FUNDAMENTALS OF OXIDATION REDUCTION POTENTIAL MEASUREMENT

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What is ORP?

- ORP stands for oxidation-reduction potential, which is a measure, in millivolts, of the tendency of a chemical substance to oxidize or reduce another chemical substance

Oxidation

- Oxidation is the loss of electrons by an atom, molecule, or ion.
- It may or may not be accompanied by the addition of oxygen, which is the origin of the term.
- Familiar examples are iron rusting and wood burning.
- When a substance has been oxidized, its oxidation state increases.
- Many substances can exist in a number of oxidation states.
- Example is iron, which can exhibit 2 oxidation states in soil ferrous and ferric Fe^{2+} and Fe^{3+}

- Substances with multiple oxidation states can be sequentially oxidized from one oxidation state to the next higher.
- Adjacent oxidation states of a particular substance are referred to as redox couples.
- In the case below, the redox couple is Fe+2/Fe
- Fe = Fe+2 + 2electron
- Iron Ferrous ion electrons
- The chemical equation shown above is called the *half-reaction* for the oxidation, because, as will be seen, the electrons lost by the iron atom cannot exist in solution and have to be accepted by another substance in solution.
- So the complete reaction involving the oxidation of iron will have to include another substance, which will be reduced.
- The oxidation reaction shown for iron is, therefore, only half of the total reaction that takes place

Reduction

- Reduction is the net gain of electrons by an atom,molecule, or ion.
- When a chemical substance is reduced, its oxidation state is lowered.
- As was the case with oxidation, substances that can exhibit multiple oxidation states can also be sequentially reduced from one oxidation state to the next lower oxidation state.
- The chemical equation shown below is the half-reaction for the reduction of chlorine

Cl2	+ 2e -	= 2Cl
chlorine	electrons	chloride ion

- The redox couple in the above case is Cl2/Cl- (chlorine/chloride)
- Oxidation reactions are always accompanied by reduction reactions.
- The electrons lost in oxidation must have another substance as a destination, and the electrons gained in reduction reactions have to come from a source.

- When two half-reactions are combined to give the overall reaction, the electrons lost in the oxidation reaction must equal the electrons gained in the reduction reaction.
- **Oxidation:** $Fe = Fe^{+2} + 2\ e^-$
- (Half- Reaction)
- **Reduction:** $Cl_2 + 2\ e^- = 2\ Cl^-$
- (Half- Reaction)
- Overall reaction: $Fe + Cl_2 \Rightarrow FeCl_2$
- In the reaction above, iron (Fe) reduces chlorine (Cl_2) and is called a *reductant* or *reducing agent*.
- Conversely, chlorine (Cl_2) oxidizes iron (Fe) and is called an *oxidant* or *oxidizing agent*

STANDARD POTENTIAL

- How easily a substance is oxidized or reduced is given by the standard potential of its redox couple, symbolized by E°.
- Standard potentials of quite a number of redox couples are available in reference books, along with their half-reactions.
- All are referenced to the redox couple for hydrogen ion/hydrogen (H^+/H_2), which is assigned a standard potential of 0 millivolts.
- Examples
- Oxidants: E° (mV)
- $O_3 + 2H^+ + 2e^- = O_2 + H_2O$ +2,007
- $HOCl + H^+ + 2e^- = Cl^- + H_2O$ +1,490
- Reductants:
- SO_4
- $-2 + H_2O + 2e^- = SO_3$
- $-2 + 2\ OH^-$ -930
- $Na^+ + e^- = Na$ -2,713

Measurement of ORP

- An ORP sensor consists of an ORP electrode and a reference electrode, in much the same fashion as a pH measurement.
- **The ORP Electrode**
- Principle behind the ORP measurement is the use of an inert metal electrode (platinum, sometimes gold),
- Due to its low resistance, it give up electrons to an oxidant or accept electrons from a reductant.
- The ORP electrode will continue to accept or give up electrons until it develops a potential, due to the build up charge, which is equal to the ORP of the solution.
- The typical accuracy of an ORP measurement is ±5 mV.
- Sometimes the exchange of electrons between the ORP electrode and certain chemical substances is hampered by a low rate of electron exchange (exchange current density).
- In these cases, ORP may respond more strongly to a second redox couple in the solution (like dissolved oxygen).
- This leads to measurement errors, and it is recommended that new ORP applications be checked out in the laboratory
- ORP measurement is never temperature compensated

Reference electrode

- The reference electrode used for ORP measurements is typically the same silver-silver chloride electrode used with pH measurements.
- In contrast with pH measurements, some offset in the reference is tolerable in ORP since, as will be seen, the mV changes measured in most ORP applications are large

ORP measurement in soil

- ORP measurement in soil assesses the oxidizing or reducing capacity of the soil, indicating whether conditions are aerobic or anaerobic.
- It's measured in millivolts (mV), with positive values signifying oxidizing and negative values indicating reducing conditions.
- Aerobic soils generally have higher ORP values due to the presence of oxygen, while anaerobic soils have lower ORP values
- This information is crucial for understanding soil health, potential for corrosion, and microbial activity.
- ORP can be used to assess the overall health and quality of the soil, as it can indicate the presence of specific compounds or microbial activity.
- In construction and infrastructure projects, ORP measurements can help determine the likelihood of corrosion in soil, especially when dealing with metallic structures.
- ORP can provide insights into the types and activity of microorganisms in the soil, as different microbes thrive under different redox conditions

Measurement Methods:

- ORP is typically measured using an electrode immersed in a soil suspension or in the field using specialized probes. The measured potential is then compared to established standards and interpreted accordingly.
- In situ field measurements using temporary or permanently installed electrodes have become routine study of soils

Factors Influencing ORP:

- Several factors can influence ORP in soil, including soil moisture content, the presence of organic matter, and the type of microorganisms present.

Limitations:

- ORP is a non-specific measurement, it reflects the combined effect of all redox-active species in the soil.
- Thorough understanding of the soil's composition and the specific redox reactions occurring is crucial for accurate interpretation of ORP data.

Reference

Rosemount Analytical Inc. 2008,ADS,43-014,Fundamentals of ORP Measurement


Thank You