

The Reason Why Chlorine-Treated Water and Peroxyacetic Acid Treated Water Register Different Oxidation-Reduction Potential (ORP) Responses

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To a first approximation, the Oxidation-Reduction Potential (ORP) measured at a platinum electrode in a water system is governed by the Nernst Equation:

$$E = E^{\circ} + 2.303 \frac{RT}{zF} \text{Log} \frac{[\text{Red}]}{[\text{Ox}]}$$

Where:

E = ORP/mV

E^o = Standard Electode Potential for the Redox Couple

R = Gas molar Constant equal to 8.314 J K⁻¹ mol⁻¹

T = temperature in Kelvin ($T_K = 273.15 + T_{\text{C}}$)

F = Faraday's Constant (the charge per a mole of electrons), equal to 96,480 C mol⁻¹ s

z = the number of electron transferred in the half-reaction

[Red] is the molar concentration of the oxidizing agent (the reduced species).

[Ox] is the molar concentration of reducing agent (the oxidized species).

The Nernst Equation is theoretical, and predicts that the ORP responds to the logarithm of the concentration of oxidizing agents present. Further discussion is below.

When peroxyacetic acid is introduced to water, an associated excess amount of hydrogen peroxide is also introduced. Therefore, the electrical potential measured at the platinum surface of the ORP electrode is actually the result of 2 redox couples. For simplicity, let's assume that the hydrogen peroxide is the dominant influence to the ORP when peroxyacetic acid is introduced to a water system, and that hypochlorous acid is the dominant redox couple when sodium hypochlorite is introduced to a water system. The two respective half reactions are:



Since, E^o for H₂O₂ is higher than that for HOCl, intuitatively one might expect the peroxyacetic acid-treated water would register a higher ORP (for a given molar equivalent charge to the system) than that for chlorinated water. However, many factors effect the actual ORP response that are not defined by the Nernst Equation. These include slow electrode kinetics, the pH effect on acid dissociation constants, electrode poisoning (clogging), dissolved oxygen, and even the flow rate of solution over the probe surface.

Note that the dissociation constant (pK_a) of hydrogen peroxide is 11.62, and hypochlorous acid (HOCL) is 7.4, expressed in terms of pH. It then becomes obvious that the peak activity of the E° for hypochlorous acid is very near the pH of the water being treated, and the H_2O_2 is considerably higher. Thus, H_2O_2 would express a much lower ORP value at pH 7.4 than would hypochlorous due to the vast difference in the pK_a constant.

Practical ORP Measurement in Agricultural Applications

Measurement of a water system's ORP is simple and it provides the operator with a rapid assessment of the system's disinfection potential. Unfortunately, as the Nernst Equation indicates, the ORP varies with the logarithm of the concentration of the oxidizing agent. This makes correlation of the ORP to an absolute concentration of a comparative oxidizing agent inaccurate at best, and plain wrong at worst. Instead, the operator should rely on previous experiences or historical measurements without drawing any conclusions as to the concentration of disinfectants present. For example, chlorination has been practiced for decades. Instinctively, and from year's of experience, users know that microbiological quality will not be compromised provided an ORP of 650-700 mV is maintained for most systems.

However, would one expect to measure a similar ORP if a peroxyacetic acid/hydrogen peroxide sanitizer was used? The answer is no due to the limitations of the ORP methodology outlined above.

A practical approach to using ORP in a peroxyacetic acid-treated environment would be first to select the desired or target concentration for the treatment program. This would depend on several factors such as the required microbiological performance, the soil-loading on the produce being treated, etc. For fresh fruit and vegetable washing and sanitation purposes, experience dictates that one start at the 40-50 ppm range, reported as peroxyacetic acid, and compare this treatment rate to the resulting ORP.

Let's assume that we wanted to maintain 40 ppm PAA and wished to control the dosing using ORP. The user should start introducing peroxyacetic acid into the water system and measure the concentration using test strips or a test kit. Once the target dose has been reached, discontinue the feed and measure the ORP of the system. It may be far lower than typically experienced in chlorinated water. The Nernst Equation and its limitations in practical applications would explain the difference. Set this ORP as the trip point on the ORP controller, which will signal the pump to turn on when the ORP is below this voltage, and off when it is reached.

At least once per week, and preferably every day, check that the target ORP still corresponds to 40 ppm PAA using a test kit or test strips. If there has been a drift, readjust accordingly. It's also a good idea to clean the ORP probe weekly as fouling is a common cause of ORP errors.

In summary, one can use ORP to control the dosage of peroxyacetic acid solutions into agricultural applications, but you must understand the limitation of the technique and frequently check that the ORP set point still corresponds to the target dose. A lower ORP reading than one would obtain for chlorination is commonplace and typical, but there are no sacrifices or concessions in microbiological control as long as one calibrates their ORP system set point to the corresponding residual of peracetic acid, and not to that of hypochlorous acid.

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