

Electrochemical Generation

The applications and scientific mechanisms of disinfectants generated on-site using salt, water and electricity

By Andrew Boal, Ph.D.

When you are researching a product, how frustrating is it to conduct your due diligence only to find answers segmented across dozens of sources? I've been there before.

That is why I wrote this digestible, technical overview of electrochemical generation, also known as on-site generation (OSG), to outline the applications and scientific mechanisms of this revolutionary technology in order to make your life easier and help you do your job better.

Many water treatment professionals are moving to OSG to produce disinfection chemistry on-demand, leaving traditional oxidizing and non-oxidizing biocides behind.

The benefits speak for themselves:

- Increased safety
- Elimination of storage and transportation of hazardous chemicals
- High quality disinfection
- Greener operations
- Substantial savings

What is on-site generation?

You may be familiar with the fundamental principles which make this technology possible, namely the electrolysis of salt water solutions, which have been known for decades. OSG uses a solution of sodium chloride (salt) and fresh water as feedstock. When electricity is applied to the feedstock, a disinfecting oxidant solution is produced.

Electrochemical generation has a number of applications for disinfection and can be a cost-effective way to replace chlorine gas, bulk sodium

hypochlorite, calcium hypochlorite, chlorine dioxide, bromine, glutaraldehyde and other traditional biocides.

Disinfection Applications of OSG Technology:

- Cooling Tower Water Treatment
- Process Water Treatment
- Drinking Water Treatment
- Wastewater Treatment
- ECA Clean-In-Place (CIP)
- Produced Water
- Hydrogen Sulfide Removal
- Aquatics and Decorative Water Features
- Surface Disinfection
- Dairy, Poultry & Swine Sanitation (drinking water, pre- and post-dip, facility)
- Irrigation Line Cleaning

How does on-site generation work?

Water coming into the OSG goes through a softener, and then splits into two lines. One line is used to feed a salt filled tank, creating a saturated brine. The other line enters the OSG, acting as a dilution stream prior to the electrochemical process. Saturated brine is then precision mixed with the softened water stream prior to entering the electrolytic cell. Application of an electrical current to the cell results in the production of an oxidant solution from the diluted brine.

After leaving the electrolytic cell, the oxidant solution is temporarily stored in an oxidant tank. As needed, the oxidant is then metered or injected into the water moving through the treatment process, typically with equipment similar to that used in a

bulk hypochlorite dosing system. Injection options include a venturi or other eductor, centrifugal feed pumps, or chemical metering pumps. Sites with multiple injection points may use a combination of these options.

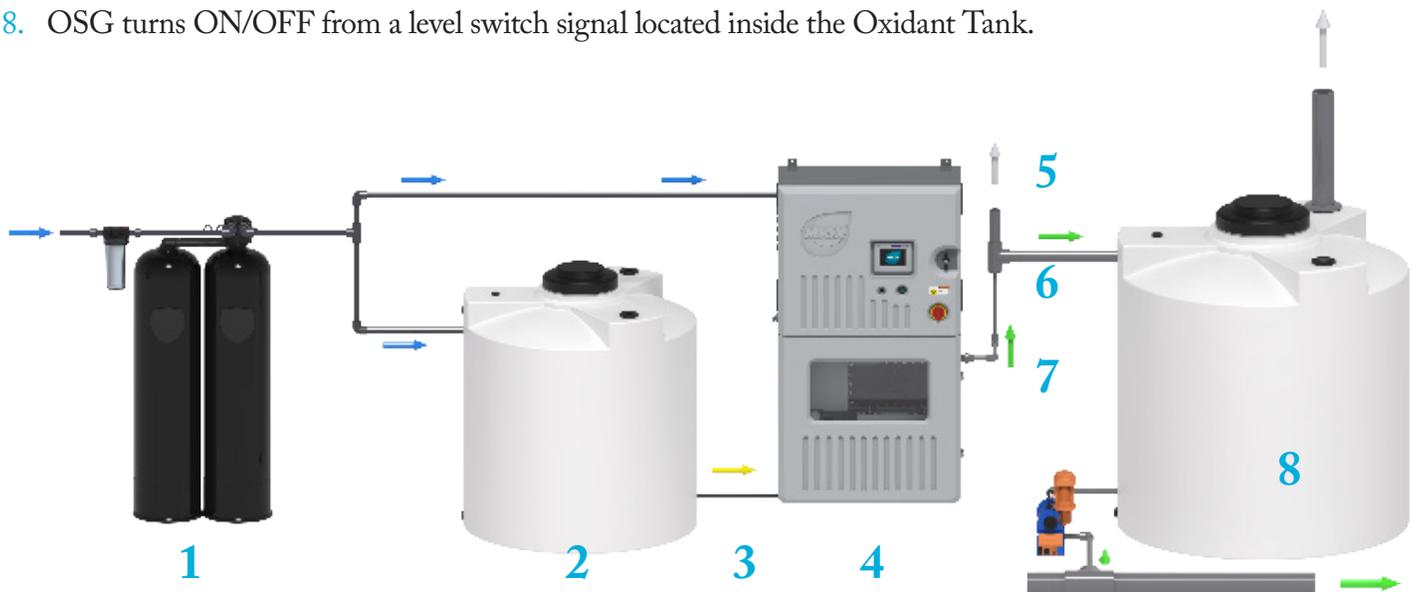
Hydrogen gas is also produced inside the electrolytic cell and is removed from the cell and the oxidant storage tank through vents and/or dilution air blowers.

The OSG operates via a signal from the level switch/transmitter located in the downstream oxidant tank. When the tank is empty, the level switch/transmitter sends a signal to the Programmable Logic Controller (PLC) and puts the OSG online. As soon as the tank is full of oxidant, the transmitter/switch sends a signal to the PLC to put the OSG in standby mode. This means very minimal operator attention is required during normal operation.

Engineering Note: A single on-site generator can be used for multiple applications at a site. This allows operators to take advantage of economies of scale provided by OSG systems that decrease per-volume disinfectant costs.

On-site generation process flow

1. Softened water to Electrolytic Cell & Brine Tank.
2. Salt and Water mix in the Brine Tank to form Saturated Brine.
3. Saturated Brine mixes with softened water and the diluted brine enters the Electrolytic Cell.
4. Electrical Current is passed through the Electrolytic Cell producing Oxidant.
5. Hydrogen Gas produced during the Electrolysis Process is vented outside.
6. Oxidant Solution leaves the Electrolytic Cell and is stored in the Oxidant Tank.
7. Oxidant Solution is dosed into the Treatment Process by a metering pump.
8. OSG turns ON/OFF from a level switch signal located inside the Oxidant Tank.



Eliminating Hazardous Chemicals

On-site generation replaces numerous delivered chemicals for water treatment, including:

Oxidizing Biocides

- Bulk Sodium Hypochlorite
- Chlorine Dioxide
- Chlorine Gas
- Iodine
- Hydrogen Peroxide
- Calcium Hypochlorite
- Ozone
- Bromine

Non-Oxidizing Biocides

(and other disinfection approaches – depending on the application and/or water chemistry)

- Glutaraldehyde
- Quaternary Ammonium Compounds
- Isothiazoline
- Silver Copper Ion
- Ultraviolet Light

The Science

The electrolytic cell, where the oxidants are produced, is central to the OSG process. Electrolytic cells built by MIOX consist of two primary electrodes, the anode and cathode, along with a number of intermediate electrodes. MIOX electrolytic cells are designed to have proprietary electrode geometries, electrolytic scheme, and solution flow characteristics in order to optimize disinfection chemistry and oxidant production efficiency.

The cells are arranged so all electrodes make contact with the water and brine solution, and when the OSG is activated, an electrical current flows through the cell. In turn, this current causes chemical reactions on the surfaces of both electrodes that eventually produce the oxidant solution.

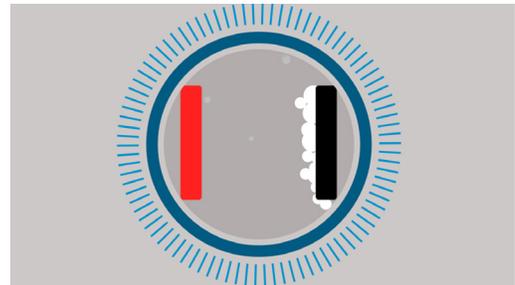
As the cell operates, calcium and magnesium scales will build up on the cell electrodes, reducing the efficiency of the OSG system. Traditionally, a manual acid washing procedure is employed to

remove these scales.

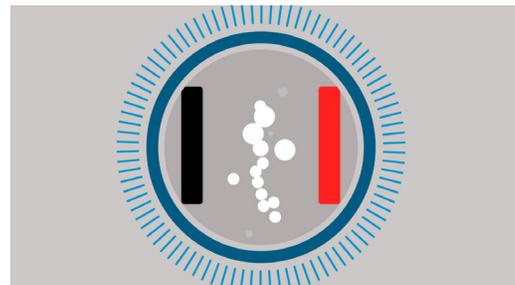
MIOX has developed a proprietary reverse polarity mechanism which can safely clean electrode surfaces. Instead of using an external acid, the direction the current passes through the cell is reversed, so positive becomes negative and negative becomes positive. When this occurs, scales are dissolved from the surface of the electrodes and removed from the OSG. This automatic process dramatically reduces the need for external acid washing.

Acid washing via reverse polarity

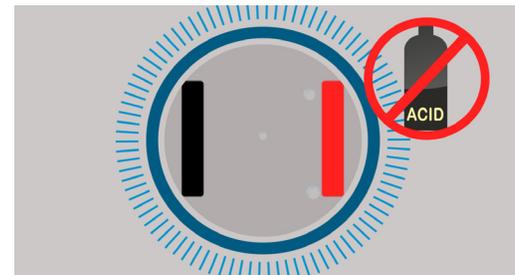
1. As the cell is run, impurities from water and salt build on electrodes.



2. The cell is cleaned by undergoing a proprietary polarity reversal sequence. Scale is removed from electrode surfaces.



3. The cell returns to normal run mode.



Electrochemical Generation of Sodium Hypochlorite

The overall chemical equation for reaction of salt (NaCl) and water (H₂O) to form sodium hypochlorite (NaOCl) is:



Oxidation reactions are carried out at the anode where two chloride ions (Cl⁻) are stripped of one electron each to produce molecular chlorine:



Depending on the physical and working parameters of the cell (e.g., electrode to electrode spacing, cell applied potential, etc.), it is also possible to produce oxidants other than chlorine, which can provide enhanced removal of microbiological contaminants from water and other benefits. After it is produced, the molecular chlorine dissolves in water to produce hypochlorous acid (HOCl) in the same way that bulk chlorine gas from cylinders acts:



Chlorine production is balanced by the reduction reactions that occur at the cathode where water (H₂O) is converted into hydroxide ions (OH⁻) and hydrogen gas (H₂):



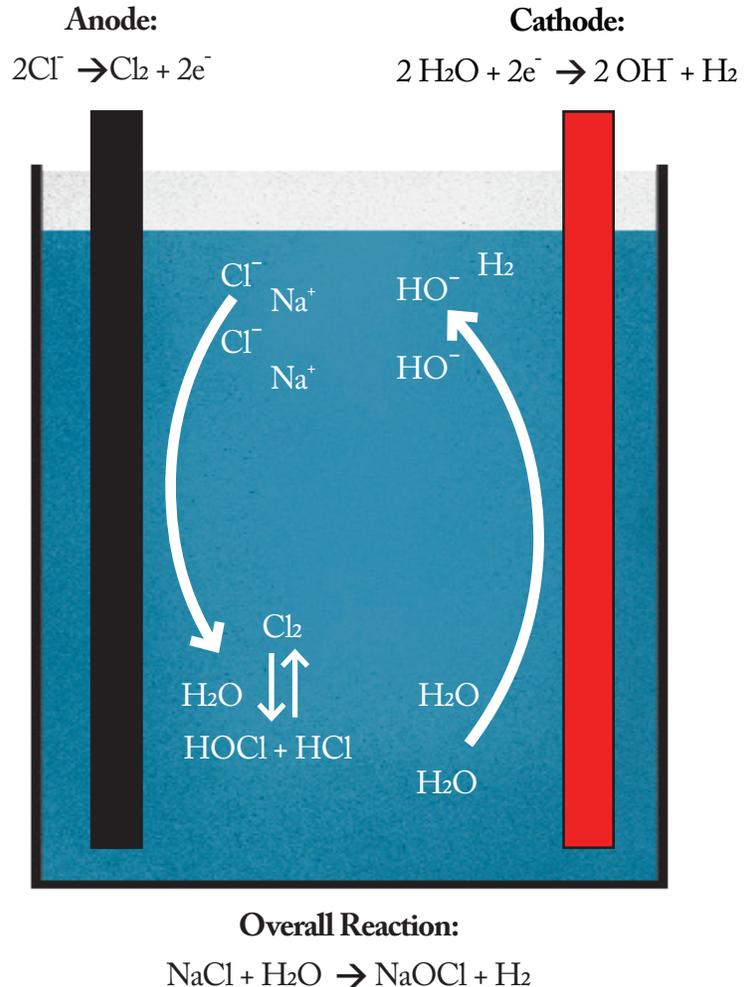
During electrolysis, hydrogen gas is produced as bubbles and must later be removed from the produced oxidant solution to prevent buildup of the gas. The hydroxide ions produced at the cathode then react with the hypochlorous acid produced at the anode, producing the hypochlorite anion (ClO⁻), which is charge balanced with sodium cations (Na⁺) that originally came from the salt:



Typically, the pH of oxidant solutions produced by OSGs are in the range of 9 - 10. Dosing water with OSG produced oxidant solutions often does not alter the pH of the water being treated since the

produced oxidant solution is used at a volume ratio of at most 1:1000 with the water to be treated under most application scenarios.

This diagram shows the different electrochemical reactions that take place inside of an OSG electrolytic cell:



Electrochemical Generation of Mixed Oxidant Solution (MOS)

MOS is a disinfectant that is produced through the electrochemical process. OSG equipment producing MOS is optimized for the highest levels of bacteria inactivation efficacy through proprietary cell design, control of power, and cell geometry.

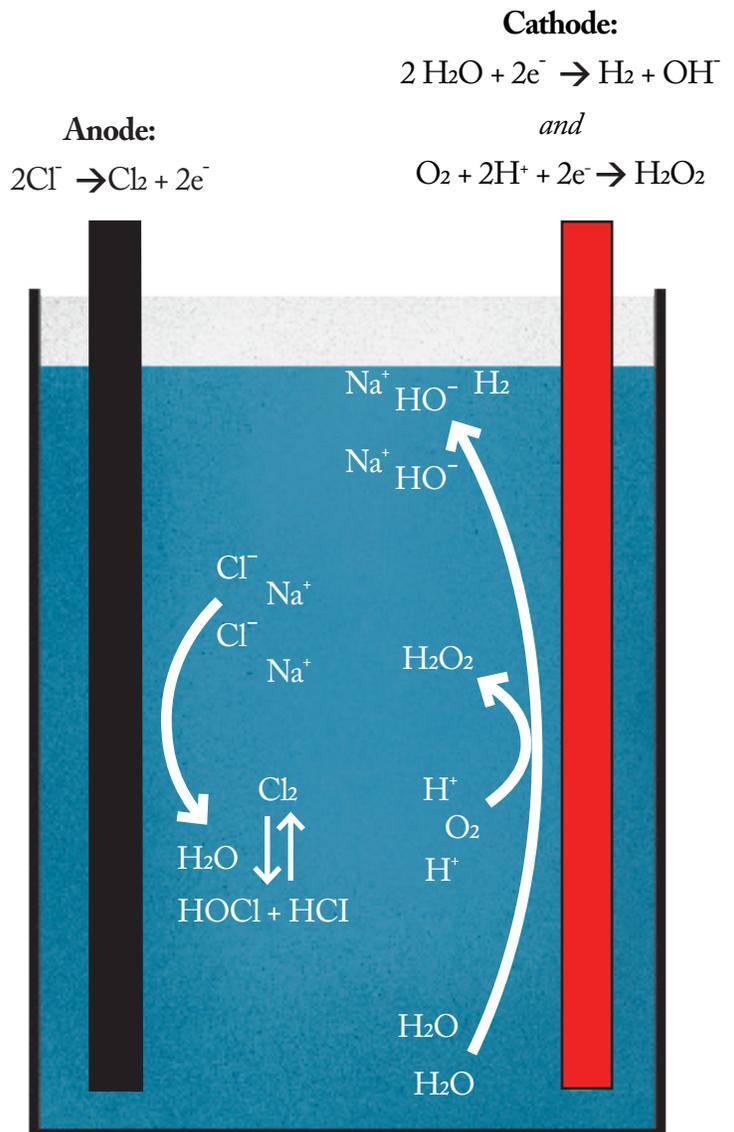
MOS is highly effective at controlling microbial populations, biofouling, and biofilm formation in water treatment applications across multiple applications and industries.

Numerous laboratory studies and customer experiences prove that MOS is a much more effective biocide than chlorine alone, a property that is a result of the synergistic antimicrobial action of the multiple oxidants contained within MOS – predominantly sodium hypochlorite with trace hydrogen peroxide.

Benefits of MOS

- Faster and more thorough microbiological inactivation (2-3 times more effective than chlorine at same FAC dose and application pH)
- Superior biofilm removal
- Elimination of Legionella counts
- Enhanced microflocculation reducing coagulant demand by up to 40%
- Effective iron and manganese oxidation, enabling removal by flocculation and filtration
- Lower required dose
- Longer residual carry in distribution systems with longer detention time
- Reduction in disinfection byproduct (DBP) formation
- Elimination of chloramine boosters
- Improves filter runs
- Lowers final turbidity
- Eliminate taste and odor problems
- Rapidly oxidizes hydrogen sulfide

This diagram shows the different electrochemical reactions that take place inside of an OSG electrolytic cell producing MOS:



Did you know? As a point of company history, MIOX actually derives its name from Mixed Oxidant Solution: **MI**-xd **OX**-idant, a chemistry originally discovered while the technology was first being developed in the early 1990s.

What are the Benefits of Using On-Site Generated Disinfectants?

There are five principal benefits associated with OSGs:

1. Improved operator safety
2. Higher quality chemicals
3. Lower disinfection byproduct formation
4. Greener applications
5. Cost savings

Improved Operator Safety

Chemicals traditionally used in water disinfection pose a variety of hazards to the operator. Chlorine gas and chlorine dioxide are probably the most hazardous disinfectants used for water treatment. Chlorine gas is toxic upon uncontrolled release and the use of chlorine gas cylinders also pose a pressure hazard for explosion or fire. Chlorine dioxide utilizes precursors – acid combined on site with chlorite or chlorate – both of which are health hazards. Chlorine dioxide production processes utilizing chlorite carry additional workplace hazards since the chlorite solutions, if spilled and allowed to dry, become a serious fire hazard. Even industrial strength sodium hypochlorite used for water disinfection is typically 12.5 percent-by-weight chlorine solution at elevated pH, and is highly caustic, requiring proper personal protective equipment (PPE) when being handled by operators. Alternatively, OSG systems use only water and salt and produce nonhazardous oxidant solutions with a chlorine content that typically contains less than 0.8 percent free available chlorine at moderate pH. Treatment plants that use OSG systems typically face less federal and state regulatory oversight, require less safety training for operators, and have less of an insurance issue compared to those using traditional forms of chlorine.

Higher Quality Chemicals

Factors such as time in storage, storage temperature, and exposure to sunlight can accelerate hypochlorite

loss through these chemical degradation pathways. As a result of this degradation, aged hypochlorite solutions will contain less and less free available chlorine (FAC) and more degradation products, effectively increasing the per-pound cost of chlorine available for treatment applications.

Storage issues mount in areas that are required to have 30-day or higher supplies of disinfectant chemicals on hand, especially when bulk hypochlorite is stored without significant environmental control in warm climate areas.

OSG systems, on the other hand, produce hypochlorite solutions that contain less than 1% available chlorine, and hypochlorite degradation at these concentrations is extremely low. Coupled with the built-in engineering controls that limit chlorine production to a one- to three-day supply results in a more cost effective production of chlorine.

Lower Disinfection Byproduct Formation

Recent research has indicated that hypochlorite storage leads to chlorate (ClO_3^-), and perchlorate (ClO_4^-) production from hypochlorite anions. Chlorate has been identified as a potential health hazard and was included on the third contaminant candidate list (CCL3) developed by the US EPA, indicating that there is a likelihood that the EPA will issue a regulatory limit of this chemical in drinking water in the future. Currently, there is a health reference level of chlorate at 210 ppb, and 37% of water samples from utilities using bulk hypochlorite as a disinfectant were found to have chlorate concentrations higher than this level. Additionally, 52% of water samples from treatment plants using chlorine dioxide were found to have chlorate concentrations above 210 ppb. Due to these findings and in anticipation of an eventual EPA regulatory limit being established for chlorate, many operators are looking for ways to reduce the introduction of chlorate into their finished water.

One way to achieve this goal is to use hypochlorite produced by OSG systems. While some chlorate is produced as an undesired side reaction in the electrolysis process, hypochlorite solutions produced by OSGs are far less concentrated than bulk hypochlorite and therefore degrade much slower.

Hypochlorite Degradation & Chlorate Production after 28 Days

(Based on Concentrations and Temperature)

Commercial Hypochlorite Initial Free Available Chlorine (FAC)	Storage Temperature	Measured FAC after 28 days	Decomposition after 28 days	Measured ClO_3^- after 28 days (g/L)
15%	55°F (13°C)	13.3%	11.6%	3.0 g/L
10%		9.0%	9.9%	1.2 g/L
5%		5.4%	---	0.5 g/L
15%	80°F (27°C)	10.8%	28%	12.7 g/L
10%		8.4%	16.5%	4.6 g/L
5%		5.0%	---	1.1 g/L

Source: Gordon, G. et al., "Predicting Liquid Bleach Decomposition" Vol. 84, Issue 4, pp.142-149, 1997.

OSG is especially beneficial for utilities that are required to have long term supplies of disinfectant on location. Bulk hypochlorite stored for extended periods of time, especially in warmer climates, can result in substantial chlorate production. In contrast, it is possible to store a long term supply of the sodium chloride feed stocks for OSG systems to meet the same requirement, and sodium chloride will not degrade upon standing.

Greener Applications

OSGs are more environmentally friendly compared to delivered chemicals. In addition to the elimination of the use and potential accidental release of extremely toxic chlorine gas, precursor explosion, accidental inhalation or chemical burn, transportation of chemicals from factories to the point of application is reduced. This is due to the fact that delivered disinfectant solutions are mostly water, therefore, delivery costs associated with aqueous biocides mostly arise from paying for the delivery of water to the application point. Decreased deliveries reduce delivery cost and logistics expenses, and also lower the carbon footprint of the treatment facility because less fossil fuel is needed to supply the disinfectant.

Reduction in Trucking

The volumetric space requirements for concentrated hypochlorite are substantially more than the salt required to generate an equivalent amount of dilute hypochlorite on site. A truckload of palletized salt consists of 18 pallets for a total of 22 tons of salt. If salt is purchased in bulk and blown pneumatically

into a brine silo, the truckload quantity increases to 24 tons of salt. At a typical OSG salt conversion efficiency of 3.5 pounds of salt per pound of equivalent chlorine, a truckload of salt would generate between 12,600 and 13,700 pounds of chlorine equivalent. In contrast, a typical truckload of concentrated hypochlorite is only 4,000 gallons, which means that it would take more than three deliveries of bleach to equal the chlorine equivalent produced by one truckload of salt.

In addition, a typical 12.5% hypochlorite solution weighs around 10.2 pounds per pound of equivalent chlorine. This means that for the same unit of disinfection, delivered hypochlorite weighs about three times more than the salt required for OSG and it carries a hazardous classification, which also garners a higher transportation cost.

Cost Advantage

The cost of bulk chemicals depends on market prices, while the cost of operating an OSG system is tied to the cost of salt and power. In general, the lifecycle cost of OSG is very competitive with chlorine gas alternatives, and is typically substantially less than delivered hypochlorite.

OSGs typically produce chlorine at a much lower cost than traditional delivery methods, primarily because there is no need to continuously purchase expensive chemicals. This is especially the case for systems using calcium hypochlorite, chlorine dioxide and other biocides used for industrial applications. Additional savings come from decreased transportation and safety-related costs,

decreased logistics effort on the part of the user, and lower insurance premiums. Although OSG systems usually present an up-front capital equipment cost, for most applications conversion to OSG results in a return on investment in OSG equipment within one to two years; or a matter of months when replacing expensive biocides like chlorine dioxide or stabilized bromine. Additionally, immediate chemical cost savings can be realized via equipment rental or lease options.

Typical operation costs for various disinfectants on a per pound basis (or equivalent to one gallon of 12.5% hypochlorite):

Operational Cost \$/lb Free Available Chlorine (FAC)	
On-Site Generated Sodium Hypochlorite	\$0.49 - \$0.56
On-Site Generated Mixed Oxidant Solution	\$0.57 - \$0.79
Chlorine Gas	\$0.50 - \$0.60
12.5% Sodium Hypochlorite (bulk delivered)	\$1.00 - \$1.60
Chlorine Dioxide	\$2.50 - \$4.00
Stabilized Bromine	\$2.00 - \$7.00

In all prospective scenarios, a thorough cost evaluation will explore operating, maintenance and capital costs to achieve a realistic lifecycle cost analysis. Possible effects on other plant processes should also be considered.

Note that inclusion of delivery costs would reflect an even more marked contrast between salt and delivered hypochlorite. Mileage, impacted by volumetric space, is the largest factor in transportation costs. Weight and chemical classification also play a role.

Operational Considerations of Using Electrochemical Generation

There are a few operational topics to consider when evaluating OSGs for a facility:

1. Hydrogen safety
2. Electrical safety
3. Water quality, temperature and pressure
4. Salt quality
5. Electrolytic cell maintenance

Hydrogen Safety

All electrochemical systems that employ aqueous solutions—disinfectant OSGs included—produce hydrogen at the cathode as a byproduct of the electrolysis process. Hydrogen is more than 13 times lighter than air, so it will rapidly dissipate from an electrolytic cell or OSG system. Because OSGs are typically installed inside a building, the system and tanks need to be properly ventilated. Hydrogen safety concerns are mitigated by careful engineering of the OSG itself, as well as good planning when the OSG is installed. When considering an OSG system for water treatment, it is important to ensure that the system meets standards set by groups such as Hydrogen Safety, LLC.

Electrical Safety

Basic electrical safety must be adhered to when working with on-site generators. This is true of all electrical equipment.

OSG voltage varies depending upon the system size and equipment manufacturer. MIOX on-site generators are designed to minimize electrical hazards. For example, MIOX's small OSG systems are far below voltages normally associated with dangerous conditions. This means that operators can work on the system, touch the electrolytic cell, and perform basic maintenance without risk of lethal shock. Larger systems have higher voltages requiring special precautions, but they are typically designed with an electrical interlock that shuts down the cell when the cell enclosure is opened. On all MIOX systems, high voltage components are isolated and rarely require maintenance.

Water Quality, Temperature, and Pressure

Water is the largest component of the salt solution that enters the electrolytic cell of an OSG and, thus, the composition of that water is important to ensure the reliable operation of an OSG system. Potable water supplies can feed most OSG electrolytic cells, but it is very important that the water be softened to maintain the feed water hardness within the maximum recommended range. If hard water is used to provide either the water or brine solutions for an electrolytic cell, scale will rapidly form on the surfaces of the cathodes, causing the electrolytic cell to fail. Similarly, the temperature of the water entering the electrolytic cell should be maintained within a range of 50 to 80°F to avoid damaging the electrolytic cell. If an OSG is installed in an area where water feeding the OSG will be outside of that temperature range, a heater/chiller unit is typically added to the overall system.

Numerous factors related to water quality and temperature can affect the oxidant demand of each individual water system, the oxidant production of the electrolytic cell, or the life of the cell itself:

Parameter	What is impacted?		
	Oxidant Demand	Chlorine Production	Cell Life
Total Hardness		•	•
Iron (Fe)	•	•	•
Manganese (Mn)	•	•	•
Fluoride (F1)			•
Silica (SiO ₂)		•	•
Bromide			•
Cyanide	•	•	•
Lead (Pb)			•
Disolved Sulfides (as H ₂ S)	•	•	
Ammonia Nitrogen (NH ₃ -N)	•	•	
Organic Nitrogen (Org-N)	•	•	
Total Organic Carbon (TOC)	•	•	
pH		•	•
Water Temperature Range		•	•

In addition, feed water pressure should be maintained between 25 and 100 psi to ensure proper OSG operation. A water boost pump or a pressure reducing valve is installed upstream of the OSG if the feed water pressure is lower or higher than the operating range.

Salt Quality

Sodium chloride is the only chemical added to the OSG water stream and is required for producing the chlorine-based disinfectants. As is the case with feed water, it is vital to use high purity salt to ensure the reliable operation of an OSG system. Some contaminants in salt, such as the calcium and magnesium found in brackish waters and sea salt, can cause damage to the electrolytic cell. Another concern is that some salts contain other chemical species that are subject to oxidation, the most common being bromide (Br⁻). In any electrochemical cell that produces chlorine, bromide will be oxidized to form bromates (BrO₃⁻), which are regulated by the United States Environmental Protection Agency to have a Maximum Contaminant Limit (MCL) of 0.01 mg/L in drinking water. Food quality salt is the most common form of salt recommended for OSGs.

Electrolytic Cell Maintenance

The electrolytic cell is the most expensive part of an OSG and appropriate care should be taken to avoid costly replacement events. Flushing the cell with soft water after every usage helps to prevent salt-deposit buildup. Most OSG systems perform this action automatically upon system shutdown. Using appropriately softened water and high-quality salt are the two most important factors of cell maintenance. Even under these conditions, though, electrochemical cells will develop scale over time. This scale will impede the ability of the cell to generate chlorine and, if left unchecked, will eventually destroy the electrodes. Wash the cell periodically by flushing it with muriatic acid (hydrochloric acid) to remove the scale and clean the electrode surfaces. How much acid is needed and how often the electrolytic cell needs to be rinsed are factors that rely on variables such as how

often the cell is in operation and the quality of water and salt that go into the cell.

Note that low-calcium salts are widely available throughout the U.S. from a variety of manufacturers. The price differential for a better quality salt usually has a nominal impact on the operational budget, so it may be worthwhile to obtain the best quality salt possible. OSG customers using good quality salt report acid-washing their cell as infrequently as once per year. For those customers that either cannot obtain high quality salt or cannot justify the higher cost, the issue can be remedied by a more frequent cell cleaning program.

About the Author

Andrew K. Boal obtained his Ph.D. in organic chemistry from the University of Massachusetts, Amherst. He has worked for Sandia National Labs, NASA, and currently is the Chief Scientist and Director of Business Development for Oil & Gas at MIOX, a company specializing in the development, manufacture, and installation of on-site generators for chlorine, mixed-oxidants and other chemistries.



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For more information about MIOX electrochemical generators for water disinfection, please visit www.miox.com.