Advances in Instrumentation Used to Monitor High-Purity Water Treatment Systems

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Abstract

High-purity water treatment technology has progressed and changed significantly in recent years. Major trends include the wider variety of membrane processes driving an increasing share of purification, more use of reclaimed and recycled water, and treatment systems with more user-friendly interface. In addition, industry pure water requirements have also changed. Pharmaceutical waters now have conductivity and total organic carbon (TOC) requirements that are most easily met with on-line measurements. The power industry has more specific water chemistry guidelines and higher priority "core parameters" to be monitored in all plants. The semiconductor industry has more stringent ultrapure water limits as well as process-specific requirements. All of these changes have raised challenges for the associated instrumentation. Application requirements also frequently point toward additional parameters, lower detection levels and lower costs. Progress in instrumentation technology and innovative design are meeting many of these challenges. Presented here is a summary of instrumentation advances that help to meet these newer application needs.

Membrane Processes

Reverse osmosis (RO) was initially introduced with cellulose acetate (CA) membranes which provided the state of the art separation at the time. Their good separation, low fouling tendency and low operating cost relative to deionization resins produced steady growth of RO in the water treatment field. However, their limited pH range between 4 and 6 generally required pH control upstream to prevent hydrolysis of CA. As a result, an on-line pH measurement and automatic or manual control system to feed acid were typically needed as pretreatment to protect CA membranes.[1]

The development of thin film composite (TFC) membranes using polyamide (PA) polymers improves separation, operates at lower pressure and lowers operating costs further. In addition, they can tolerate a much wider range of pH which eliminates the need for pH control and acid addition in most cases. However, TFC/PA membranes are very vulnerable to oxidation from even the low levels of chlorine in municipal water supplies. Where chlorine is added for disinfection ahead of pretreatment filters there is even more potential for damage. Some deionization resins are also attacked by chlorine.

Dechlorination is therefore an essential step in pretreatment. This is accomplished either with a granular activated carbon (GAC) filter or with the injection of bisulfite which reduces chlorine to harmless chlorides. Dechlorination is illustrated in Figure 1, including both a carbon bed and bisulfite feed, although in practice only one would be used. Dechlorination is an oxidation-reduction reaction, where electrons are transferred between reactants. Chlorine takes on electrons which reduce it to chloride ion. At the same time bisulfite ions lose electrons and are oxidized to bisulfate.
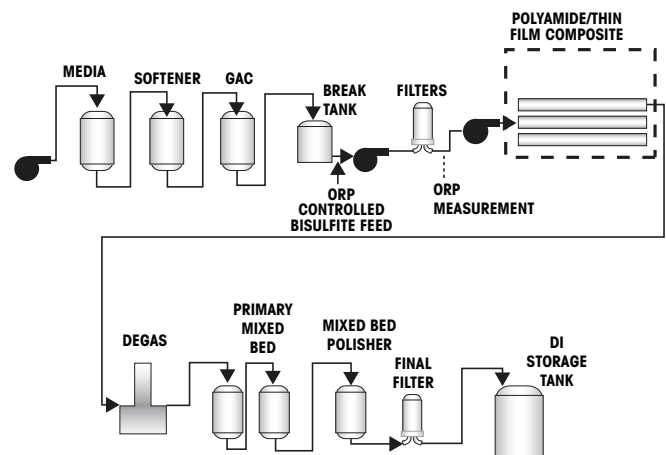

Figure 1. Dechlorination shown with both Granular Activated Carbon and Bisulfite

With either bisulfite or a carbon bed, ORP (Oxidation Reduction or redox Potential) is most commonly used to monitor this stage. It is a simple millivolt reading from the surface of a platinum electrode, with the measuring circuit completed through a reference electrode, the same as used for pH. ORP is proportional to the logarithm of the ratio of oxidizing and reducing materials present in the water, including chlorine, chloride, sulfite and sulfate. It is also influenced by minerals, pH and dissolved oxygen so every installation gives slightly different control values.

Although a carbon bed does not contribute an obvious reducing agent to the stream, its effluent still shows the reducing characteristic of a low ORP value. ORP is measured in millivolts and does not correspond directly to concentration due to its logarithmic ratio relationship. Figure 2 illustrates the kind of ORP response obtained in a laboratory titration (where small amounts of bisulfite are added to a fixed volume of sample and the resulting ORP is recorded). The same response would be seen on-line if the bisulfite feed were discontinued and then gradually restored. The steep equivalence point is where all chlorine is reacted. Below that there is an excess of bisulfite. For control purposes with this curve, a value near 425 mV would assure all that chlorine was reduced, with a safety margin, but without wasting much bisulfite. Other water compositions or pH levels could shift the curve up or down and different control values would apply, but the basic shape would remain the same. Additional information on ORP measurement is available.[2]
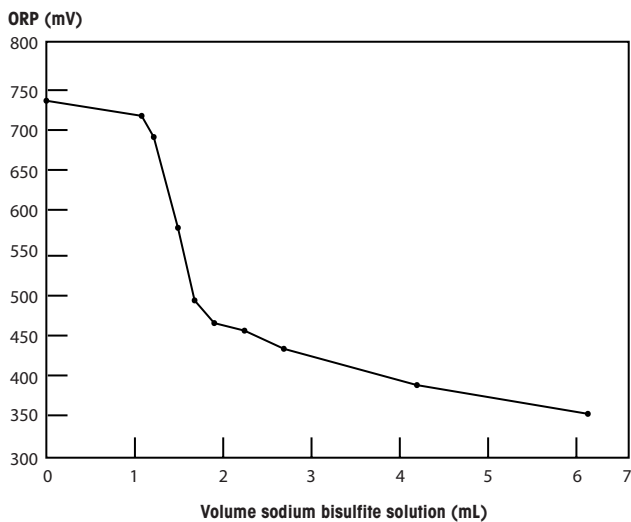

Figure 2 – Dechlorination ORP Titration Curve

Reagent feed systems using pulsing metering pumps for pH or ORP control produce slugs of concentrated reagent along the length of the pipe, especially if they operate at low frequency. For this reason, the reagent should be injected ahead of a pump or filter to encourage thorough back-mixing.

The mixing across the pipe cross-section as provided by in-line mixers, elbows, etc. is not sufficient. There must be mixing along the length of the pipe to smooth any pulses created by the metering pump or slugs of reagent at the measurement will be erratic and will not allow accurate measurement, let alone control. Moving the measurement a long way downstream is not recommended since that would add deadtime to any closed loop control and that could produce its own oscillation.

Double Pass Reverse Osmosis is another more recent development in membrane treatment systems. High rejection rates are further improved by passing through two membranes in series as shown in Figure 3. When at least the second membrane is the TFC/PA type that can tolerate a wide range of pH, it allows the opportunity to increase the pH with a trace of caustic before the second pass. This shifts the carbon dioxide equilibrium into the ionic bicarbonate form which the membrane can reject to a much greater degree. Thus pH is a desirable control variable for interpass treatment. However, this means that the pH of relatively pure water must be measured, which can be a challenge.

High purity pH measurement has been made on power industry samples for decades but with varying degrees of success. Requirements for reliable measurement include a low pressure, low flowrate side-stream sample passing through a stainless steel housing which is usually earth grounded. It should also have a flowing junction reference electrode—one that forces a small flow of electrolyte through the junction to provide similar junction conditions both during calibration in buffer solution and when measuring in high purity water. Figure 4 illustrates this type of specialized pH sensor assembly which includes a pressurized gel reference electrode. Measuring pH in a side-stream is generally recommended for highest accuracy, longest electrode life and ease of maintenance, but for high purity samples, it is mandatory unless a more highly pressurized electrolyte system is provided. Additional precautions and techniques for successful high purity pH measurement are provided in an ASTM standard.[3]
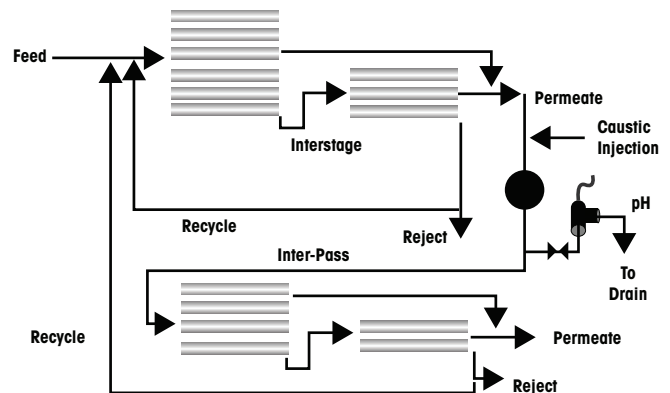

Figure 3 – Double Pass RO System with Interpass pH Adjustment

Figure 4 – High Purity pH Sensor Assembly

Nearly all membrane performance criteria include real time percent salt rejection calculated from the conductivity values of product and feed water. The calculation is available in most good quality multi-channel conductivity instrumentation. It indicates the relative health of the membrane and quickly detects any flaws or significant deterioration. The calculation is simply,

% Rejection = [1 − product conductivity / feed conductivity] x 100   eq (1)

Of interest especially where water is scarce is the percent recovery of water. This computation is available in some multi-channel flow instrumentation as,

% Recovery = [product flow / (product flow + reject flow)] x 100   eq (2)

Continuous Electrodeionization (CEDI) has come into its own in the last decade with a steady stream of improvements making it more and more attractive. Its fundamental ability to produce very pure waters without chemical regeneration of resins is a major operating advantage. Electrical current is used to attract ionic impurities through ion-selective membranes to yield pure product water. As with RO, conductivity measurements can provide % rejection as well as product water quality indication. Because of the high electrical currents running through a CEDI system, it is always a good practice to provide earth grounded fittings or rods at the inlet and outlet of the system to prevent interference with electrochemical measurements such as conductivity, pH or ORP.

Typical measurements needed to monitor and control a CEDI system include feed and product conductivities and flowrates plus the voltage and current being applied to the plate stack. Multiparameter instrumentation has kept pace with this need by providing input circuitry and enough channels to handle all these measurements in a single compact unit as shown in Figure 5.

- Feed conductivity
- Product conductivity
- % Rejection
- Product flowrate
- Concentrate flowrate
- Voltage
- Current

Figure 5 – Multiparameter Approach Provides for CEDI Measurements in a Single Unit

Deionization Regenerant Measurements

In traditional deionization systems, control of chemical regenerant concentrations is critical to produce efficient and complete regenerations. Acid and caustic supplied in concentrated form must be diluted on site to the optimum concentration. These concentrations are usually measured on-line using high range conductivity with software to provide temperature compensation and conversion to concentration units.

The sensors for these measurements have varied widely. Conventional high-constant 2- electrode sensors have been used for many years to make these measurements. However, they have small passages that in some installations are vulnerable to plugging or trapping air bubbles that interfere with the measurement. Another approach has been to use inductive or toroidal conductivity sensors but these usually require extra large pipe sizes to prevent interference with cell constant and the need for specialized calibration. The 2-electrode sensor has very small passages while the inductive sensor requires oversized pipe in many cases. A "just right" alternative is a recent 4-electrode sensor design that installs in a 1" NPT port and presents a flat, smooth measuring surface, as shown in Figure 6.

Figure 6 – Four-electrode Conductivity Sensor for Deionizer Regenerant or Wastewater

Recycle, Reclaim & Waste Water

With water in ever shorter supply, reuse becomes an economic, environmental and/or political necessity in many situations. The criteria for recycling or reclaiming versus disposal of contaminated water are frequently evaluated with on-line conductivity or in some cases TOC measurements.

For conductivity measurement of highly conductive waters, the same sensor considerations apply as for deionizer regenerant measurements described above. The 4-electrode sensor design has distinct advantages. Where TOC is a deciding factor, an especially fast response is paramount to prevent delays in diverting contaminated water. TOC instrumentation with response as fast as 15 seconds was developed in recent years.[4]

pH neutralization of wastewater requires continuous pH sensor exposure to the conditions of the wastewater. As reference electrodes have become more robust, with solid polymer gels and similar enhancements, they are more tolerant of these difficult conditions. However, in batch neutralization it is still not a good practice to allow a pH sensor to go dry between batches. The sensor should be mounted low enough in a tank or in a low section of recirculation piping so that it always remains wetted, as shown in Figure 7A.

With semiconductor etching wastewaters containing acids and fluorides, direct attack of the glass pH electrode is likely. If treatment is done in batches as in Figure 7A, with filling, neutralizing and pumping out, then the pH sensor could be exposed to hydrofluoric acid all through the long filling cycle. In that situation a special HF-resistant pH sensor is recommended. This sensor will extend the life in HF but its exposure should still be minimized as much as possible.

On the other hand, if treatment is continuous with gravity overflow as in Figure 7B, then the tank should be near neutral most of the time and the pH sensor is not subjected to hydrofluoric acid. A conventional electrode should be satisfactory in this case unless there is poor mixing or frequent control upsets. There is also no time when the sensor is left dry with continuous treatment.
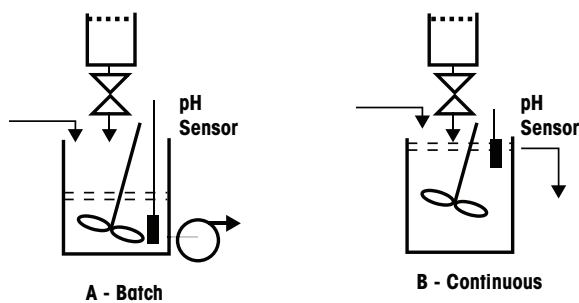

Figure 7 – pH Neutralization System Configurations

Industry Requirements for Conductivity Temperature Compensation

Pharmaceutical water measurement requirements have been drastically revised in the last decade. The U. S. Pharmacopoeia changed its requirements for Water For Injection and for Purified Water to use conductivity and TOC measurements to replace antiquated wet chemical methods in USP 23 effective November 1996. This had a distinct impact on instrumentation supplied for this purpose. In particular, the conductivity measurement was required to be non-temperature compensated in order to eliminate the ambiguities of various manufacturers' compensation techniques and to match the conductivity properties of previous ionic contaminant limits across the temperature range. The new requirements define the conductivity limits as a function of temperature in a table of values. To satisfy this requirement, some conductivity instruments allow convenient disabling of temperature compensation and provide a setting for "USP setpoints". An alarm can be set up to activate when the measured conductivity exceeds the USP limit for the measured temperature. For further flexibility there is also a safety margin adjustment to make the alarm activate when the conductivity reaches a value that is a set percentage below the USP limit. For example, the USP conductivity limit at 35°C is 1.3 µS/cm. If the safety margin were set to 25% then the alarm would activate when the conductivity exceeded 0.975 µS/cm at 35°C.

The power industry has greatly advanced its knowledge of corrosion and scaling mechanisms and has developed a series of improved cycle chemistry treatment regimes and associated guidelines for their operation. Turbine warranties also have requirements for water quality monitoring and control. As these limits and guidelines become more stringent and have greater visibility, the accuracy of measurements becomes more of an issue. Power plant samples are seldom controlled to exactly 25°C so temperature compensation is an important factor. However, it had been found that the temperature compensation for specific and cation (acid) conductivity measurements in most power plant instrumentation had very poor accuracy and would typically be the largest source of error in these measurements. Considerable work was undertaken to improve this situation and the result has been the improvement in accuracy of one to two orders of magnitude with our instrumentation.[5,6]

Semiconductor manufacturing uses ultrapure water with extremely low levels of contaminants. High purity non-linear temperature compensation coupled with very accurate temperature measurement is appropriate for these applications. Some locations have standardized on resistivity data from earlier studies and their needs can be accommodated with a compensation algorithm that matches that data. There are also a few specialized applications that use isopropyl alcohol or ethylene glycol solutions and these have much different temperature characteristics. In addition, they may have resistivity values that go well above 18.2 Mohm-cm which places greater demands on the measuring circuit. These also need specialized temperature compensation algorithms to obtain accurate results. All of these capabilities are now available in standard instrumentation.

Instrument Standardization

Within a plant or on a company-wide basis, the standardization of instrumentation makes life much easier in designing, operating and maintaining water treatment systems. The ability to field-select from a variety of accurate, application-specific, temperature compensation algorithms and other specialized functions is therefore of considerable value. The temperature compensation characteristics and requirements are very different in the pharmaceutical, power and semiconductor industries, as well as for different applications within each of these industries. Nevertheless, a single model instrument can provide uncompromised performance for each of these if it has sufficient memory to include all the leading algorithms.[7] A water treatment system using such instrumentation that is supplied to any of these industries will be welcomed by users who recognize its performance capability in their applications. This allows them to use the same instrumentation in their water treatment, core process and wastewater, with the best available accuracy and key functions in all three.

Another contributor to standardization in water treatment instrumentation is the multiparameter approach. A single instrument platform can provide input capability for analytical (conductivity, pH, ORP) as well as physical (flow, pressure, level, temperature) and electrical (voltage, current for CEDI) parameters. The multi-parameter system uses Smart sensors that automatically communicate their identity and calibration data to the instrument as soon as they are connected. The multiparameter concept provides flexibility in signal handling much like a programmable logic controller (PLC). In our implementation, it accepts four of any of the above sensor types plus two pulse flow sensors. It allows defining and custom labeling multiple measurements directly or by calculation from those sensors. For example, from a flow sensor it can measure flow and compute totalized flow. From a conductivity sensor it can measure conductivity and temperature plus calculated % rejection (in conjunction with a second conductivity sensor) or deionization capacity (in conjunction with a flow sensor).[8] Each measurement can be displayed, can activate a setpoint and relay and can go through to analog and digital outputs.

Conclusion

Water treatment trends including the development of different RO membrane materials, multiple pass systems, and CEDI require different measurement and control parameters. Increasing reuse of waters adds measurements to discern water quality at the critical diversion points as well as in final wastewater treatment. Industry process requirements differ widely in their needs for conductivity temperature compensation and other functions. The inclusion of all these capabilities in multi-parameter, field-configurable instrumentation greatly simplifies this part of water treatment system design, fabrication, training, operation and maintenance.

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Notes