

# WTR OSG

# Advanced Oxidation

# An Introduction

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# **I: WTR Mineral Complex Buffer Properties**

#### Introduction

The purpose and function of adding **WTR Mineral Complex**, a buffer, to a hypochlorite solution is to increase oxidation energy, i.e. improve the oxidation potential (ORP) when added to a water stream. By definition, the properties of a "buffer" are to increase the presence of hydroxyl radicals. By dissociating the hypochlorite source into hydroxyl and other oxygen complexes, oxidation energy is increased and the process mimics "advanced oxidation process". The ionic nature of mineral salts (buffers) is to generate complex conformations of ionically bound (chelated) ions. When introduced into a water stream, the properties and behavior of this chemistry is that of an advanced oxidation process and "biologic water". That is, when mineral and metal ions are introduced in concentrations measured in very low concentrations, they do not interfere with each other but as in biologic processes, these active ions interact with water and substrates generating hydroxyl and other radicals.



A typical curve disclosing the relationship between ORP and ppm of chlorine

Conditions: Sodium hypochlorite solution (with and without buffer) was titrated in deionized water of pH 7. The ORP was measured in relationship to 0.2 ppm increments of chlorine

How this is accomplished is by mimicking nature in how oxygen radicals are interconverted, how oxygen radicals are managed and how oxygen radical reactions are catalyzed. Hence the generation of a dynamic environment in which oxygen **is** the active ingredient and the presence of minerals, metals and water play subordinate and supporting roles.

#### Minerals and metals in biologic systems

The science of oxygen species describes active oxygen species as very good oxidizers and are generated in water environments. Metals play an important role in the generation and decomposition of active oxygen species due to their ability to participate in oxidation-reduction reactions. Their variable valency allows them to act as donors and acceptors of electrons. The decomposition of water, and oxo-compounds, generate several oxygen products. These oxygen products are various oxidation states of oxygen called: superoxide  $[O_2^-]$ , hydroxyl  $[OH^-]$ , nascent oxygen  $[^1O_2]$ , hydroperoxyl  $[HO_2^-]$ , and peroxide  $[O_2^{2-}]$ .



These oxygen radicals play a double role of both oxidant and antioxidant. As oxidant, oxygen species exert harmful effects on living water organisms. Oxygen species also are very important antioxidants transferring pollutants present in lakes and rivers into nontoxic products by their oxidative degradation, usually in the free radical and singlet oxygen way. The hydroxyl radical has a very high oxidation potential (2.8V), compared to singlet oxygen (2.7V). Additionally, hydroxyl and singlet radicals show very high values of second order rate constants for organic compounds. This means after an oxygen radical initially reacts with organic material, substantial energy is available to continue breaking down the organic compound, i.e. the oxygen radical is not limited to reacting with organic material just once. Also, with **WTR OSG** (On Site Generation oxidizer) oxygen radicals are generated during the combination with the metal/mineral constituents of **WTR Mineral Complex**. These reactions are referred to as "Haber-Weiss" and "Fenton" reactions.

1.  $Me^{[n+1]+} + O_2^- -----2H^+--- \rightarrow Me^{n+} + H_2O_2$ 2.  $H_2O_2 + Me^{n+} ---- \rightarrow HO^- + HO^- + Me^{[n+1]+}$ 

The enhancement of the toxicity of oxygen radicals caused by specific minerals and metal ions is observed in many biologic processes. It is this property of **WTR OSG** that enables reliable and effective ORP measurement, catalyzed oxygen reactions with organics,



improved second order rate reactions, and low concentrations of chemistry vs mg/l concerns with conventional treatment protocols and makes **WTR OSG** effective as:

- Disinfectant; kills bacteria and viruses
- Oxidation of organics
- Oxidations of inorganics
- Color removal
- Odor removal; sulfur and organic odors
- Algae control
- Micro coagulation aiding filtration
- BOD/COD reduction
- VOC elimination

#### **Chelation in Biologic systems**

When evaluating the principles of inorganic chelates, molecular cell biology (how biologic processes manage oxygen to build and destroy), and principles of water chemistry, there is commonality as to how specific minerals and metals chelate (ionically bind) conformations of oxygen radicals to prevent the oxygen radical energy from immediately being exhausted as seen with ozone and peroxides.

A second function of these oxygen chelates is, when in contact with organic matter, the presence of the minerals and metals catalyze the oxygen reactions with the organic material.

#### Discussion

The **WTR Mineral Complex** "buffer", which consists entirely of micronutrient elements, that when blended with the oxygen and chlorine of a hypochlorite solution, form hydroxyl "mineral"-oxychloride ions. The balance, ratio and valence of these elements are critical to optimizing the oxidation potential when introduced into a water stream. As in biologic processes, when mineral/metal ion valence is not correct, nothing happens, if concentrations are "low" there is a "deficiency" and the desired reaction(s) do not take place. Conversely, if the ion concentration is "too high" then there is an interference to desired reaction(s). Hence

there is a bell curve of diminishing returns. That is, there is a narrow area of the curve in which specific valence and ion concentration that optimizes oxidation potential. On either side of this curve, the improved oxidation potential is not there.

The addition of buffer to a hypochlorite solution not only increases oxidation energy by 30%-40%, but also catalyzes oxygen radical reactions within a water stream. The result is being more effective in controlling microbes with less chemistry and being able to maintain disinfection while keeping required chlorine concentrations well under MCL. An example of this is by maintaining an ORP above 450 mV with **WTR OSG** in a clarifier, the algae, bacteria and biofilm disappeared and the clarifier stays clean while chlorine concentration is held below 0.2 ppm.

# II: Biologic Water

Important to biochemistry, and biologic functions, is ionic equilibria. For the majority of biologically important reactions, very low concentrations of the hydronium ion, along with ions of Mn, Mg, Fe, and Ca are significant driving forces.

Biochemical ionic reactions are *acid* - *base* reactions that are pH and temperature sensitive, and follow the Bronsted definition of an *acid* as a proton donor and a *base* as a proton acceptor. Because water is amphoteric, it is important to understand the biochemistry of water and its contribution to biologic ion driven reactions.

Within biologic systems, oxygen species are generated to oxidize and be anti-oxidants. The production, delivery, and attenuation of oxygen specie reaction rates, is dependent on the biochemical properties of water and the other ions carried with it. Because water auto-ionizes, forms polymers, encapsulates (forms shells and clusters) simple and complex ions, it attenuates the oxidation potential and reaction rates of ion complexes.

**WTR OSG** is an ionic solution that mimics biochemical water in the production of oxygen species, and in the conservation of ionic energies (oxidation potential). **WTR OSG**, like biochemical water, has pH and temperature sensitivities identical to biochemical water.

# WATER

Understanding water, or more correct, to understand what we think we know about water is the first step necessary for understanding ionic solutions and how biologic systems use ionic solutions to their benefit and/or to their detriment.

Water,  $H_2O$ , two molecules of hydrogen and one molecule of oxygen, has a specific shape (conformation) that is instrumental to the behavior of water. Oxygen has two locations for bonding with other atom(s), and two locations where bonding can only be covalent. These four locations, equally spaced, form the four points of a tetrahedral (three sided pyramid). In the case of water, the two bonding locations are occupied with hydrogen atoms and the two ionic locations are filled with electrons.



#### WATER: GROUND STATE

In order for a water molecule to form, an oxygen atom must be in its "ground state". This ground state has two bonding locations it wants to fill. This "need" to fill makes oxygen "electronegative" (negative charge). Hydrogen, conversely, has an electron it wants to give up, making hydrogen "electropositive" (positive charge). If the hydrogen atoms, attached to the oxygen, were 180 deg opposite each other, the negative/positive charges would cancel each other, and water would not have any "magnetic" properties to it. But, the tetrahedral conformation puts the hydrogen atoms at an angle (105 deg) in relation to each other and the oxygen atom.



This means that the negative character of the oxygen, and the positive character of the hydrogens, do not cancel each other. The result of this bonding angle between the oxygen and hydrogens gives the molecule both positive *and* negative *charge* fields similar to a magnet.

This specific property is what makes water a *universal* solvent.



Because it is both a polar substance (+/- ends) and a hydrogen bonding molecule, water dissolves many substances that are ionic and polar compounds. This is important to both biologic and industrial processes.

### STRUCTURE OF WATER- WATER AS A POLYMER

In liquid water, each oxygen atom forms two covalent bonds via the two locations adjacent to where the hydrogen atoms are bonded, with two hydrogen atoms. This "hydrogen bonding" may be with adjacent water molecules, hydrogens of other solvates. Because hydrogen bonding is transient, and the matrix generated by just water-to-water hydrogen bonding is also transient, the exact structure of liquid water is still unknown. It is believed to contain many hydrogen-bonded networks that are presumably so transient that "stable" water is never formed.



What is known is that water molecules have a high affinity for each other. Many water molecules will link to form clusters of up to six water molecules. These clusters will also join together to *form polymers*. This transient bonding, and polymerization, is what gives water its viscosity, it's property to hold heat, and why no two snow flakes are alike (transience frozen in time like a photograph).

# SELF IONIZATION OF WATER

This transience of covalent and hydrogen bonding, of water molecules, causes a self-ionization (or autoionization), a reaction in which two like molecules react to give ions. In the case of water a proton from one  $H_2O$  molecule is transferred to another  $H_2O$  molecule, leaving behind an  $OH^-$  (hydroxyl) ion and forming a  $H_3O^+$  (hydronium) ion.

 $H_2O[L] + H_2O[L] \leftarrow ---- \rightarrow H_3O^+[aq] + OH^-[aq]$ 

This autoionization makes water amphoteric, meaning that water can act as either an acid or a base. Methods of manipulating water pH (acid/base properties) include stripping water of either ion generated, electrolysis, radiation, heat, or the addition of ionic substances that will favor the production of either ion.

# WATER COMPETES FOR HYDROGEN BONDS- WATER SHELLS

The polarity, and hydrogen bonding, of water makes it a highly *interactive molecule*. The consequence, is that water weakens electrostatic and hydrogen-bond interactions between

other molecules. This dielectric property of water is an expression of its polarity, and its capacity to form an oriented solvent shell *around an ion*.

*If water is manipulated to generate ions*, and additional ions are then added, to capture and form more complex ions, that portion of water that is not ionized will form *shells* [water molecules surrounding the ion] around each ion complex.



Because of the dipole property of water, it can be argued that water is a solvent of ionic complexes. But, because of the water shells around ion complexes, water conserves ionic energies [oxidation potential], it attenuates the reactions and reaction rates of ion complexes with organics, and it provides a raw material source for oxygen species. Hence, water is not just a carrier, but an active ingredient.

These shells will attenuate the electrostatic interaction of one ion with another. These oriented solvent shells produce electric fields of their own, which oppose the fields produced by the captured ion/ion complex. This shell field will also be attracted to electrically weak locations on an organic molecule, and during the hydrogen bonding exchange the ion/ion complex is released to react with the weakened organic molecule.

# **IONIC INTERACTIONS: ATTRACTIONS BETWEEN OPPOSITELY CHARGED IONS**

Compounds that are composed of atoms, of varying electronegativity, are easily dissolved in water. Because the different charged components of a compound separate and are shelled by water molecules, these now separated components are ionized.

Ionized atoms/molecules *do not share an electron with water* (bonding), *but rather conduct ionic interactions* with the water shell around them. Positive ions will have a water shell surrounding it, with the oxygen atom of water orientated inwards, towards the ion. Negative ions will have a water shell with the water hydrogen atoms oriented inwards, towards the ion.

Unlike other bond formations, ionic bonds do not have fixed or specific geometric orientations because the electrostatic field around the ion is uniform in all directions. In biologic systems, the water shell around ions of Na, K, Ca, Mg, Mn, Cl, Fe, as well as various hydrophilic polar oxides, is key to the transport and behavior/reactivity of the ion.

# Chapter Three: GENERATION OF REACTIVE OXYGEN SPECIES

In biologic systems, pH and temperature are critical to the generation of ion complexes, the stability of ion complexes, and the reactivity of ion complexes. Oxo-complexes work well in the pH range of 6.5 - 7.4, with the majority of oxidation reactions occurring at pH 6.8 - 7.2.

The water shell around a given ion complex is sensitive to the kinetics of temperature. The higher the temperature, the more kinetic energy there is in a solution that will break a water shell and the retained oxidation potential will be lost. In coordination with pH, oxo-complexes and their associated water shells, are best stable at a temperature range of 10 - 20 deg C.

Various forms of energy decompose water molecules. Energy that will decompose water may come from cosmic rays to UV radiation, alkaline complexes and transition metal complexes, photosensitized pigments, organic compounds that are contaminants, and metabolic enzymes.

The loss of a second proton from coordinated water can lead to the formation of oxocompounds. The oxygen of water can form a single bond bridge between two clusters, a conjugated end/branch of a cluster, or become a core atom for oxo-centered complexes.



Two coordinate oxygen compounds are linear. Three coordinate oxygen complexes are pyramidal and planar, and are associated with hydronium and oxonium ions. Four coordinate oxygen are tetrahedral in conformation and found in polynuclear complexes. Five and six coordinate oxygen is the least common, but are found in polynuclear complexes with a core of Mn<sup>+4</sup>, Mn<sup>+3</sup>, Mn<sup>+2</sup>, and other metal ions.



The decomposition of water, and oxo-compounds, generate several oxygen products. These oxygen products are various oxidation states of oxygen called: superoxide  $[O_2^-]$ , hydroxyl  $[OH^-]$ , nascent oxygen  $[^1O_2]$ , hydroperoxyl  $[HO_2^-]$ , and peroxide  $[O_2^{2^-}]$ .



\*Superoxide & Hydroperoxyl

In aqueous solution the superoxide anion exists in equilibrium with its conjugate acid, the hydroperoxyl radical. The stability of superoxide and hydroperoxyl products are only a few seconds in alkaline solution, and in both acid and neutral pH, superoxide and hydroperoxyl will dismutate to form molecular oxygen.

$$HOO^{\cdot} + HOO^{\cdot} - - - \rightarrow H_2O_2 + O_2^{-1}$$

$$O_2^{--} + O_2^{--} - - - \rightarrow O_2^{2^-} + O_2$$

\*Peroxide

Catalytic and non-catalytic dismutation of superoxide will lead to the production of peroxide. Hence, peroxide is always present, in all systems that produce superoxide anions.

$$Me^{[n+1]+} + O_2^{-} - - - 2H^+ - - \rightarrow Me^{n+} + H_2O_2$$

#### \*Hydroxyl radical

Superoxide and peroxide are relatively non-toxic per se but they are precursors of the most powerful oxidant, the hydroxyl radical. The detection of the hydroxyl radical is difficult because of its very short half life and exceptionally fast reaction rate constant. Its detection is generally inferred from its strong oxidative properties.

$$H_2O_2 \dashrightarrow HO^- + HO^-$$

$${}^1O_2 + H_2O \dashrightarrow HO^- + HO^-$$

$$H_2O_2 + Me^{n+} \dashrightarrow HO^- + HO^- + Me^{[n+1]+}$$

\*Nascent Oxygen

Superoxide anion, peroxide and hydroxyl radicals are water decomposition products, are normal to biochemical processes, and their interconversion reactions will generate an energetically richer form of oxygen by-product called nascent oxygen. The life time of nascent oxygen is only a few milli-seconds.

$$H_2O_2 + HOO^- \dashrightarrow H_2O + HO^- + {}^1O_2$$
$$O_2^- \dashrightarrow \to {}^1O_2 + e^-$$

# III. ROLE OF TRANSITION METAL IONS IN GENERATION OF OXYGEN SPECIES AND THEIR INTERCONVERSION

All the above mentioned oxygen species are very short lived, always present in aqueous environments, and in biologic systems. It is also a normal phenomena that they interconvert into each other. Transition metals (iron, manganese) play an important role in the generation, interconversion, and decomposition of these oxygen species due to their ability to participate in oxidation-reduction reactions. Iron and manganese have variable valences that allow them to take part in radical reactions, and can act as both donors and acceptors of electrons.

When considering the total mass of organics in a given stream/system, e.g. the total mass of bacteria to be killed, there are relatively few reactive sites on each bacterium/organic that can be attacked by an appropriate ion to kill and/or render an organic compound non-toxic. Biologic systems know this, and appropriately generate an ionic concentration just enough to do the job.

The relevant subject here is the stability and behavior of dilute ionic solutions. The normal considerations of aqueous equilibria are the reactions of cationic and anionic acids and bases with water, association equilibria, and dissociation equilibria. Wherein ionic energies are lost quickly. But, in dilute ionic solutions, these considerations are reversed, and take on a different physic because it is the water that is the principle agent.

In dilute, low concentration, ionic solution, the reduced kinetics between ion complexes means that the biochemistry of water, at biochemical pH and temperature ranges, is able to conserve oxidation potential, and deliver that potential to the reactive site of an organic.

#### \*Manganese

Manganese has oxidation states from -3 to +7. Associated coordination numbers will range from 2 to 8. The cations of Mn will form extensive soluble salts with many anions. Many of these salts form hydrates with water shells of up to 6 water molecules. In the presence of chlorine, manganese salts may form polymeric chains (Cl acts as a bridge) with octahedral sharing edges.

Mn  $^{+3}$  ion plays a central role in the complex redox reactions of higher oxidation states of manganese in aqueous solutions. It can be oxidized to a Mn $^{+4}$  by electrochemical oxidation. Associated manganic compounds may have oxo-centered cores and form complex conformations with multiple valences



In the +2 and +3 oxidation states, manganese is susceptible to bridging by chlorine and calcium. In the +4 oxidation state, manganese forms oxo-compounds with oxo bridges. A common feature of such species is their reduction in 1e (1 electron) steps to the corresponding +3/+4 and +3/+3 complexes.

The more complex species, of oxo-compounds, can have structures built up of different core units.



The Mn<sub>4</sub>O<sub>4</sub> cubes can have different charges, e.g.  $4+(Mn^{+3})$ ,  $8+(Mn^{+4})$ ; there are also rings of various conformations, and clusters such as  $[Mn_4 O_2]^{8+}$  and  $[Mn_{18} O_{16}]^{22+}$  in which 18 Mn<sup>+3</sup> ions are linked by 16 O<sup>2-</sup>.

\*Iron

Iron has valences from -2 to +6. Coordination numbers for these ions range from 2 to 8. The transient  $Fe^{+4}$  O species appear to be involved in the chemical oxidation of  $Fe^{+3}$ . The dismutation of peroxide, and the oxidation of saturated hydrocarbons, in the presence of Fe  $^{+2}$  will proceed through an Fe  $^{+5}$  =0 intermediate species.

In aqueous solutions, iron cations form salts with anions. In complex ionic solutions,  $Fe^{+2}$  forms hydroxo complexes, and  $Fe^{+3}$  forms hydolyzed complexes, along with  $Fe^{+4}$  oxo species.

A simple oxo-anion is  $[O_2FeOFeO_2]^{6^-}$ . More complex conformations arise with increased coordination number, i.e octahedral, trigonal bipyramidal and dodecahedral for the respective 6, 7, and 8 coordinate iron ions.



In the presence of chlorine and calcium, these iron oxo-complexes will form polymers with Cl and Ca bridges.

A characteristic property is the formation of oxo and/or hydroxo bridges. Binuclear systems may be [a] doubly bridged and [b] singly bridged. Hydroxo bridges are common on mutidentate ligands. More complicated conformations of polymeric oxo species will have a centrosymmetric eight member ring of alternating iron and oxygen atoms.



### **IV: OXIDATION POTENTIAL**

Formation of the metal-oxy-complex, which is a diamagnetic molecule, removes the restrictions for the oxygen reactions with molecules in the singlet state. These complexes also decrease the ionic activity of the metal ions. In general, there is a stabilization against reduction of metal ions (of low concentration) by these complex formations. Coordination with a donor group increases the oxidation potential and thereby increases the relative stability of the higher oxidation states (valences).

Metal-oxy-complexes cause an increase in the oxidation properties [potential] of the oxygen complex compared to the oxygen molecule alone. The change in the redox behavior of the metal ion, and its oxidation state, results from the interaction with oxygen, the type of ligand formed and its field geometry.

Metals will form oxy-complexes that will release superoxide, hydroxyl and nascent oxygen ions. These reactions cause a valence change in the metal, which then catalyses the reaction with superoxide to produce peroxide. Peroxide, in the presence of metal ions, will decompose to hydroxyl radicals. The interconversions of these ions produce nascent oxygen.

$$\mathsf{Me}^{[\mathsf{n}+1]_+} + \mathsf{O}_2^- \longleftrightarrow \mathsf{Me}^{\mathsf{n}+} + \mathsf{H}_2\mathsf{O}_2 \ \longleftrightarrow \mathsf{HO}^{\cdot} + \mathsf{HO}^{-} + \mathsf{Me}^{[\mathsf{n}+1]_+}$$

The stability of the oxy-complexes strongly depends on the pH and the matrixes formed between and with minerals and metals. In the presence of proton donors, they undergo decomposition to yield peroxide. Furthermore, it is generally accepted that peroxide yields hydroxyl radicals as a result of catalytic reactions in the presence of metal ions. By this mechanism, the oxy-complex of the metal would produce hydroxyl radicals on contact with organic material at the point where the metal is bound. This reaction will also place the metal in a higher valency state, which is also a highly oxidizing species.



#### V. WTR: PROPERTIES OF METAL-OXY-COMPLEXES

The formation of metal oxy-complexes results in the loss of "normal" chemical reactions of metal ions in solution. The fact that metal ions do not behave as expected is an indication that these ions are present in very low concentrations. What would normally precipitate a metal ion from a solution, will not work with metal-oxy-complexes because the metal, while in an oxy-complex formation, is "deactivated" from its expected behavior. Metals are normally expected to precipitate as an oxide, but the formation of mineral-metal-oxy-ion, *shelled by water*, keeps the metal in solution, thus de-activating the metal from normal behavior. Under this condition, no precipitation occurs until the concentration of the metal ion rises to a value such that the solubility product of the insoluble salt is exceeded.

Di-positive ions, (Ca, Fe, Mg, Mn) will form monohydroxy complexes and at pH above 9, these oxy-complexes are *continuously converted* to oxy-complexes having two or more hydroxyl groups. They also form interconnected matrices of a transient nature.

Ionized atoms/molecules do not share an electron with water (bonding), but rather conduct ionic interactions with the water shell around them. The formation of metal-oxy-complexes are accompanied by a *decrease* in ionic activity of the metal, and hence, an *increase* in its oxidation potential. In general, coordination with a donor group (oxygen species) increases the oxidation potential, and increases the relative stability of the higher valence state. It is these kinetics that defines the variability of **WTR Oxidizer**.

It is known that an ion has a negative contribution of entropy (randomness) which is due to the restriction of degrees of freedom of water molecules in the vicinity of the ion and that the effect is greater the greater the charge of the ion. When a metal in a simple ionic state is oxidized, the entropy contribution decreases. Conversely, an increase in valence of a metal ion, when it exists in a negative anion (oxy-complex), results in a decrease in the charge of the ion and in a corresponding entropy increase. The increased entropy (randomness of structure) means that the oxidation state of both the metal and oxygen ions are maintained by the resonance of complex and rapidly changing matrixes of these ion complexes.

The *alteration in the rate of reaction*, through formation of metal-oxy-complexes, always result in a *reduction in the rate of what is considered to be the "normal" reactions of these metals* in solution. Metal-oxy-complexes always result in a reduction in the rate of reaction. For example: when iron (a hexacoordinate bivalent ion) combines with oxygen anions (a tetradentate tetravalent anion), a water soluble anion, containing the metal and up to four oxygens (ferrate), is formed. In the presence of Ca, K, Cl, Mg, and or Mn, bridging weak bonds are made between oxy-complexes of these compounds, forming transient matrixes. Although the solution may show no apparent changes accompanying the metal-oxy-complex formation, the reactivity of the metal is first limited to be a catalyst between the oxygen and a reactant (organic compound), and then secondly by its transitional oxidation state(s), when all oxygen molecules are released.

Water, by forming a shell around a metal-oxy-complex, enables the complex to *retain its energy* for extended times (residual ORP). This water shell, because of its hydrogen bonding with organics, becomes a bridge that delivers the metal-oxy-complex to a weak spot on the organic compound. Depending on the properties of the organic reactant, the water shell will either help the metal-oxy-complex regenerate (regain active oxygen species) or decompose (loose all active oxygen molecules).

The metal-oxy-complex has specific and significant reactions not shown by either metal cation or oxygen anion alone. Although the metal-oxy-complex is destroyed in the course of reactions, and all minerals and metals return to their ground state of oxidation, the net effect of the reduction of oxidative state, is said to be catalytic. This catalytic property lowers the activation energy required for the oxidation of many organic materials.

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