Water Remediation using Aqueous Chlorine Advanced Oxidation Processes

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Petroleum Production Water Treatment Challenges

Water used in petroleum production operations is highly treated before and after use (physical modification, disinfection, etc.).

As freshwater use is restricted, technologies that allow for the reuse of water during production operations are highly sought after.

Disposal and post-use treatment of waters used in petroleum production, specifically the removal of organic and inorganic contaminants, is a major challenge facing the industry.
Introduction to On-Site Generation

On-Site Generation (OSG) of custom chemicals enhances water treatment by producing high value chemistry at the point of use. Benefits of OSG include:

- **Inexpensive and safe chemical feed sources** - enhances worker and site safety while decreasing operational expenses
- **Chemistry produced on demand as needed** - decreases loss due to degradation and minimizes hazardous waste due to unused chemical
- **Decreased reliance on chemical delivery to remote sites** - facilitates and simplifies logistics surrounding deployed oil and gas production operations
- **Improved Operations** - benefits of on-site oxidation can ease logistics, separations and operations
OSG Chemical Processes

OSG works through the combination of salt (NaCl), water, and electricity to produce chlorine-based disinfectant solutions:

In the electrochemical cell, chloride ions are oxidized to produce hypochlorous acid and hypochlorite ions.

Water is reduced at the anode to produce hydroxide ions and hydrogen gas.

Chemistry can be enhanced by using salts and salt blends beyond NaCl.

![Diagram of OSG process]
Mixed Oxidant Solution

- Electrolytic cells are optimized for the highly efficient production of sodium hypochlorite solutions

Hypochlorite

- Electrolytic cells are optimized for the production of the most effective biocide

Mixed Oxidant Solution (MOS)

Sodium Hypochlorite

Mixed Oxidant Solution

B. g. spore inactivation test

Sodium Hypochlorite

Mixed Oxidant Solution
Applications of OSG in Petroleum Production Water Treatment

Upstream
- Hydraulic fracturing
- Enhanced Oil Recovery
- Down-Hole disinfection
- Off-shore disinfection using seawater

Downstream
- Refineries
- Cooling Towers
- Production water reuse
- Remediation of production water
Production Water Reuse

MIOX is currently involved in the full scale biocide treatment of reuse water for hydrological fracturing operations in the Fayetteville shale in Arkansas.
MOS has been shown to be highly effective at controlling the microbial population, including Acid Producing Bacteria (APBs) and Sulfate Reducing Bacteria (SRBs), in this water.

Raw Water
APBs: $10,000,000,000\,(10^{10})\text{ cfu/mL}$
SRBs: $100,000,000\,(10^{8})\text{ cfu/mL}$

Treated with MOS
APBs: 10 cfu/mL
SRBs: 100 cfu/mL
Viscosity Reduction with MOS

MOS has also been field tested as a polymer breaker for the reuse of treated waters.

Here, MOS doses of 125 mg/L or higher resulted in a greater than 30% reduction in viscosity.

- Viscosity in this water resulted from prior treatment with a high molecular weight polyacrylamide polymer.

Increased contact time resulted in marginal increase of viscosity reduction.

- Reaction between the polymer and MOS is rapidly completed.
Technology Innovation

MIOX is the OSG industry leader in technology innovation

- Mixed Oxidant Solution (MOS), a chlorine-based biocide with superior microbial inaction efficacy
- OSG systems with self-cleaning functionality
- OSG systems capable of utilizing low quality brine sources

OSG system platforms offer a wide range of choices to meet any application

- Individual hand-held systems for military personnel and outdoors enthusiasts
- Static installed systems for potable and industrial water applications capable of treating 186 MGD
- Fully field-deployable OSG systems capable of treating over 100 barrels of water per minute
Chemistry Innovation

- Integrated Advanced Oxidation (iAO)
- Quaternary Ammonium Hypochlorite (eQuat Hypo)
- Non-traditional Disinfectants (NH₂Cl, HOBr)
Advanced Oxidation Processes (AOPs) are chemical treatment technologies that produce hydroxyl radicals \textit{in situ} during treatment.

- Hydroxyl radicals are short lived (microseconds), highly reactive oxidant species.
AOPs Target Organic Chemicals

Hydroxyl radicals are very reactive, non-specific oxidants

Oil field chemicals that can be degraded using AOP:

- Benzene, toluene, ethyl benzene, and xylenes (BTEX)
- Oils and hydrocarbons
- Naphthalene, phenanthrene, and dibenzothiophene (NPD)
- Polyaromatic Hydrocarbons (PAHs)
Chlorine AOPs

• Chlorine/UV (Cl₂/UV) based AOPs are a topic of increasing research and technology development

• Production of hydroxyl radicals from aqueous chlorine is more efficient than from hydrogen peroxide

• Hydroxyl radical recombination with hypochlorous acid is very slow

• Aqueous chlorine, especially produced through OSG, is a much safer and less expensive chemical compared to ozone and hydrogen peroxide
The photochemistry of aqueous chlorine is highly complex:

- Aqueous chlorine speciation is highly pH dependent.
- Hypochlorous acid (HOCl) and hypochlorite ions (ClO⁻) have different UV absorption profiles.
- HOCl reacts much slower than ClO⁻ with hydroxyl radicals.

![Graph showing the % Composition of HOCl and ClO⁻ vs pH](image)

![Graph showing the Absorbance vs Wavelength for different pH and MOS](image)

**Graphical Abstract:**
- % Composition of HOCl and ClO⁻ vs pH.
- Absorbance vs Wavelength (nm) for different pH and MOS.

**Legend:**
- 100 mg/L pH 6 MOS
- 100 mg/L pH 6.5 MOS
- 100 mg/L pH 7 MOS
- 100 mg/L pH 7.5 MOS
- 100 mg/L pH 8 MOS
- 100 mg/L pH 8.5 MOS
- 100 mg/L pH 9 MOS
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Ultraviolet light is used to activate the aqueous chlorine molecules, producing short-lived but extremely reactive hydroxyl radicals.
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Hydroxyl radicals rapidly react with organic molecules present in water, effecting complete oxidative mineralization of the organic molecules producing water, carbon dioxide, and nitrogen.
Destruction of Organic Chemicals

1,4-dioxane is commonly used as a model compound to test AOP treatment processes

- 1,4-dioxane is a very common groundwater contaminant in the US

Treatment solution pH was found to be critical in achieving high removal rates of 1,4-dioxane

- Differential treatment outcomes are linked to both the initial photo processes of aqueous chlorine as well as the reactivity of hypochlorite with hydroxyl radicals
UV lamp selection (LPUV vs. MPUV) is a critical factor in determining the outcome of Cl\textsubscript{2}/UV AOP treatment.

- Both LPUV and MPUV produced equivalent results at low pH.
- MPUV produced superior results at high pH.

Other water quality parameters can also impact the outcome of a Cl\textsubscript{2}/UV AOP treatment process.

- Alkalinity, temperature, background Total Organic Carbon, presence of ions that can interfere with hydroxyl radicals.

Comparative testing on real waters is required to fully evaluate the various aspects of Cl\textsubscript{2}/UV AOP treatment and compare with traditional AOPs.

![Bar chart showing Log Removal of 1,4-Dioxane at pH 6 and pH 9 for LPUV and MPUV.](chart.png)
**Compound Destruction**

### Volatile Organic Compounds (VOCs)
- 1,2-dichloroethane
- Trichloroethylene (TCE)
- 1,1-dichloroethane
- 1,2-dichloroethane
- Chloroform
- 1,1-dichloroethylene

### Persistent Flame Retardant Chemicals
- Tris-(2-chloroethyl)-phosphate (TCEP)
- Perfluorooctanoic acid (PFOA)

### Pesticides
- Atrazine
- N,N-diethyl-meta-toluamide (DEET)

### Organic Contaminants
- 4-chlorobenzoic acid
- 2-Methylisoborneol (MIB)
- 1,4-dioxane
- N-nitroso-N-dimethyl amine (NDMA)

### Pharmaceuticals
- Ibuprofen
- Fluoxetine
- Primidone
- Carbamazepine
- Gemfibrozil
- Atolol
- Dilantin
- Meprobamate
Field Testing of iAO Technology

Field testing of iAO technology has been accomplished at several sites:

- Industrial groundwater remediation, municipal groundwater, municipal surface water

Pilots focused on the removal of specific contaminants:

- 1,4-dioxane, trichloroethylene, 2-methylisoborneol

Pilot protocols were designed to evaluate several aspects of treatment:

- Overall capability in the removal of targeted contaminant
- Economic data to enable a comparison of traditional AOPs with iAO treatment
- The production of disinfection byproducts (DBPs) and impact of treatment on the toxicity of the treated water
Field Testing of iAO Technology

Data acquired from pilots demonstrated the cost-effectiveness of iAO technology:

- iAO was able to meet or exceed treatment levels obtained with traditional AOP in three of four sites tested.
- iAO technology is less expensive than traditional AOP at three of four sites tested.
- Additional field data will help predict \textit{a priori} when iAO will work better than traditional AOP treatment.

No significant increase in the formation of DBPs were observed as a result of iAO treatment.

Whole effluent toxicity was also tested at two sites and water treated by iAO was found to be non-toxic.

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![Graph showing treatment cost comparison between H$_2$O$_2$/UV, Cl$_2$/UV, and Cl$_2$/UV with pH Adjustment.](Image)
AOP Applications in O&G

MIOX’s iAO Technology can be combined with UV to enhance and improve the treatment outcome

Production water remediation/reuse through the removal of organic compounds

Technology limitation: similar to UV in that waters with low UV transmittance are challenging to treat with this technology
How Can MIOX Help Your Oilfield Water Treatment Needs?