How good is on-line zeta-potential measurement in water treatment?

Use at Aurora Water demonstrates feasibility, reduces chemical coagulant usage about 17 percent

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The benefits of using zeta potential measurement to determine water-treatment plant-control strategies are extensively documented. Zeta potential is a measure of the charge on particles in a system and is known to correlate with coagulation performance. It's already used for quality control and to optimize chemical flocculent addition.

Even more intriguing, however, is the idea of using zeta-potential as part of "on-line" continuous process monitoring and eventually, automated process control.

Zeta-potential monitoring benefits are illustrated by the experiences of Aurora Water, water-treatment utility for Aurora, Colorado. One Aurora Water facility uses zeta potential as both an off- and on-line tool. Results show how on-line technology can reduce chemical usage costs and simplify process operation.

Aurora Water provides water for about 340,000 people and has three water purification facilities in the metro Denver-Aurora area.

Some background

The chemical and physical processes employed at water-purification facilities eliminate harmful organic, inorganic and bacterial contaminants to meet potable-water quality standards. Yet many water-purification facilities can't respond rapidly or efficiently to raw water chemical- or physical-characteristic fluctuation; nor can they assess the system alteration impacts on purification performance.

Typical water treatment begins with physical contaminant removal via sedimentation. Gravity separates out suspended material. In other words, once particles reach a certain mass, the gravitational forces inducing sedimentation are sufficient to offset the surface-chemistry interactions keeping them in suspension. The result is sedimentation of the contaminated material, i.e., its separation to the tank bottom.

The typical size range of suspended materials within untreated water is relatively small ($< 1000\ \mu m$), making natural sedimentation a lengthy process. Therefore, to make treatment viable, contaminants are "encouraged" to clump together, or coagulate, increasing sedimentation rate to improve process efficiency.

Water impurities tend to be anionic in charge and therefore charge stabilized. That leads to use of positively charged additives, such as aluminum sulfate, cationic polymers and other cationic moieties. Neutralizing the water impurities' surface charge allows effective coagulation and sedimentation of most contaminating material. Depending on method employed, resulting flocculent either settles prior to filtration or is transferred direct to filtration.

Maintaining initial coagulation and flocculation, given variable raw water quality, is crucial for optimizing treatment and ensuring safety. Floc impacts the downstream process: a floc with poor characteristics can break up, resulting in carryover on filters, greater particle loads, turbidity breakthrough and reduced filter run times. Well-maintained flocculation can reduce chemical use.

What doing all this takes is a relevant measurement technique for process monitoring that enables timely and effective control.

Answers of the past

Historically, water-treatment facilities monitor flocculation with "jar tests" that take two hours to perform. A jar test simulates the coagulation process. A water sample is dosed with a concentration of coagulant. The floc formation is then assessed under standard conditions. This analysis gives a relative indication of plant performance but is highly subjective and, like all manual techniques, prey to operator-to-operator variability. Furthermore, practicalities dictate that jar testing misses rapid changes in contaminant concentration. The technique may offer little on optimizing chemical usage following poor results.

Consequently, jar-test use often results in a tendency to overdose the water to ensure regulatory compliance, even in the event of rapidly changing seasonal variations in water composition. Considering flocculent costs, this is unsatisfactory. In addition, overdosing contaminants can reverse the surface charge, thereby building a particle-surface cationic charge and re-stabilizing the water contaminants.

Turbidity tests also can indicate and control organic-matter presence, doing so by measuring cloudiness as a quality indicator. Highly turbid solutions can cause filtration-system blockages. Even low turbidity prevents effective tertiary chlorination treatment. Turbidity meters

Top image. Malvern Instruments Zetasizer Nano

and bench turbidity make this measurement. However, they don't deliver feedback or predictions to improve in-situ water treatment. Nor are they relevant for an industry transitioning from manned to unmanned operations.

On the other hand

Zeta-potential measurement assesses stability in colloidal systems and is increasingly used to monitor water-treatment flocculation. Laboratory-based electro-phoretic light-scattering zeta-potential measurements are not subject to operator-to-operator variability. Data indicates how to change the process to improve performance.

Zeta potential measures the magnitude of electrostatic or charge repulsion between particles at the boundary layer surrounding the particle, rather than on the particle itself (see Figure 1).

Zeta potential therefore quantifies the balance of repulsive and attractive forces that particles experience as they approach one another. At a zeta potential near zero, a system is unstable and highly prone to aggregation. A pronounced negative or positive zeta potential (+/-30 mV), on the other hand, is indicative of an electro-statically stable system that will resist particle aggregation. Monitoring the zeta potential of water treatment streams therefore provides a way of maintaining optimal conditions for flocculation. Typical raw water zeta potential is around -15 to -20 mV and not naturally prone to aggregation.

The last decade, some water treatment plants worldwide have successfully monitored zeta potential with lab measurements.Zeta potential is measured by applying an electric field across a dispersion sample. Particles within the dispersion, with a zeta potential, migrate toward the electrode of opposite charge at a velocity proportional to the magnitude of that zeta potential.

The velocity at which the particle moves is measured using laser Doppler anemometry. The frequency or phase shift of an incident laser beam caused by the moving particles is measured to determine particle mobility. This is converted into zeta potential values, using knowledge of dispersant viscosity, through the application of Smoluchowski or Huckle theories.

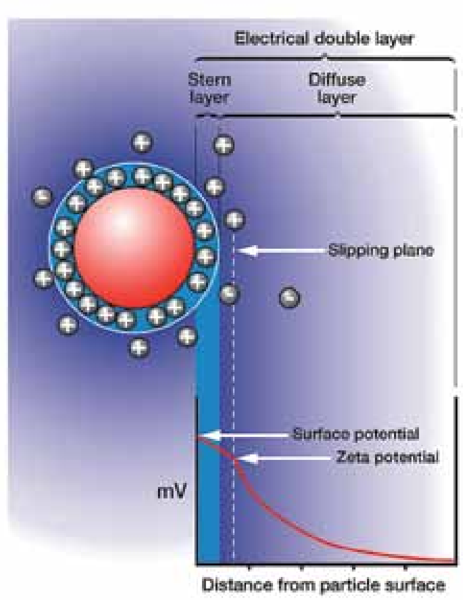

Figure 1. Schematic representing the measurement of zeta potential, a parameter which indicates particle charge and can be used to assess the tendency of a system to coagulate.

It's all about on-line

While zeta potential is at the forefront of water treatment as a lab technique, advances that bring it on-line are welcome.

The water industry is keen to access on-line measurement and move towards automated coagulant dosing. Streaming current detectors (SCD) on the process line are used this way within many treatment facilities, albeit with varied levels of success.

This method should help regulate coagulation, with the streaming current correlating, if not directly comparing with, zeta potential. However, in practice, many operators find these systems unreliable. Crucially, many variables can affect the charge measurement, leading to erratic readings, particularly at high flocculent concentration. Many water treatment facilities consider SCD an inherently flawed technique and too subjective to rely upon for process control.

Robust and sensitive on-line zeta-potential measurement is a potential solution to the problem of automated flocculation monitoring. Initial trials conducted with the Zetasizer Nano from Malvern Instruments demonstrated the feasibility of this approach.

At Aurora Water

The Aurora Water treatment facility has been using an online zeta potential system from Malvern Instruments since early in 2012 to monitor plant performance.

The online Zetasizer Nano is integrated into the water purification process, as illustrated in Figure 2. Water from the process line is pumped into the sampling loop at a controlled flow rate and directed, through an automated system of filters and valves, to a header tank, which ensures a constant analyzer sample supply. Post measurement, samples are disposed to open waste. Automated valves enable analyzer system by-pass and drainage, as required, for operational maintenance.

The system is reliable and produces useful operational data. It is more sensitive and informative than alternatives such as SCD, and measurement

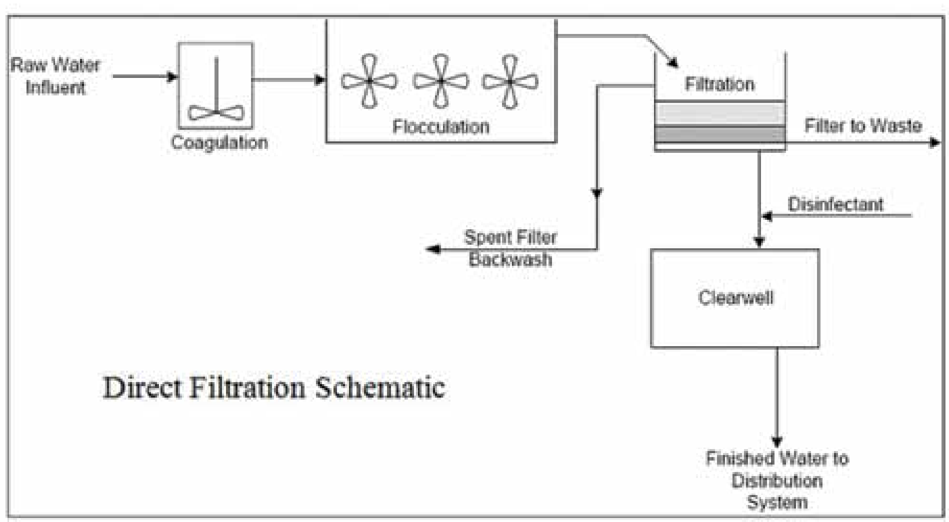

Figure 2. Plant schematic showing the treatment steps involved in producing clean water.

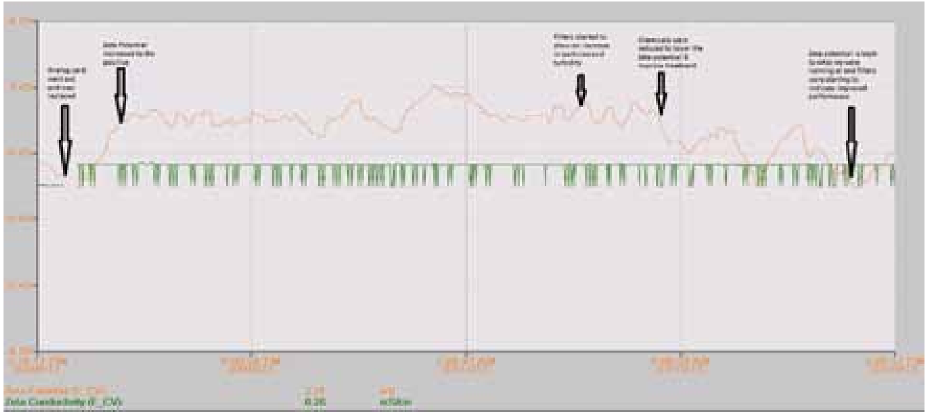

Figure 3. Screen shot showing on-line zeta potential measurements following the PLC shutdown. A sharp increase in zeta potential is eventually brought down by reducing coagulant dose.

frequency allows quick response to process changes. Adjusting chemical dosage rates to maintain zeta potential close to zero, within the range +3mV to -3mV, is effective for flocculation control. If zeta potential goes negative, chemical dosage rates are increased to restore it to around zero and likewise chemical additions are reduced if zeta potential shifts towards the positive.

Data received from the on-line system are corroborated by the lab-based Zetasizer. The high measurement frequency and instantaneous feedback unit presents an opportunity for advanced plant control, reduced labor costs and optimized chemical dosing.

Troubleshooting and efficiency

In February 2013, the plant suffered a major PLC fault. Once the problem was fixed, the plant was reset and operation continued. Immediately following the outage, however, the on-line zeta potential measurements became strongly positive (see Figure 3), a result that was confirmed by off-line laboratory analysis. Further evidence of a developing problem was an increase in suspended particles that led to the filters being taken off on breakthrough.

With no indication that water physical or chemical characteristics had changed, it was assumed the indicated water-flow rate was higher than the volume actually coming into the plant, causing the ratio of chemical addition to water to be overly high and account for the positive zeta-potential reading. Coagulant concentration was therefore lowered to bring zeta potential back to neutral.

This initial change seemed to move the plant in the right direction and further reductions were made. Overall coagulant addition was reduced by 17 percent, relative to pre-PLC shutdown levels, and this brought zeta potential back close to zero. At the same time, effluent particle concentrations dropped back to pre-shutdown values, turbidity readings improved and filter run times became longer, all confirming a plant moving back towards a better operating regime.

Further investigation of the water flow rate produced evidence that the water rate had not changed significantly pre- to post-shutdown. At the same time, it was determined that the rapid mixer used to stimulate flocculation had been left off, in manual mode, following the PLC reboot. This was switched back on and a strong negative shift in zeta potential was immediately observed.

This brief experiment suggested that rapid mixing was in fact detrimental to coagulation, resulting in more chemicals addition than would otherwise be required. This finding is supported by evidence from the published literature that slower flocculation can be beneficial. The decision was made to leave the rapid mixer off, saving energy and chemicals.

The online system quickly picked up the initial zeta potential change and also tracked the negative shift when the mixer was turned back on — real-time information needed for the efficient plant-performance investigation.

The problems might have eventually manifested themselves in filtration challenges, but online measurement allows rapid adjustments without upsetting plant performance.

Final comments

By using on-line zeta potential, Aurora Water has decreased chemical coagulant usage by around 17 percent while at the same time eliminating the need for a rapid mixer.

Research suggests that zeta potential measurement can be important to water treatment. Online zeta potential analysis will be part of a growing trend toward developing proactive, as opposed to reactive, water treatment methodologies.

Experience shows the Zetasizer Nano can be used for automated online zeta potential measurement. The technology is especially useful in responding to sudden changes in raw water quality and for troubleshooting.

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Malvern Instruments, Malvern, U.K., says it provides the materials, biophysical characterization technology and expertise that enable scientists and engineers to understand and control the properties of dispersed systems.

Malvern Instruments

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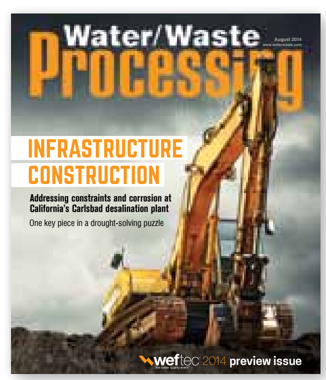

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