compliance And RO Membrane Protection

Optimizing chlorination/dechlorination procedures — for wastewater discharge compliance or reverse osmosis (RO) membrane protection — is a delicate balance. Inaccurate measurement can cause excessive chemical treatment costs, compromised effluent standards, or premature membrane failure. Here is how new ultra-low-range (ULR) chlorine instrumentation offers hope for more cost-efficient wastewater treatment and RO membrane management practices.

The Ups And Downs Of Chlorination/ Dechlorination

Chlorine is a common oxidizing agent for neutralizing biocontamination growth in numerous water applications— e.g., drinking water, wastewater, and industrial process water — but can create negative implications downstream in certain instances. Whether the treated flow is being discharged directly into the environment or going to RO membrane filtration for clean water uses in steam generation, semiconductor manufacturing, food and beverage production, or general water reuse, all of those applications demand accurate readings of residual chlorine for managing dechlorination steps that remove it from the flow. Even for those who advocate The Contrarian Use of Chlorine to Control Biofouling in RO Membranes as a means of winning the battle between biofouling and RO membrane longevity, the need for accurate chlorine measurement is critical.

The Give And Take Of Biofouling, Cleaning, And RO Membrane Protection

The ability of RO membranes to pass water through pores as small as 0.0001 microns can easily be compromised by larger particles blocking the flow. And when those particles include living microbes that foul the membrane surface, flow restrictions can develop quickly. On one hand, frequent cleaning to remove fouling can damage membranes and shorten service life. On the other hand, dosing source water with chlorine to minimize potential biocontamination growth requires a thoroughly controlled dechlorination process to minimize the risk of degraded long-term RO performance.

Guidelines for membrane maintenance state that salt passage doubles after 1,000 ppm-hours of chlorine exposure. To achieve an average membrane life expectancy of 3 to 5 years, that requires consistently maintaining chlorine levels below 38 parts per billion (ppb).

The two primary methods used to dechlorinate water before it passes through final RO filtration each come with their own performance advantages, potential concerns, and need for accurate chlorine monitoring:

- **Sodium Sulfite.** Adding SO2 gas, sodium sulfite, bisulfite (SBS), or metabisulfite (SMBS) are popular approaches to neutralizing chlorine in high-volume water treatment for industrial applications such as power and steam generation. Overdosing such chemicals can create a variety of problems, thereby magnifying the importance of accurate chlorine measurement.

  First, excessive chemical additions drive up chemical costs, wasting $3,500 or more annually when overdosing by as little as 10 gallons of SBS per day. Second, excess sulfur can create its own problems by promoting anaerobic bacterial growth that fouls RO membranes or by depleting dissolved oxygen from a wastewater discharge, which can harm wildlife.
- **Granular Activated Carbon (GAC).** This approach tends to be used for treatment of lower volumes of water in applications such as food and beverage. With an appropriate empty bed contact time (EBCT), a properly maintained GAC tank will adsorb chlorine from the water filtering through it. As the bed captures more chlorine over time, however, its ability to remove chlorine degrades until the point where the carbon needs to be replaced or regenerated. Because of that and because of possible channeling or leakage of untreated water through the bed, some users will test the outflow to check for trace amounts of chlorine breakthrough, while others might add an SBS treatment to reduce margin for error.

With either approach, optimized dechlorination depends on knowing just how much chlorine is present in the water at the appropriate stage of the process. Until recently, there had been no online instrumentation sensitive enough to measure total chlorine at the low levels needed to protect sensitive RO membranes.

Evaluating A Better Way To Optimize Dechlorination Control

- Among the common methods used to detect and quantify chlorine presence in order to establish SBS dosage or GAC contact time at optimal levels, each has its advantages and limitations (Figure 1).
- **Oxidation Reduction Potential (ORP/Redox).** ORP sensors use a potentiometric method to provide a quick response from continuous readings. But it provides an indirect and relative measurement that is affected by water temperature, pH, flow, etc. Also, an ORP reading can be deceiving in that it does not provide a direct correlation to total chlorine but rather only shows the balance among all oxidizers and reducers present in the sample, indiscriminately.
- **Amperometric Sensors.** Measuring the change in current/voltage across two electrodes can provide a fast indication of changing chlorine concentrations in water and can be correlated with absolute chlorine concentration. But this method is calibration dependent and is influenced by changing water matrix states and conditions (pH, temperature, flow/pressure, etc.). Also, amperometric sensors can lose their sensitivity to chlorine after long periods without chlorine exposure, resulting in delayed notification for sudden chlorine breakthroughs.
- **Colorimetric DPD (N,N-Diethyl- P-Phenylenediamine) Method.** Direct-read technology, which has long been used to control chlorine feeds, can now be used to aid in the removal of unwanted chlorine down to minimal levels for wastewater discharge or RO membrane protection. Unlike older colorimetric instruments and near-instantaneous electrochemical methods, however, newer ULR colorimetric instruments can measure total chlorine in the ultra-low range — accurately detecting its presence at levels as low as 8 parts per billion (ppb) with + 3 ppb precision (Figure 2). The automated batch measurement takes just 2.5 minutes per cycle and is unaffected by changing sample matrix conditions.

Avoiding 'Rock vs. Hard Place' Dilemmas

ULR colorimetric instrumentation adds a new option between the analytical accuracy of direct total-chlorine readings and indirect readings from ORP or not- very-selective amperometric sensors for satisfying the demands of specific applications. Users can even employ ULR colorimetric technology in concert with ORP technology to gain the best of both worlds — accuracy and fast response. For example, continuous ORP readings can respond in seconds to identify sudden spikes in chlorine readings, while ULR colorimetric

Analytical Technology	Measure Principle	Main Benefits	Major Deficiencies
Oxidation-Reduction Potential (ORP)	Electrochemistry (Potentiometry)–change in mV output proportional to change in oxidation potential	Fast response to appearance of oxidants in water, reagentless	Indirect, non-specific, matrix influence (sample pH, flow/pressure, etc.) non-linear response
Amperometric	Electrochemistry (Amperometry)–change in current/voltage across electrodes proportional to chlorine concentration	Fast reaction to changes in chlorine concentration in the water, reagentless	Calibration-dependent, matrix influence (sample pH, flow/pressure, etc.), may lose sensitivity to chlorine
Colorimetric	Colorimetry–change in color intensity proportional to chlorine concentration	Direct and accurate measurement, independent of sample conditions, stable calibration	Non-continuous response (batch analysis), reagents

Chart courtesy of Hach.

Figure 1. Colorimetric measurement of chlorine concentrations in wastewater discharge or RO process water provides direct, accurate readings down to 8 ppb in less than 3 minutes.

measurement provides a more accurate confirmation of total chlorine within minutes to inform the most cost-efficient SBS feed requirements.

These new choices give users better options to reduce operating expenses for excessive chemical costs and/or overly frequent clean-in-place membrane maintenance — without risking fines for non-compliant discharge and without unexpected capital expense for premature membrane replacement.

Figure 2 (at right). Highly accurate readings from this ULR online analyzer automate the process of monitoring chlorine levels in water to promote RO membrane protection and regulatory compliance. Its accurate, unattended operation for weeks at a time compares favorably to the indirect readings of ORP sensors, to intermittent grab sample measurements, and to the frequent calibration demands of amperometric instruments.

Photo courtesy of Hach.

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