

CHEMISTRY AND IMPLEMENTATION OF MINERAL OXYCHLORIDE REAGENT

The mineral oxychloride reagent is a second-generation advanced oxidation formula based on the Fenton-Haber-Weiss chemistry. It is commercialized ready-to-use in liquid form with a long shelf life for applications in water treatment, gas scrubbing, petroleum industry, aquaculture, agriculture, and for general use as a potent ecofriendly oxidizer and disinfectant. Its operation does not require an external energy source and has no risk of flammability or explosion.

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CHEMISTRY

Mineral Oxychlorides represented by the formula $M_xO_yCl_z$ are a family of chemical compounds that contain both oxygen and chlorine molecules bound to transition mineral elements. There is a tight in-plane M-O (mineral/metal-oxygen) chemical bond while weak out-of-plane Van der Waals interactions between adjacent Cl-Cl (chloride ions) layers.

The structures of the mineral oxychlorides in aqueous media, $[(M_xO_yCl_z)(Aq)]$, support their high-efficiency photocatalytic activity for water splitting and generation of highly reactive oxygen species (ROS) that maximize their application as an advanced oxidation process (AOP) and powerful water treatment chemical. The molecules are purposely designed to be weakly bound together such that when it comes in contact with inorganics, microorganisms and organic matter, it readily gives off oxygen atoms that aggressively oxidize all desired contaminants. Unlike the well-known fungicide copper oxychloride $[Cu_4(OH)_6Cl_2]$, whose inhibitory activity is based on copper's antifungal effectiveness, the reactive oxygen species are the active agents in the mineral oxychloride solution when it interacts with water.

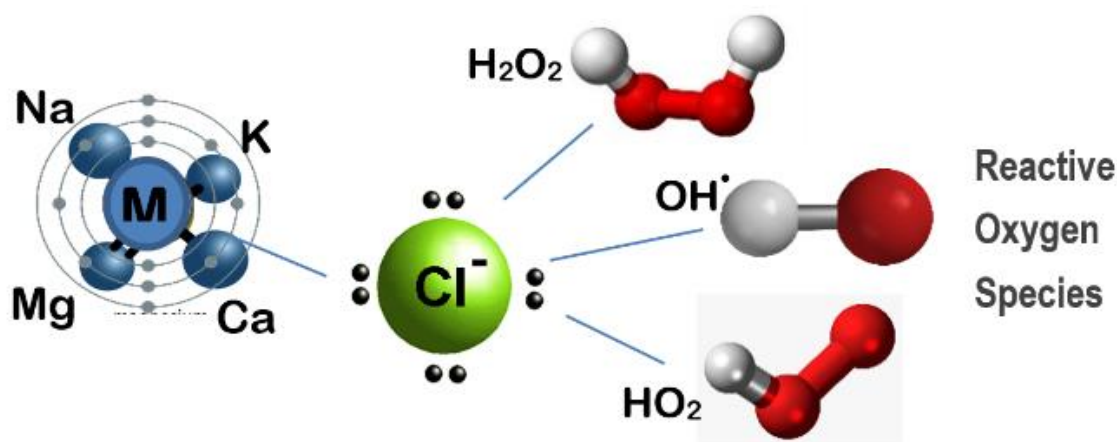


Figure 1: Proposed structures for mineral oxychlorides

The definition and development of AOPs had evolved since the 1990s, when it was proposed that solely the effective generation of hydroxyl radicals defined an advanced oxidation process. Nowadays, AOPs include various methods for generating hydroxyl radical as well as other reactive oxygen species, including superoxide anion radical, hydrogen peroxide, and singlet oxygen. However,

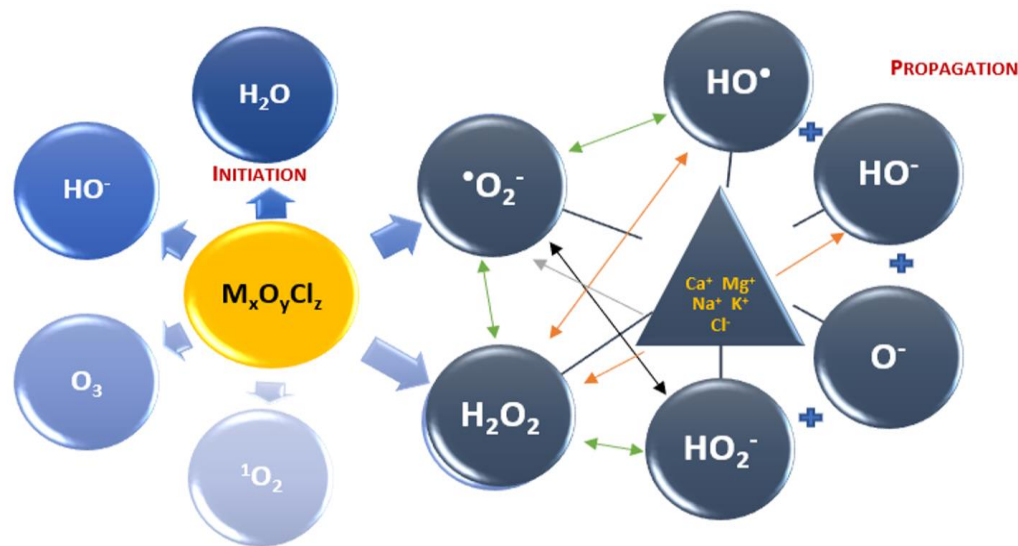
hydroxyl radical is still the species most tied to the effectiveness of AOPs.

The mineral oxychloride solution is a modified Fenton reagent, and predominantly hydroxyl radicals are produced. The Haber-Weiss reaction simplifies the principal conversion pathway:



In addition, to OH^\bullet , it contributes as well with large quantities of hydroxyl and singlet oxygen ions, both very reactive oxidants, and superoxide, hydroperoxide anions, and perhydroxyl radicals, the most reactive reductant trio. The mineral oxychloride solution is catalyzed by the transition minerals' internal vibrational energy, which activates the reactive oxygen species. In this very energy-efficient process, all the generated power is created and used at the atomic level.

Figure 2 below: Chain reaction phases of mineral oxychloride reagent: initiation, propagation, and termination



The mineral oxychloride solution, or mineral oxychloride reagent, is a chemically based, homogenous advanced oxidation technology. It is powerful and fast-acting, with reliable effectiveness against all known microorganisms which cannot survive the level of oxidative stress driven by its ROS. It is a novel sanitizer certified by the National Sanitation Foundation (NSF) and authorized for use in potable and non-potable water systems for disinfection, oxidation, corrosion and scale control, and elimination of biofilm, among others. In 2018 it was approved by the USA Environmental Protection Agency Antimicrobial Division for various water treatment, agricultural, post-harvest applications.

Hydroxyl radical, having the oxidation potential of 2.8 mV, just second to fluorine with 3.1 mV, is considered the maximum reactive oxidant for the

MECHANISM OF ACTION

Advanced oxidation processes involve generating hydroxyl radicals in sufficient quantity to effect significant changes in water contaminants at the molecular level and improve the quality of the water by degrading most compounds to its elemental, harmless form. They have shown tremendous promise in water purification and treatment, including the destruction of naturally occurring toxins, contaminants of emerging concern, pesticides, and other harmful recalcitrant pollutants.

degradation of water contaminants because fluorine is not used in the industry as such.

Hydroxyl radicals endorse the mineral oxychloride reagent electrochemical potential, the highest in the water treatment industry, estimated to be in the range of 2.80 mV to 2.90 mV. The minerals act as catalysts to dynamize the formation of reactive oxygen species through interaction with water. The mineral oxychloride reagent is the advanced oxidation technology that produces the most amount of reactive oxygen species as a whole, brought about with a synergistic effect.

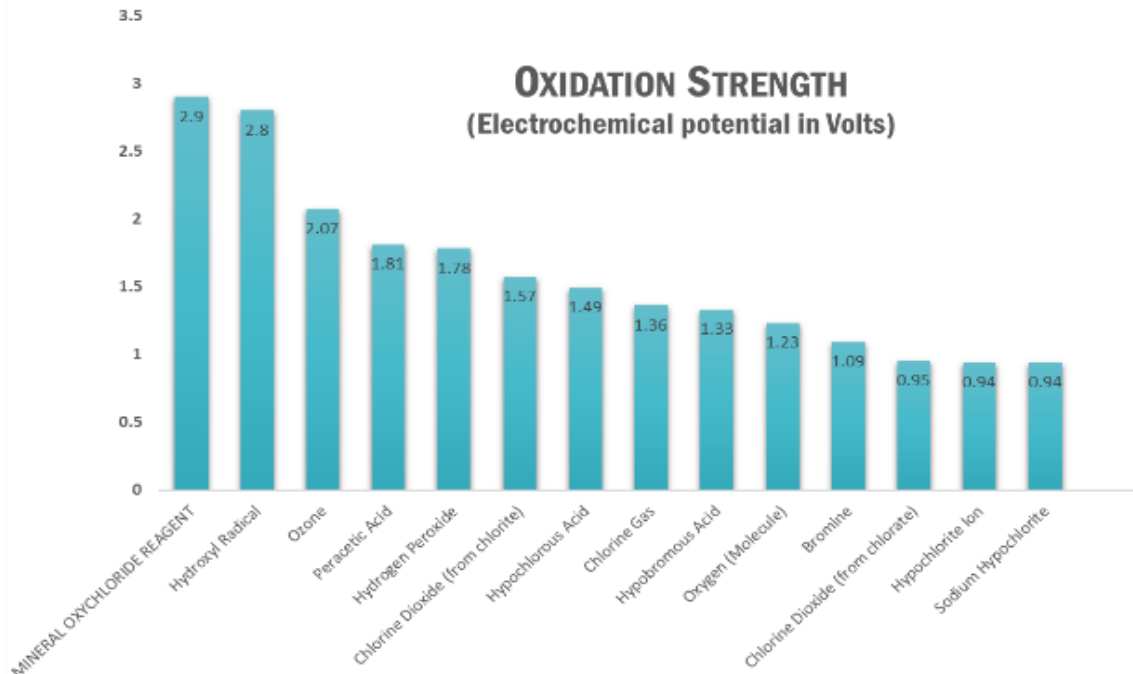
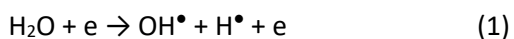


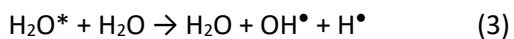
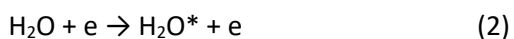
Figure 3: Oxidation potential of various water treatment chemicals

The combination of the resulting ROS assembly will achieve higher levels of oxidation potential than each of the species alone and will depend on the coordination environment of the minerals, the pH, and the biochemical properties of water and the other ions carried with it that encompass the redox equilibrium of the water system. Hydroxyl radicals are generated in larger amounts than the rest and can follow more than one pathway. It is principally the result of dissociation, excitation, and ionization of water molecules with the catalytic effect of the transition minerals. As described in equations (1) to (5), water dissociation generates hydroxyl radicals, excitation reactions also yield OH^\bullet , and the ionization reactions also end up with the generation of OH^\bullet .

Dissociation:

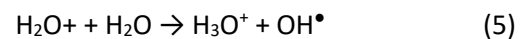
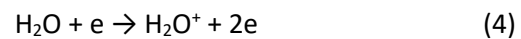


Excitation:



The mineral oxychloride reagent is not linear pathway oxidation. It is a continuous chain reaction autocatalyzed by the inherent catalysts. It will stay active, protecting the water, and its residual oxidative energy will not diminish until new contamination is allowed in the system.

Ionization:



The degradation of organic and inorganic compounds by hydroxyl radicals is robust and extremely fast, making the mineral oxychloride solution a prominent tool for their elimination. The combination of reactive oxygen species can degrade the pollutants in water very efficiently and disintegrate them into non-reactive and nonhazardous substances and non-toxic biodegradable intermediate products, which further undergo mineralization and yield CO_2 and H_2O .

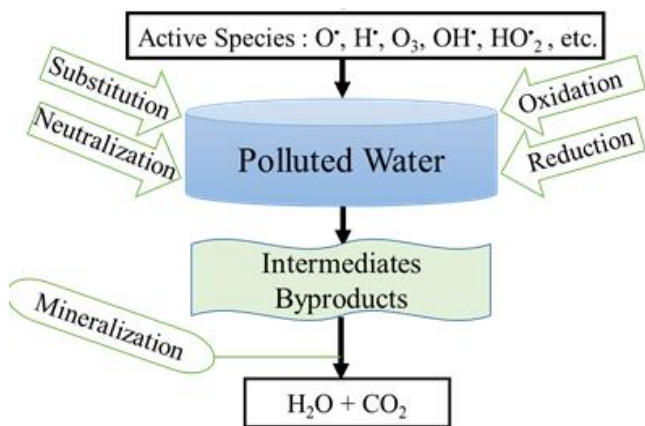


Figure 4:

Degradation of pollutants in water by advanced oxidation

The oxidation reactions with organic pollutants can be categorized in the addition or elimination of hydrogen atoms, electrophilic substitution of the unsaturated bond, and electrons' transfer. They can yield carbon-centered radicals (R^\bullet or $R^\bullet-OH$) that might react with molecular oxygen and be converted to organic peroxy radicals (ROO^\bullet), ultimately producing a host of oxidation products, that is, ketones, aldehydes, and alcohols. Hydroxyl radical can also abstract an electron from electron-rich substrates to form a radical cation, which in aqueous media is readily hydrolyzed, ultimately leading to an oxidized product, more susceptible to bioremediation. When mineral oxychlorides are used, the peroxy radicals undergo subsequent reactions, which can spawn additional reactive species such as H_2O_2 and superoxide ($O_2^{\bullet-}$). Hydrogen peroxide is generated as an intermediate, and it reacts to produce new hydroxyl radicals in second-rate reactions and with the presence of the mineral catalysts.

When the redox level of the water environment treated with mineral oxychloride reagent approaches a state of saturation, meaning that the processes of oxidation and reduction are changing oxidation states of the compounds present in the water without a significant change in the number of newly formed compounds, reactive chlorine species can be generated and provide a measurable chlorine residual. Depending on the pH value, the concentration of hypochlorous acid (HOCl) is related to the concentration of hypochlorite ions (OCl^-): $HOCl + H_2O \rightarrow H_3O^+ + OCl^-$, in the same way that it happens with chlorination water treatment.

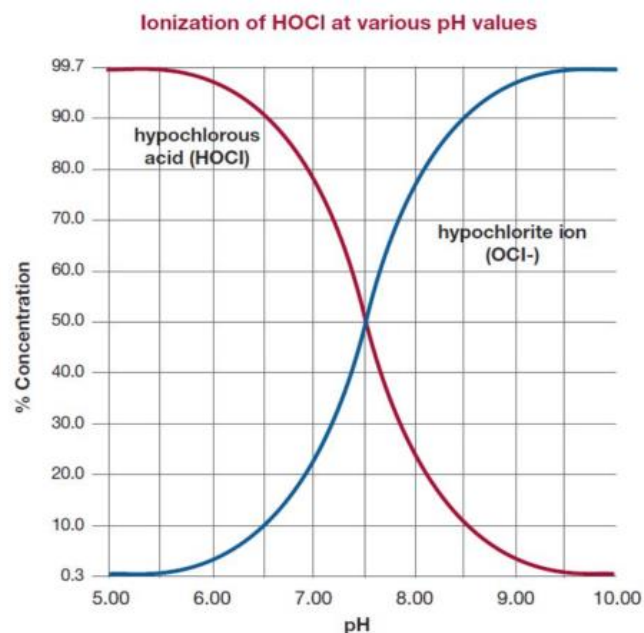


Figure 5:

Ionization of reactive chlorine species at different pH values

When monitoring ORP levels of mineral oxychloride applications, it will be noted that as pH goes down, the ORP will increase. In traditional water chlorination, disinfection efficacy is determined by pH. The maximum level of hypochlorous acid (HOCl) occurs when pH is between 4 to 5.5 pH, and ideal water disinfection will happen when the pH is between 5 and 7, as then an optimal level of hypochlorous acid (HOCl) is present with moderate risk of corrosion. In advanced oxidation applications with mineral oxychlorides, a lower pH will enhance the process; however, the reactive oxygen species with the hydroxyl radicals as the lead agent will always dominate over chlorine species. ROS are so fast-acting that they will satisfy the oxidative and biocidal demand ahead of the reactive chlorine species and realize an increase in the free chlorine residual by the presence of the unused HOCl and OCl^- . Furthermore, hypochlorous acid can provide a new pathway supporting advanced oxidation by augmenting hydroxyl radicals resulting from second-rate reactions.

The biocidal function of hydroxyl radical is characterized by oxidative stress that damages DNA, proteins, lipids and causing cell death by lysis. Numerous scientific studies have demonstrated that it is effective in destroying biofilm and planktonic life with minimal contact time. Biological

membranes are made up of unsaturated fatty acid chains and are easily oxidized. OH^\bullet radicals attack the double bonds of these structures and leave an unpaired electron in the chain that will bind to an oxygen molecule to re-stabilize, giving rise to a

peroxyl radical. This peroxidation of the fatty acids in the membranes decreases their functionality irreversibly since it changes its spatial distribution, causing instability.

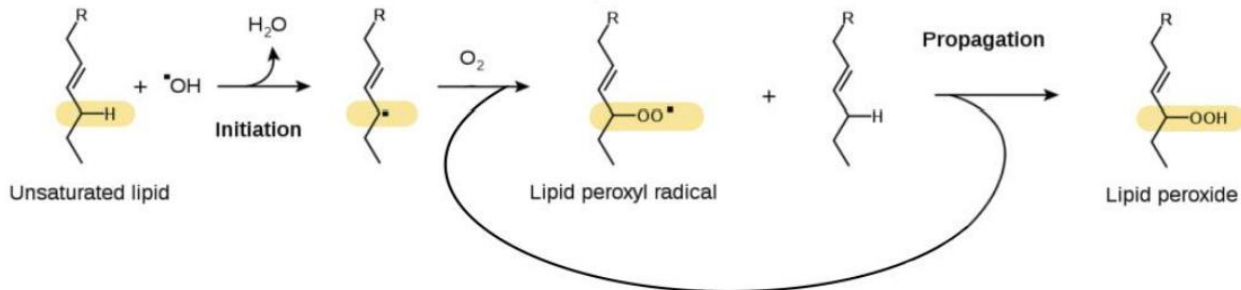


Figure 6: OH^\bullet oxidizes cell membrane unsaturated fatty acids and propagates ROS

The main effects of the cluster of reactive oxygen forms occur as direct oxidation on membranes, lipids, and sulfhydryl bonds of DNA's proteins and nucleotides. Free radicals cause changes in the molecular structure of amino acids by modifying their charge, which can end up breaking the polypeptide chain, and fragmenting the protein. It also occurs as indirect oxidation, producing lipid peroxidation. The resulting peroxides initiate a catalytic chain reaction leading to further loss of unsaturated fatty acids and extensive membrane damage. They also make cross-links between proteins by forming disulfide bonds and mutations in the genetic material of the microorganisms.

IMPLEMENTATION IN WATER TREATMENT

Traditionally, advanced oxidation processes were reserved for treating challenging effluents, like those with high COD levels, and were not a widespread consideration for improving water quality or simple water disinfection applications.

The reason could be one or a combination of the complexity of the implementation, the need for specially trained technicians, on-site energy demand, the volume of water, treatment goals, energy source, high operational cost, and capital investment. However, new emerging treatment challenges and failure to achieve reliable disinfection have motivated water professionals to look for new treatment solutions. The mineral oxychloride reagent has started a new narrative that overcomes all the above considerations and provides the highest level of disinfection and water purification at almost the same cost as traditional chlorination. When chlorine alone is not delivering results, and your treatment protocol needs to compensate by adding more chemicals or incorporating new process steps, there is an excellent chance that advanced oxidation with mineral oxychloride reagent will save you money while improving the quality of the finished water and helping achieve all your treatment goals.

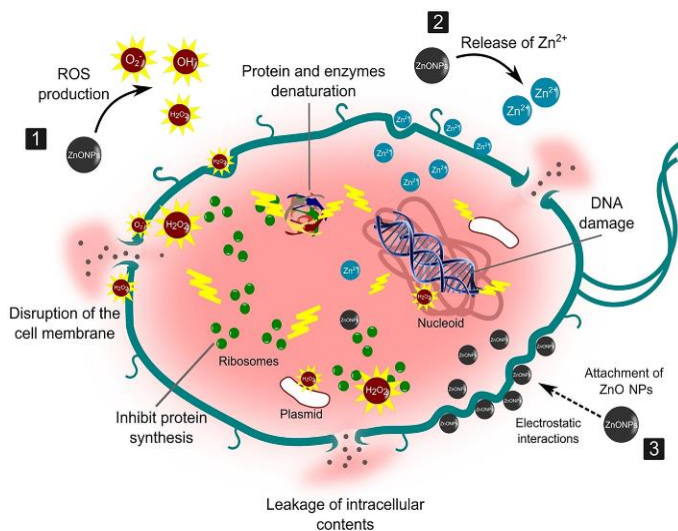


Figure 7: ROS cell destruction

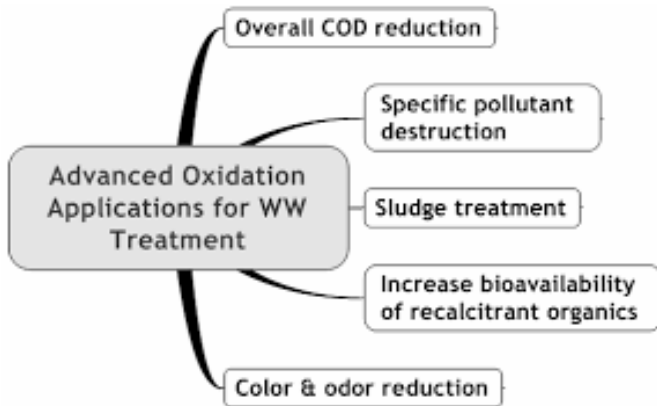


Figure 8:

Typical applications of AOPs for wastewater treatment

As it stands today, the mineral oxychloride reagent is the only advanced oxidation technology that meets all 12 principles of green chemistry as defined by the US Environmental Protection Agency. When applied correctly, it does not create disinfection byproducts and can break down organic byproducts after they are formed.

In a general sense, the mineral oxychloride solution is a tool to increase the oxidative energy of the water environment, and by doing so, it will improve the entirety of the treatment process by enhancement of the effectivity of subsequent chemical and biological treatment, and better biofilm elimination and biofouling control.

It does not produce bromate even when bromide is present in the water in a significant amount.

As a ready-to-use on demand chemical, the mineral oxychloride solution is easy to scale up and down, and can be a quick and inexpensive fix for an aging water treatment facility or an inefficient purification protocol. It can be applied together with most water treatment chemicals. Every treatment process step downstream from its application, like coagulation, flocculation and filtration is expected to improve by increasing efficiency and reducing chemical use and contact time. Even biological processes improve because the degradation of complex molecules will provide the microorganisms easier to absorb micronutrients.

The chemistry of the mineral oxychloride operates seamlessly with chlorinated compounds. It can be used as an adjuvant of existing chlorination protocols and boost the oxidative energy with ORP management to promote the effectivity of the current treatment and avoid violations. It can retrofit ozonation and UV radiation systems to enhance their operation and reduce energy demand. It will increase effectivity of all disinfection chemicals and technologies. All that is required to start using the mineral oxychloride is a liquid dosing system operated with an automatic ORP controller.

IMPLEMENTATION OF THE MINERAL OXYCHLORIDE SOLUTION IN WATER TREATMENT OPERATIONS

Capital investment	Often negligible. Only requires a liquid dosing system with automatic ORP controller.
Complexity of operation	It is very simple to operate with ORP monitoring. Does not need specially trained personnel.
Maintenance	Very low maintenance on equipment and system.
Hazards	It is highly corrosive in its concentrated form. However, it is not flammable and there is no risk of explosion.
Stability	Minimum shelf life of 6 months for maximum performance.
Physical blueprint	Very small. Dosing and monitoring systems can be mounted on a wall.
Storage	Normal storage conditions protected from direct sunlight.

EFFECTIVENESS OF THE MINERAL OXYCHLORIDE SOLUTION IN WATER PURIFICATION

<i>Oxidation of water contaminants</i>	Excellent. It supports advanced oxidation process with 2.8 mV – 2.9 mV electrochemical potential. Reactivity has been found as less than 1 mg/L per mg/L of inorganics; and 1 to 8 mg/L per mg/L of organics.
<i>Taste, color, and odor</i>	Excellent. It starts oxidizing the taste and odor compounds easily at an ORP of +350 mV. Higher ORP is necessary to remove color.
<i>BOD and COD</i>	Excellent. In industrial effluents it has been found in the range of 1 mg/L per 5 to 15 mg/L of COD
<i>Hydrogen sulfide, iron, and manganese</i>	Excellent. It will eliminate hydrogen sulfide at a ratio of 1 mg/L per 2 mg/L H ₂ S.
<i>Disinfection of bacteria, parasites, viruses</i>	Excellent. By oxidative stress and cellular lysis. Very fast acting. Reactivity can be in the range of 1 mg/L per 1,000 to 10,000 mg/L pathogens.
<i>Disinfection of amoeba and protozoa</i>	Excellent. Hydroxyl radicals have been found effective at attacking the membranes and achieving quick inactivation.
<i>Biofilm control</i>	Excellent. Destroys biofilm by oxidizing extracellular polysaccharide matrix structure. It disturbs the chemical integrity of the matrix and interferes with cell signaling.
<i>Solubility in water</i>	100% instant solubility.
<i>Organic DBPs</i>	Very good at reducing precursors. It does not create any DBPs. It can breakdown existing organic DBPs.
<i>Brominated DBPs</i>	It does not react with bromide and does not create bromate.
<i>Chlorinated DBPs</i>	Reactive oxygen species are the active oxidizing agent and therefore its application, even when generating a chlorine residual, will not affect a significant contribution of chlorite or chlorate.
<i>pH sensitivity</i>	Effective at an ample pH of 4 to 9
<i>High temperature</i>	Higher temperature increases reactivity. It will not degrade or gas off from water.
<i>Residual Protection</i>	Excellent. At an ORP of +700 mV and above the system is clean and the residual protection is maintained by the oxidative energy in the water. Measurable residual is provided by free chlorine level.

For additional information, please visit the website www.jenfitch.com or send an email: charles@jenfitch.com