What every operator should know about ORP

Ronald G. Schuyler

Knowledge	Principle	Practical consideration
Chemistry	Oxidation–reduction potential (ORP).	Potential is an electrical voltage, not the "potential" for someone to succeed. It is the solution voltage developed between a noble metal and a reference electrode, such as hydrogen, calomel ($Hg/HgCl_2$), or silver/silver chloride. The ORP probe is attached to a pH meter. ORP is read on the millivolt (mV) scale.
History	ORP competed with dissolved oxygen (DO) for process control. ORP changes when DO is present and even when DO reaches 0.0 mg/L.	In the 1930s and 1940s, ORP was considered a main control parameter for the activated sludge process, but it was not used seriously until the 1980s and 1990s to help optimize nitrification/denitrification systems. The information presented here deals specifically with using ORP for biological process control.
Oxidation/reduction	Oxidation is the loss of electrons, while reduction is the gain of electrons.	The ability of a solution to oxidize or reduce can be measured by ORP. Higher ORP values represent oxidized conditions, while lower values suggest reduced conditions.
Nernst equation (modified)	This is what your ORP meter-readout is based on, but you never see any of this on the meter. $ORP = E^0 + (2.303RT/nF)Log(A_{ox}/A_{rd})$. Don't worry about E^0, the standard state ORP, or the (2.303RT/nF) term. Focus instead on $Log(A_{ox}/A_{rd})$, which is the logarithm of the activity of the oxidized substances divided by the activity of the reduced substances. At the low ion concentrations involved with wastewater, think of activity as concentration.	If A_{ox} is greater than A_{rd}, then A_{ox}/A_{rd} is greater than 1.0, and the logarithm is positive. Thus, the value of $(2.303RT/nF)Log(A_{ox}/A_{rd})$ is added to E^0. However, if A_{ox} is less than A_{rd}, then A_{ox}/A_{rd} is less than 1.0, and the value of $(2.303RT/nF)Log(A_{ox}/A_{rd})$ is negative and subtracted from E^0. The result is that solutions with higher concentrations of oxidized substances tend to have positive ORPs, while those with higher concentrations of reduced substances have negative ORPs.
Anoxic selector	A small tank receiving influent or anaerobic selector effluent, return activated sludge, and recycled mixed liquor with no aeration provided. This tank has nitrate/nitrite available but no DO; thus, it is anaerobic but has nitrate available.	Even though a system at zero DO is anaerobic, there are different degrees of anaerobic. Anoxic is a special case of anaerobic. The anoxic zone has zero DO but has nitrate available, so the ORP is in the upper end of the anaerobic range. Typically, anoxic selectors run best in the ORP range between zero and −150 mV. This range is anaerobic enough to make sure most of the nitrate/nitrite has been denitrified but not anaerobic enough to produce organic acids as an anaerobic selector does.

<table>
<tr><th>Knowledge</th><th>Principle</th><th>Practical consideration</th></tr>
<tr><td>Reference electrode</td><td>The actual ORP reading depends on the specific reference electrode being used in conjunction with the noble metal. Typical reference electrodes include standard hydrogen, saturated calomel electrode, or silver/silver chloride electrode.</td><td>Different electrodes produce different ORPs for the same solution, based on the specific reference electrode used. For example, a solution showing zero mV with a hydrogen electrode would read these approximate values from other electrodes:
<table>
<tr><th>Reference electrode</th><th>ORP (mV)</th></tr>
<tr><td>Standard hydrogen electrode</td><td>0</td></tr>
<tr><td>Saturated calomel electrode</td><td>−241</td></tr>
<tr><td>Silver/silver chloride, 1 M KCl*</td><td>−236</td></tr>
<tr><td>Silver/silver chloride, 4 M KCl</td><td>−200</td></tr>
<tr><td>Silver/silver chloride, saturated KCl</td><td>−197</td></tr>
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* Silver/silver chloride electrodes can use different concentrations of potassium chloride (KCl) electrolyte.</td></tr>
<tr><td>Biochemical activities</td><td>Each type of biochemical activity occurs within its own range of ORP.

Research by Mervyn Goronszy on sequencing batch reactors revealed standard ORP ranges using silver/silver chloride reference.

Exact ORP values should be verified at each plant, since basic water quality can affect these values, as do various conditions within the plant. Also note that flow-through systems differ from sequencing batch reactors.

Chemical discharges from industries also can directly affect ORP readings.</td><td>An ORP probe and mV meter may be useful in determining the type of biological activity occurring at any point in the process.
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<tr><th>Biochemical activity</th><th>Approximate ORP range*</th></tr>
<tr><td>Carbon oxidation (carbonaceous biochemical oxygen demand stabilization)</td><td>+50 to +200</td></tr>
<tr><td>Polyphosphate accumulation</td><td>+50 to +250</td></tr>
<tr><td>Nitrification</td><td>+150 to +350</td></tr>
<tr><td>Denitrification</td><td>−50 to +50</td></tr>
<tr><td>Polyphosphate release</td><td>−40 to −175</td></tr>
<tr><td>Acid formation</td><td>−40 to −200</td></tr>
<tr><td>Sulfide formation</td><td>−50 to −250</td></tr>
<tr><td>Methane formation</td><td>−200 to −400</td></tr>
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* Using silver/silver chloride reference.</td></tr>
<tr><td>Anaerobic selector</td><td>A small tank receiving influent wastewater and return activated sludge with no aeration provided, and which runs with zero DO and no nitrate remaining. While a DO meter will only indicate the lack of DO, ORP indicates what is happening, even at zero DO.</td><td>Typical ORPs will be low in selectors due to the high organic and ammonia concentrations and the organic acids produced. These are all reduced compounds.

ORPs between −100 and −250 mV are common. Higher values (closer to zero) mean that the system is not as anaerobic as it should be.</td></tr>
<tr><td>Aeration tank</td><td>A larger aerobic tank for carbonaceous biochemical oxygen demand (CBOD) removal, nitrification, and biomass stabilization.</td><td>Typical ORPs may range from +100 to +250 mV as CBOD is converted to carbon dioxide and biomass, and ammonia is converted to nitrate/nitrite.</td></tr>
<tr><td>Aerobic digester</td><td>An aerated tank typically used for waste activated sludge stabilization.</td><td>Typical ORPs may be more than +200, but this reading usually means that the digester is being overaerated. ORPs between −50 and 50 usually mean the solids are stabilized, the ammonia is nitrified to nitrate/nitrite, and the nitrate/nitrite is denitrified to nitrogen gas, nitric oxide, or nitrous oxide – this is the best condition.</td></tr>
<tr><td>Anaerobic digester</td><td>A nonaerated tank for stabilizing primary and waste activated sludge in some cases.</td><td>Typical ORPs will be quite low, averaging less than −200 mV. This ensures that organic acids form and methane is produced.</td></tr>
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