



Oxidation Reduction Potentials (ORP)

In this month's Peroxygen Talk, Frank Sessa, of Environmental Solutions team, discusses measurement of the Oxidation-Reduction Potential (ORP). Mr. Sessa earned a BS in chemistry and physics from the South Connecticut State University and a master's in electrochemistry from the University of Connecticut. Mr. Sessa has been with us for the past ten years and provides expertise in chemical oxidation and aerobic bioremediation.

In an aqueous solution where the processes of oxidation and reduction are occurring, one measures the potential to determine if this is an “oxidizing” or “reducing” environment. Like pH the ORP represents an intensity factor, it does not characterize the capacity of a system for oxidation or reduction similar to the way pH does not characterize the buffering capacity of a solution. To better understand this measurement we must start at the definition of ORP and progress through its limitation and interferences, as well as, its application in the remediation field. The measurement of Oxidation-Reduction Potential as a tool to assess the site condition for application of bio-remediation is somewhat removed from its original intent and therefore the use of this measurement must be judicious to arrive at an appropriate conclusion.

Definition

According to the EPA field manual, the “Oxidation-Reduction Potential (E_h) is a measure of the equilibrium potential, relative to the standard hydrogen electrode, developed at the interface between a noble metal electrode and an aqueous solution containing electro-active redox species”. This definition is similar to those found in instrumental chemistry books, “Electrode potentials are defined as cell potentials for a cell consisting of the electrode in question behaving as a cathode and a standard hydrogen electrode acting as the anode. The electrode potential is in fact the potential of an electrochemical cell involving a carefully defined reference electrode.” One key takeaway is that measured potentials are in fact relative to a specific reference cell, such as the hydrogen electrode.

Half Reaction

The half reaction is:



Where v is the valence state of the target species prior to reduction, n is the number of electrons transferred and $(v-n)$ is the reduced species valence state. This is called a half reaction because we are only seeing one half of the oxidation/reduction couple, the other half reaction is hydrogen oxidation measured at the reference hydrogen electrode.



Hydrogen and Reference and Sensing Electrodes

The hydrogen electrode is a reference electrode that has its potential arbitrarily set at 0.0 mV. However, because the hydrogen electrode is difficult to use in the field or laboratory, other electrodes are used as the reference electrode. These electrodes are characterized by having very stable potentials and are highly reproducible. For example two widely used reference electrodes are:



As a result, the measured value of ORP will vary depending on the reference electrode chosen. Additionally the correct filling solution for the electrolyte in the reference electrode of choice must be used. Knowing which reference electrode is being employed allows it to be related back to the hydrogen electrode reference.

The sensing electrode is usually a platinum surface where the Redox reactions occur. In the case of measuring pH, the sensing electrode it is a glass electrode. Like a pH electrode that uses buffer solutions to standardize the instrument, there is a reference solution, ZoBell's ($E^\circ = 430$ vs. E_h at 25°C) that is used to standardize ORP instruments.

Redox measurements (E_h) on a platinum electrode are valid only in solutions that contain electro-active species present in solution. Measurements should not be carried out without an awareness of the interferences and limitations inherent with ORP method. Organic matter and sulfide may cause contamination of the electrode surface which can cause erratic performance. In addition, hydrogen sulfide can produce a coating on platinum that can interfere with measurement. Platinum single or combination electrodes may yield unstable readings in solutions containing chromium, uranium, vanadium or titanium ions, as well as other ions that are stronger reducing agents than hydrogen.

ORP Measurement

As pH is a measure of the hydrogen ion concentration in water or the acidity or alkalinity of a system. ORP is a measure of the overall oxidizing or reducing condition of a system. The ORP measurement is a direct potentiometric measurement of the equilibrium established between ALL oxidizing and reducing reactions in solution and is governed by the Nernst equation

$$E = E_o + RT/nF(\ln A_{ox}/A_{red})$$

E = potential developed at the electrode

E_o = Constant dependent on reference electrode

R = gas constant

T = temperature in $^\circ$ Kelvin

n = number of electrons transferred

F = Faraday's constant

A_{ox} = activity of oxidized species [directly related to the concentration of oxidized species]

A_{red} = activity of the reduced species [directly related to the concentration of reduced species]



The ORP reading should be reported versus the normal hydrogen electrode

$$E_h = E_{obs} + E_{ref}$$

Measurement of ORP is made using an electrode pair consisting of an electrode pair consisting of a reference electrode, sensing electrode and a high input impedance meter.

As an example, take the redox couple Fe(II) and Fe(III) with the following equation



From the Nernst equation:

$$E = E_0 - \frac{0.1987(t+273.15)}{n} \log \frac{[Fe^{+2}]}{[Fe^{+3}]}$$

, where t is the temperature in C, n = 1 for this case.

At 25 C, if the ratio of Fe⁺² concentration to Fe⁺³ concentration is a factor of ten, then E = -59.2 mv. If the concentration ratio is a factor of 0.1, then E = 59.2 mv.

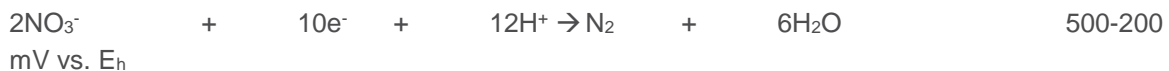
Use of ORP readings

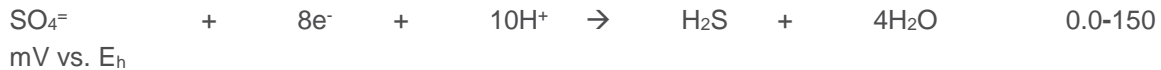
Bioremediation processes may be monitored indirectly by measuring the Oxidation - Reduction Potential. However this measurement must be accompanied by pH, temperature and oxygen content, electron acceptor/donor concentration and concentration of breakdown products. Some of the biological breakdown reactions as a function of the redox potential are shown below

Aerobic



Anaerobic





These equations are for very specific reactions. The E_h value is highly dependent on the pH [H⁺]. Note that the potential of two of the anaerobic reactions nitrate and manganese dioxide reduction can be within the aerobic potential range. As a result conclusions based on ORP measurement should not be in isolation, and should be supplemented by other measurements to have a meaningful relationship to the processes that are in the environment. However, ORP measurement is useful in assessing the general overall electro-potential state of the environment, indicating the general presence of oxidized or reduced states of metals and salts, thus giving an indication of the potential predominant chemical and biological processes that may be occurring.

The Impact of pH

pH can have a profound influence on ORP measurements. As an example, a common chemical reaction that takes place during bleaching or disinfection with chlorine is:



In writing out the Nernst equation, [H⁺] appears:

$$E = E^0 - \frac{0.1987 (t + 273.15)}{2} \log \frac{[\text{Cl}^-]}{[\text{HOCl}][\text{H}^+]}$$

As a result, electrode potentials specifically can be a function of pH [hydrogen ion concentration]. As a demonstration, an Accumet ORP probe (Cat# 13-620-115) with platinum tip was used to determine ORP and an Accumet Ag/AgCl Reference electrode (Cat# 13-620-53) was used as a reference. The Accumet reference probe was filled with 4M KCl. These electrodes were connected to a Fluke 21III Multimeter to determine voltage from the system. The ORP of distilled water as a function of pH is shown in Table 1.

| pH | Actual pH | mV |
|----|-----------|-------|
| 9 | 9.05 | 163.4 |
| 10 | 10.03 | 83.6 |
| 11 | 10.99 | 59.2 |
| 12 | 11.99 | 22.9 |

Table 1: Center of Distilled water ORP as a fxn g pH

As pH increases, the measured ORP value decreases.

Several users of Klozur® Persulfate have remarked that the ORP of a concentrated solution of persulfate and sodium hydroxide (batched in preparation for high pH – activated persulfate ISCO field remediation) are more negative after addition of the sodium hydroxide. Table 2 shows the decrease in ORP measurement for a 20 wt% sodium persulfate solution with an increase in pH (measured under the same conditions as Table 1):



| pH | Actual pH | mV |
|----|-----------|-----|
| 9 | 8.95 | 685 |
| 10 | 10.01 | 627 |
| 11 | 10.98 | 606 |
| 12 | 11.96 | 575 |

Table 2: Klozur SP Solution as a fxn g pH

Thus, even in the presence of a highly oxidizing species such as persulfate, the ORP values can be greatly impacted by an increase in pH, and in some instances, negative ORP readings have been reported for NaOH – persulfate solutions. This does not mean that persulfate is no longer acting as an oxidizer. For a given pH, as long as the potential of the half cell reaction for persulfate is more positive than the corresponding potential of the half cell reaction for the contaminant reaction, persulfate will act as an oxidant, even if the persulfate half cell is negative with respect to the reference electrode. It is the relative difference of the two half-cell potentials that dictate the oxidation - reduction reactions, instead of the absolute, measured ORP value.

Conclusions

ORP measurements are an invaluable tool to measuring changes in subsurface chemistry. However, their value is diminished if used in isolation without understanding other groundwater parameters such as pH and metal concentrations. In isolation, and ORP measurement can be misleading. It is best to use ORP change as a tool to look at the impact of chemical and biological changes on groundwater chemistry.

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