

Redox measurements

1. What is Redox?

Redox means reduction-oxidation. It is also known as oxidation-reduction potential (ORP). A Redox measurement reflects the ability of chemical species to oxidize or reduce other chemical species in solution. All redox active species present in solution contribute to the oxidation-reduction potential of that solution. Redox is measured as a single voltage in millivolts (mV). Oxidizers – like O_2 , H_2O_2 and Cl_2 – have a positive Redox value, while reducers – like Fe, C and H_2S – have a negative Redox value.

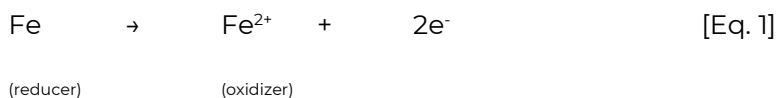


Photo 1. Mississippi swamp: reducing conditions – methane production (pixabay.com)

Photo 2. Madagascar red earth: oxidising conditions – iron oxide rich sediments (pixabay.com)

2. Oxidation and reduction

To understand Redox measurements, some basic knowledge of oxidation and reduction reactions is necessary. Oxidation is the loss of electrons by a chemical species (atom, molecule or ion). The oxidation of Fe to Fe^{2+} is an example of an oxidation reaction (Eq. 1):



Reduction is the net gain of electrons by a chemical species (atom, molecule or ion). The reduction of Cl_2 to Cl^- is an example of a reduction reaction (Eq. 2):



The chemical equations of the oxidation and reduction reactions are called half-reactions, because electrons lost by a reducer (e.g. Fe) cannot exist in solution, they must be accepted by an oxidizer (e.g. Cl_2). So, the complete reaction involves 2 half-reactions: an oxidation and a reduction reaction. In our example, the overall reaction of both half-reactions becomes (Eq. 3):



In this reaction, the electrons lost in the oxidation reaction are equal to the electrons gained in the reduction reaction.

3. Measuring Redox

Redox measurements are performed with an inert electrode (i.e. electrode does not take part in the oxidation-reduction reactions) and a reference electrode. The chemical potential at the inert electrode is compared to the chemical potential of a reference electrode in a mV measurement.

Platina (Pt) is commonly used as the inert electrode material, but e.g. gold (Au) and glassy carbon (C) can also be used.

A reference electrode consists of a chemical system with a fixed chemical potential. Several types of reference electrodes exist, a.o. the Standard Hydrogen Electrode (SHE), the Saturated Calomel Electrode (SCE) and the Ag|AgCl KCl electrode. The SHE (H^+/H_2 redox couple) has, by definition, a standard potential of 0 mV. Since the SHE is not practical/suitable for everyday use, other reference electrodes like the SCE and Ag|AgCl KCl electrode are commonly used.

Redox mV readouts obtained with, for example an Ag|AgCl 3M KCl reference electrode, can be converted to mV values as if the measurements were performed with a SHE. For example, at 20°C, the Redox value obtained with an Ag|AgCl 3M KCl reference electrode is +213 mV versus the SHE. When the voltage measurement of an Redox electrode versus the Ag|AgCl 3M KCl reference is +220 mV (e.g. tap water), Redox equals +433 mV versus the SHE.

4. Applications

Since Redox measurements are cost effective, they are commonly used to monitor a variety of processes. Applications include:

- Soil and (natural) water quality monitoring
- Water disinfection monitoring
- Wastewater treatment monitoring

Soil and (natural) water

In the natural environment, the range of redox potentials is limited by the stability of water. At a very high redox potential, water would decompose into oxygen and protons. At a very low redox potential, hydrogen would form. As the decomposition reactions of water involve protons, the redox potential at which water decomposes varies with acidity (pH). At a pH of approximately 7 to 8 (near neutral), the redox potential can vary between -400 and +800 mV versus the SHE. At pH 4 (acidic), redox potentials may rise to +900 mV, while at pH 9 (basic) redox potentials may be as low as -600mV.

In most soils and natural waters various chemical species can be present that take part in redox reactions. Some examples of redox couples that can occur in nature are shown in Fig. 1. In an ideal situation, reacting redox couples are in equilibrium and have a relatively large exchange current. This is, for example, the case for Redox standard solutions (e.g., Zobell's solution) and for the Fe^{2+}/Fe^{3+} redox couple commonly present in soils. In these situations, the redox potential can be measured accurately (within 1 - 5 mV). In practice, most natural systems are not in a state of equilibrium and exchange currents of present redox couples are relatively small (e.g., oxygen). Therefore, redox potentials measured in natural system, are often mixed potential which cannot be measured very accurately (within 10 mV). The measured potential in natural systems is a response to all redox active species present, weighted by the exchange current of the redox couples. Thus, the Redox measurement does not give you the direct concentrations of redox-active species present in your sample. Only when your samples contain a single, very active species (high exchange current), like is the case with chlorine in pool water, Redox correlates with concentration. In the case of soil and natural waters, users should be careful not to over-interpret the Redox data. Specific site information is often necessary to help interpret the Redox data.

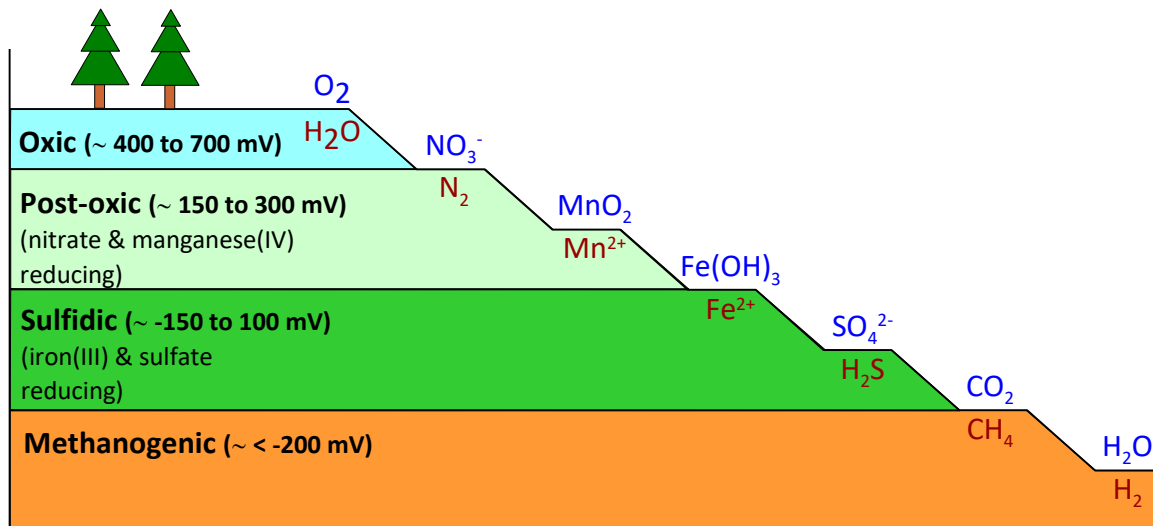
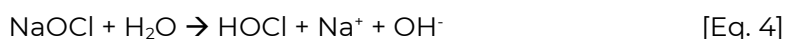


Fig. 1. The redox ladder for natural systems.

Water disinfection

Chlorine is most likely the most widely used disinfecting agent in aqueous solutions. Its powerful disinfecting capabilities are related to its ability to bond with and destroy the membranes/cell walls of bacteria and viruses. There are various possibilities to add chlorine as a disinfectant to water: e.g., 1) by adding chlorine gas to water, 2) by adding sodium or calcium hypochlorite or 3) by in-situ production of chlorine using anodic oxidation. The different forms of chlorine that can be distinguished – pH and temperature dependent – are Cl_2 (chlorine), hypochlorous acid ($HOCl$) and the hypochlorite ion (OCl^-). Of these 3, hypochlorous acid is the most biocidal form in water. Hypochlorous acid is unstable because the chlorine molecule is lightly bound and therefore reacts quickly.

Based on temperature and pH the following reactions can occur when adding, for example, sodium hypochlorite:



Between pH 5 and pH 8.5, this reaction is incomplete and both species are present in water to some degree. By adjusting the water pH, the ratio between $HOCl$ and OCl^- can be varied.

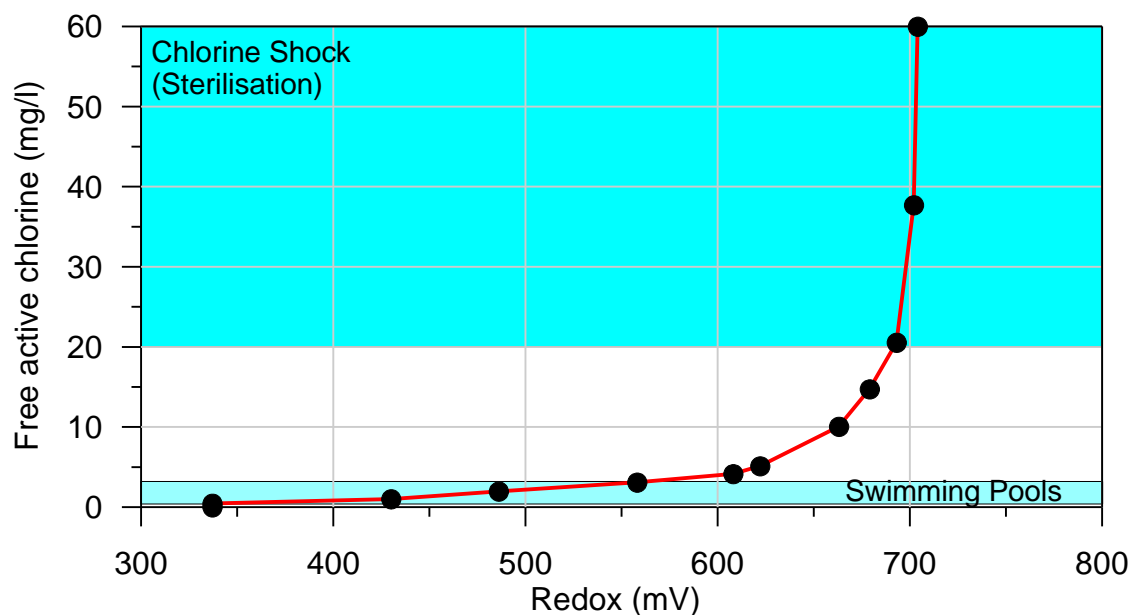


Fig. 2. Redox (mV vs. saturated KCl Ag/AgCl reference electrode) versus free active chlorine concentrations (sodium hypochlorite added to local tap water).

The amount of HOCl present in water can be determined by measuring the Redox value of treated water. This is called free available chlorine. When pH and temperature are measured, together with Redox, the OCl⁻ concentration can be calculated. The sum of HOCl and OCl⁻ is called total free chlorine. Fig. 2 shows the relationship between the measured Redox values (in mV) and free active chlorine (in mg/l). Redox values for chlorine disinfection in swimming pools and shock dosing (sterilisation) are also indicated Fig. 2

Wastewater treatment monitoring

In wastewater treatment Redox measurements are performed to determine the ability or potential of wastewater to permit the occurrence of specific oxidation-reduction reactions. According to Gerardi (2007) these are the important oxidation-reduction reactions – with corresponding Redox values – in wastewater treatment:

- Nitrification: 100 to 350 mV
- cBOD degradation: 50 to 250 mV
- Biological phosphorus removal: 25 to 250 mV
- Denitrification: 50 to -50 mV
- Sulfide (H₂S) formation: -50 to -250 mV
- Biological phosphorus release: -100 to -250 mV
- Acid formation (fermentation): -100 to -225 mV
- Methane production: -175 to -400 mV

The oxidation-reduction processes that occur in a wastewater treatment plant also occur in soils (see Fig. 1). By measuring Redox in wastewater, the plant operator knows what reactions are occurring and can influence these reactions. For example, if the formation of H₂S (toxic and malodorous) must be prevented, a Redox value of > -50 mV should be maintained. By maintaining Redox values of > -100 mV, the formation of malodorous volatile acid formation is avoided. For more information, see Gerardi (2007).

5. References

Gerardi, M.H. (2007). Oxidation-Reduction Potential and Wastewater Treatment. IWRE, Winter 2007.