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Whitepaper

Quenching the Growing Thirst for Water:
Understanding how new developments in Advanced Oxidation Processes (AOPs) can improve water and wastewater treatment in EMEA regions

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Introduction:

In recent years, denser urban population concentrations in Europe and increasing water scarcity in the Middle East and North Africa have presented significant challenges to municipal water & wastewater treatment planners in those regions. Regulatory bodies and treatment process designers are looking for better solutions to treat non-conventional water resources, such as industrial wastewater, produced water from oil reservoirs, industrial-polluted water, brackish water, or seawater. Along with improving wastewater reuse, planners are also considering ways to make better use of natural, but marginal, surface and subsurface water sources.

Decision-makers saw an array of technologies when considering how to treat water and wastewater more effectively. Advanced Oxidization Processes (AOPs), especially those using ferrate oxidizing agents, are among the most effective treatment methods available today compared to the expensive conventional AOP systems.

The recent developments in AOP technologies are able to meet EMEA water/wastewater treatment goals and environmental requirements economically.

Advanced Oxidation Chemistry

Where marginal underground and surface freshwater sources are available, many well-established water treatment technologies can be applied. These technologies fall into two functional categories:

1) **separating liquids** from solids;
2) **using filters** to capture solids from liquids.

There are hundreds of separation and filtration technologies available, each with varying levels of effectiveness.

Where seawater resources are available, a common process is to use reverse-osmosis desalination along with various pre-treatment methods to reach final water quality objectives. Again, there are many pre-treatment clarification processes and membranefiltration technologies to choose from. Each has varying capabilities to control scaling, silt density index (SDI), and other factors that affect the efficiency of costly reverse-osmosis desalination processes.

Another tactic is to design processes for reclaiming and reusing wastewater. Again, this involves selecting from a wide range of filtration and industrial wastewater treatment technologies too numerous to discuss here.

Regardless of the various tactics and technologies employed, practically any water and wastewater treatment operation can be optimized--and even superseded--by applying AOPs.

Viewed collectively, AOPs are a set of water/wastewater treatment procedures that use chemicals to generate sufficient hydroxyl radicals (OH-) to remove organic material, organic contaminants, and many inorganic pollutants. Depending on the type of AOP technology selected, specific benefits include:

- **Destroying biofilms** and bacterial and viral pathogens
- **Eliminating organic** compounds, such as pharmaceuticals, hormones, and detergent
- **Removing sulfides** and NH_3
- **Degrading hydrocarbons,** Total Organic Carbons (TOCs), and Volatile Organic Compounds (VOCs)
- **Removing heavy** metals (Lead, Copper, Arsenic, Zinc, Cadmium, etc.) as precipitates

The hydroxyl radicals, OH- is the most reactive oxidizing agent in water treatment, able to reduce the concentration of many different contaminants from several hundred parts per million (ppm) to less than 5 parts per billion (ppb) when properly applied[1].

AOP involves three steps:

1) **formation of** hydroxyl radicals, OH-
2) **initial attack** on target pollutants
3) **subsequent attacks** then form metal salts or minerals to be disposed of as sludge from the reactor vessel allowing the treated water to be used as needed

Because hydroxyl radicals are very effective oxidizing agents, reactions quickly occur *in situ* within the treatment vessel. Formation of by-products is negligible, so impact on the environment is insignificant.

Hydroxyl radicals that drive AOP can be derived from many different chemistries. The mechanism of OH- production depends on the specific AOP technique used. Three techniques predominate. There are advantages and disadvantages to each technique, which include:

1) **Photocatalytic oxidation** using ultraviolet light (UV) with hydrogen peroxide (H_2O_2) or titanium dioxide (TiO2). Advantages include low operating cost and no sludge production, depending on the target pollutants. Disadvantages include usage limitations with only a few contaminants and high capital expenditure (CAPEX).
2) **Ozone-based systems** using either direct O_3 with UV, or O_3 with H_2O_2. Advantages include usage with a broad range of contaminants. Sludge production is non-existent depending on the target pollutants. Disadvantages are stringent handling and safety requirements for O_3, which is very

1 Munter, Rein (2001). "Advanced Oxidation Processes–Current Status and Prospects". Proceedings of the Estonian Academy of Sciences. Chemistry. 50 (2): 59–80.

reactive, and high CAPEX and operating expense (OPEX).

3) **Ferrous-based systems** using Fenton reagent, which is a solution of hydrogen peroxide with positively charged ferrous (iron) ions in the form of Fe^{2+} as a catalyst to produce hydroxide radicals. This is the oldest and most common AOP treatment method. Similar to ozone-based systems, advantages include usage with a broad range of contaminants. Sludge production is non-existent depending on the target pollutants. Disadvantages include stringent handling and safety and high CAPEX and OPEX.

Unfortunately, the cost and logistics of applying common AOP technologies are problematic in many EMEA locales. AOPs require hydroxide radicals and other reagents proportional to the quantity of contaminants. As a result, synthesizing and supplying continuous input of chemical reagents is required to maintain operation, which is not feasible in many EMEA sites.

However, a new development in Reduction-Oxidation (RedOx) chemistry now offers an extremely high redox potential for enhanced AOP. The result is greater efficiency, economy, environmental sustainability, and transportability to provide one AOP solution for water/wastewater-treatment sites in remote and urban EMEA areas.

Even more advantages with ferrate-based AOP—and still one disadvantage

To generate hydroxyl radicals, Negatively charged iron anions in the form of $(FeO_4)^{2-}$, written as Ferrate(VI), are also used. Today, Ferrates plays multiple roles in water/wastewater treatment, commonly used as an oxidant/disinfectant for water and for remediation of wastewater contaminated with metal complexes.

To understand why ferrates are so useful, it helps to understand its chemistry. In most of its compounds, iron (Fe) occurs in two stable oxidation states: positively charged Fe^{2+} ferrous(II) ions and Fe3+ ferric(III) ions. Higher oxidation states also occur.

Negatively charged ferrate(VI) $(FeO_4)^{2-}$ anions with an oxidation state of 4+ are very powerful oxidizing agents. When negatively charged $(FeO_4)^{2-}$ anions attract electrons from other chemical species, oxidization occurs; when the anion gains electrons, reduction occurs.

In general, as in the formation of rust, the movement of electrons in reduction-oxidation (redox) reactions occur slowly, but not with ferrate(VI).

Just as in an electrical circuit, the movement of electrons in redox reactions is measured in volts (V). The ability of an oxidizing agent to gain or donate electrons is known as *redox potential*. The redox potential of non-ferrate chemicals used for AOP range from 1.78 (for H2O2) to 2.08 (ozone). The redox potential of ferrate(VI) is 2.80. That makes ferrate(VI) a far stronger oxidizing agent capable of performing redox operations on many different kinds of contaminants.

Today's new generation of AOP technologies utilizes ferrate(VI) chemistry. Its high redox potential confers significant advantages in different AOP operations.

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Generic Ferrate environmental advantages:

The final end product of ferrate(VI) treatment is ferric hydroxide in the form of Fe(III), a non-toxic, environmentally benign compound. Ferrate(VI) redeploys the power of chlorine for water treatment without producing disinfection by-product DBPs. Chlorination in the presence of organics creates DBPs, such as trihalomethanes (THMs) and haloacetic acids (HAAs).

Furthermore, no ozone by-products are generated. Therefore, the possibility of ozone reacting with naturally occurring bromine to form bromates, also a carcinogen, is not a problem with ferrate(VI) AOP.

The generated sludge from a Ferrate-based oxidation process is also environmentally friendly and can be disposed as non-hazardous material.

Generic ferrate logistical disadvantage:

The ferrate(VI) anion is inherently unstable and is only available in solid form as an alkali salt (e.g., Li_2FeO_4, Na_2FeO_4, K_2FeO_4, etc.). Nevertheless, ferrate products cannot be easily synthesized, stored, and transported. These characteristics have prevented large chemical suppliers from producing commercial amounts of ferrate as a product. Previous attempts to commercialize this valuable commodity were unsuccessful due to the cost (over $100.00 USD per pound of $[FeO_4]^{2-}$) of producing a high-purity ferrate product and continuously delivering it to the treatment site.

Realizing the full advantages of ferrate AOP with FeOxy

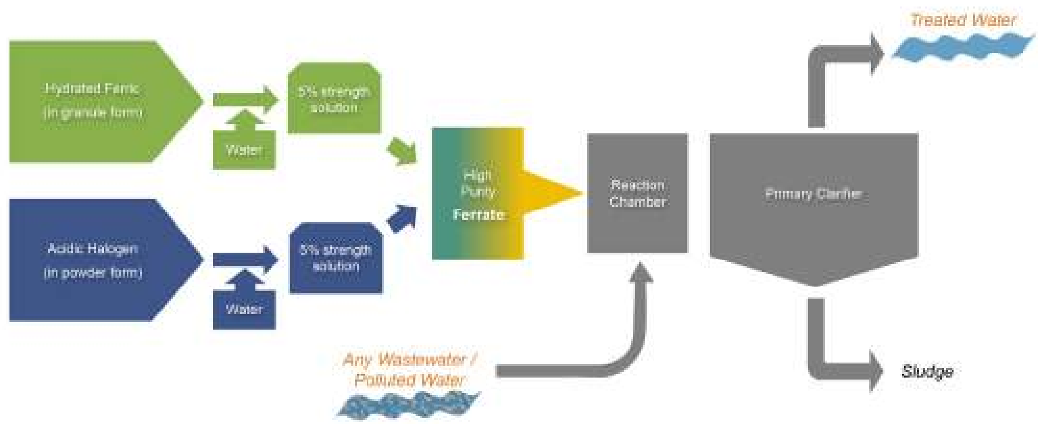
Until recently, ferrate-based AOP has been problematic for remote locations, such as Middle East oil fields, for cost-sensitive facilities in developing nations, and for centralized urban water and wastewater treatment plants with regulatory and space constraints.

After many years of research and experimentation in pilot studies, CECO Peerless is now able to offer a safe ferrate(VI) compound for AOP that overcomes these logistical and economic obstacles. The ferrate(VI) process branded as “FeOxy” is a proprietary blend of ferrate(VI) now available as an inexpensive, safe, commercially available feedstock. When reacted under proprietary conditions, FeOxy production results in an economical, concentrated ferrate(VI) solution that is stable for weeks.

FeOxy economic advantages:

FeOxy is produced through a cost-effective, modular, and scalable proprietary process (Figure 1). FeOxy production is accomplished using proprietary technology on-site employing inexpensive substrates. And FeOxy is also available in a high-purity dry powder that is stable, easy to handle, and ready for application. The versatility of FeOxy product allows ferrate(VI) to be continuously generated near its point of use. As such, FeOxy can be made readily available for use in remote locations, such as Middle East oil fields, or in a centralized urban water/ wastewater treatment plant.

Figure 1: Modularity of the FeOxy production process



FeOxy logistical advantages:

CECO Peerless's technology partner designs, fabricates, tests, installs, and maintains all components for site-specific designed FeOxy–based AOP systems.

FeOxy production systems can be scaled to any size application. The modular design of the system allows easy transport to any location. FeOxy systems can be stand-alone, or interface with existing facilities.

FeOxy systems can interface into any existing water, wastewater, or industrial waste treatment system. To meet project requirements, FeOxy AOP treatment systems can be purchased outright (standard design) or as a bespoke unit.

As a complete solution, FeOxy AOP can completely replace biological technologies, especially where COD and BOD5 levels are considered high to be treated as biological matter or in the case where COD is classified as non-degradable matter.

FeOxy AOP can also be integrated with conventional treatment technologies, such as:

- Pretreatment for desalination / reverse osmosis
- Tertiary treatment for produced water treatment system

The total treatment system design includes proprietary FeOxy synthesis, feed systems, flash mixing, flocculation, and clarification systems as required.

Facilities for storage and handling of feedstock chemicals (hydrated ferric compound, acidic halogen agent, flocculant-adsorbent agent) can also be designed and fabricated if the feedstocks are not already present at the site.

All FeOxy systems and design options are fully process controlled and can be remotely controlled from central locations.

Integrating FeOxy AOP into an existing traditional water treatment system can simplify compliance with changes in environmental regulations without involving a completely new system design. By efficiently oxidizing practically any water contaminate at a diffusion-controlled reaction speed, FeOxy AOP can complement and, in some cases, replacing conventional water/ wastewater treatment equipment.

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FeOxy environmental advantages:

FeOxy substrates (the "ingredients") are the safest and most stable of any ferrate formulation. Competitive AOP processes use bleach (hazardous and mostly banned disinfectant/oxidant in O&G facilities), caustic soda (which requires utmost care in handling), or ferric chloride (unstable and colorises the treated water if not fully reacted). After undergoing FeOxy AOP, wastewater can be reintroduced into sewage treatment, reinjected into an Enhanced Oil Recovery (EOR) reservoir, or discharged into an open body of water (e.g., streams, lakes, seawater).

FeOxy AOP Applications:

The multimodal action of Ferrate(VI) makes it possible to accomplish multiple treatments within the FeOxy Process, which also utilizes ferric(III) and ferrous(II) chemistry in a single reactor. In a single treatment, FeOxy AOP can simultaneously oxidize, coagulate, and disinfect (Figure 2). It can replace the use of coagulants such as ferric chloride, alum, and polymers for the removal of metals, non-metals, and humic acids. It outperforms other disinfectants, such as UV, hydrogen peroxide, and chlorine. It can also kill many chlorine-resistant organisms such as aerobic spore-formers and sulphite-reducing clostridia.

Figure 2: Multimodal action of FeOxy performs more treatment function than other AOP oxidizing agents.

Technology	Bacteria	Biofilm	Minerals	Scale
Chlorine AOP	X			
Chlorine Gas AOP	X	X		
Chlorine Dioxide AOP	X	X		
Hydrogen Peroxide AOP	X	X	X	
Polyphosphate AOP			X	X
Filtration System			X	X
Ozone AOP	X	X		X
UV AOP	X			
RO AOP			X	X
FeOxy	X	X	X	X

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FeOxy AOP Applications:

Municipal Wastewater Treatment

- Sulfide removal
- Ammonia reduction
- Degradable & non-degradable chemical oxygen demand (COD) removal
- Biological oxygen demand (BOD5) removal
- Heavy metals removal

Industrial Wastewater Treatment

- Sulfide removal
- Ammonia reduction
- Degradable & non-degradable chemical oxygen demand (COD) removal
- Biological oxygen demand (BOD5) removal
- Heavy metals removal

Municipal Drinking Water Treatment

- TOC removal
- THM reduction
- Algae control

Produced Water (Oil Field) Treatment

- Biocide for sulfur-reducing bacteria
- TDS reduction
- Sulfides removal
- Chemical oxygen demand (COD) reduction

Expert resources to meet AOP water and wastewater treatment challenges in EMEA regions

Many different technologies can be applied for water and wastewater filtration and separation and for AOP. Although factors will differ depending on the water source, target pollutants, and contaminants, CECO Peerless engineers and partners can facilitate AOP operation by implementing FeOxy production on site. For a total solution, a FeOxy AOP solution can be designed as a stand-alone system or interfaced with an existing treatment facility. With the full suite of CECO Peerless technologies, operators can be assured of meeting critical water and wastewater treatment requirements and environmental regulations in EMEA regions—backed by a performance guarantee that ensures success.

CECO Peerless broad field experience can have approximate predictions of most treatment performances without any necessary field tests. But when a complex water is involved, CECO Peerless usually recommends to perform bench-scale or Pilot-scale testing enables to verify the best feasibility of the proposed advanced oxidation process.

There are available pilot units for rental or purchase.

CECO Peerless can also build bespoke pilot units to solve problems occurring in existing facilities of our customers.

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