Groundwater Remediation using a Chlorine/Ultraviolet Advanced Oxidation Process

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MIOX Corporation Background

MIOX Corporation is a technology company focused on the application of On-Site Generation technologies to a variety of water treatment markets.

- **Potable Water**: 200 People to 10 Million People
- **Groundwater Remediation**: 50,000 gal/day to 50 MGD
- **Pools & Spas**: 10,000 to 1 M Gallons
- **Dairy Farms**: 100 to 5000 Milk Cows
- **Waste Water**: 1,000 Gallons to 100 MGD
- **Produced Water**: 0.5 to 5 MGD
- **Frack/Flood Water**: 10 to 100 Barrels / Minute
- **Cooling Tower**: 50 Tons to 200,000 GPM

Additional Information:
- 1 to 3000 lb/day per generator
- Temporary Treatment / Site Assessment
Advanced Oxidation Processes (AOPs)

AOPs use in situ generation of highly reactive hydroxyl radicals to oxidize and destroy organic contaminants in water.

Numerous methods can be used to initiate an AOP treatment process.

Most commonly deployed AOPs use combinations of hydrogen peroxide, ozone, and Ultraviolet (UV) light.
Chlorine/Ultraviolet AOPs (Cl$_2$/UV AOPs)

*Cl$_2$/UV AOPs combine aqueous chlorine and ultraviolet light to produce radicals*

Photolysis of aqueous chlorine primarily results in the production of hydroxyl radicals

- Chlorine and oxygen-based radicals are also produced in this process

Production of hydroxyl radicals from the photolysis of aqueous chlorine is mediated by a number of parameters

- Water pH: Cl$_2$/UV AOP is more effective at lower pH
- Type of UV light source (Medium vs. Low Pressure): Medium Pressure UV light tends to be better for Cl$_2$/UV AOP
Benefits of Cl₂/UV AOPs

Cl₂/UV AOPs have several advantages over traditional AOPs

Decreased Chemical Usage
- Cl₂/UV AOPs typically use lower oxidant doses as compared to traditional AOPs

Use of Less Hazardous Chemicals
- Use of on-site generated chlorine in place of bulk oxidants increases worker safety

Decreased UV Energy Usage
- In some Cl₂/UV AOP treatment scenarios, UV energy is used more efficiently, adding to cost savings
Cl$_2$/UV AOP Technology Development at MIOX

*MIOX, working with partners in industry and academia, has been conducting industry leading applied research on Cl$_2$/UV AOP technology for over four years*

Collaborators

- Dr. Shane Snyder, University of Arizona
- Drs. Benjamin Stanford and Erik Rosenfeldt, Hazen and Sawyer, PC
- Dr. Aleks Pisarenko, Trussell Technologies
- Dr. Michael Watts, Florida State University

Publications

- “Groundwater Remediation using Chlorine/Ultraviolet Advanced Oxidation Processes” Boal, A. K. *et. al.* Manuscript being prepared for *Ground Water Monit. R.*
Groundwater Remediation at Aerojet Rocketdyne

Aerojet Rocketdyne treats groundwater at a rate of over 25 MGD

Groundwater Extraction and Treatment (GET) facilities are used to treat water.

Remediation goals include the elimination of several contaminants:
- Perchlorate ($\text{ClO}_4^-$), N-nitrosodimethyl amine (NDMA), Volatile Organic Carbons (VOCs)

GET facilities use a site-specific blend of technologies to meet remediation goals:
- Hydrogen peroxide/UV AOP is primarily used to remove VOCs
GET A has a treatment capacity of 400 gal/min

**GET A water quality**

- Alkalinity: 86 mg/L
- pH: 7.06
- NDMA: 1,143 ng/L
- Total VOCs: 32.2 μg/L

**Cl₂/UV AOP testing involved chlorine doses of between 0.8 and 7.7 mg/L**

- Acidification of the water lowered the pH by 0.2 pH units
Cl₂/UV AOP Test Design

Sample acquisition protocol for the GET A facility

Oxidant and acid injection

Influent Water

UV Photoreactors

Air Stripper

Effluent Water

Raw Water Analysis:
- NDMA
- VOC
- Toxicity

Photoreactor Influent Analysis:
- Cl₂/H₂O₂ concentration
- pH

Photoreactor Effluent Analysis:
- Cl₂/H₂O₂ concentration
- pH
- NDMA
- VOC
- Toxicity
Treatment Overview: GET J Facility

GET J has a treatment capacity of 4,000 gal/min (10x greater than GET A)

GET J water quality:
- Alkalinity: 130 mg/L
- pH: 7.69
- NDMA: 32 ng/L
- Total VOCs: 8.6 μg/L

Cl₂/UV AOP testing involved chlorine doses of between 1 and 6 mg/L
- Water pH was not adjusted at this site
Cl₂/UV AOP Test Design

Sample acquisition protocol for the GET J facility

- **Influent Water**
  - **IX Filter**
  - **Oxidant injection**
  - **UV Photoreactors**
  - **Carbon Filter**
  - **Effluent Water**

**Raw Water Analysis:**
- NDMA
- VOC
- Toxicity

**Photoreactor Influent Analysis:**
- Cl₂/H₂O₂ concentration
- pH

**Photoreactor Effluent Analysis:**
- Cl₂/H₂O₂ concentration
- pH
- NDMA
- VOC

**Filter Effluent Analysis:**
- Cl₂/H₂O₂ concentration
- pH
- VOC
- Toxicity
Testing Methodology

**VOC Analysis**
- Duplicate 40 mL samples collected, quenched, and sent to Eaton Eurofins for analysis
- Samples analyzed for trichloroethylene (TCE), 1,2-dichloroethylene (1,2-DCE), 1,1-dichloroethylene (1,1-DCE), and vinyl chloride (VCL)

**NDMA Analysis**
- 1 L samples were collected, quenched, and sent to Eaton Eurofins for analysis

**Oxidant Concentration and pH**
- Measured on-site using HACH chemistry and a commercial pH probe

**Toxicity**
- 1 gallon samples collected with no quenching
- Acute toxicity towards *Ceriodaphnia dubia* measured by Summit Environmental
VOC and NDMA Removal: GET A

Nearly all Cl₂/UV AOP conditions resulted in the total removal of VOCs and NDMA.

Acidification of these waters had little impact on VOC removal

- Likely due to the large amount of UV fluence used at GET A

NDMA was removed under all Cl₂/UV AOP treatment conditions tested

- NDMA detection limit was 2 ppt

No Cl₂ residual was measured in the UV photoreactor effluent for any treatment condition

<table>
<thead>
<tr>
<th>Natural pH</th>
<th>Acidified</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UV Effluent VOC Concentration (µg/L)</td>
</tr>
<tr>
<td>Cl₂ Dose (mg/L)</td>
<td>UV Effluent VOC Concentration (µg/L)</td>
</tr>
<tr>
<td>0.8</td>
<td>1.22</td>
</tr>
<tr>
<td>2.8</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>4.3</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>5.7</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>7.7</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
VOC and NDMA Removal: GET J

Cl₂/UV AOP alone removed up to 80% of the VOCs

- VOC removal increased with a function of increasing Cl₂ dose up to ~3 mg/L.
- It is likely that decreasing the pH of the water would have increased VOC removal by Cl₂/UV AOP.
- All VOCs remaining in the water after the AOP step were removed by the carbon filters.
- NDMA was removed under all treatment conditions tested.
- No Cl₂ residual was measured in the UV photoreactor effluent for any treatment condition.
# Whole Effluent Toxicity Data

*Nearly all samples resulted in 0% mortality of C. dubia*

<table>
<thead>
<tr>
<th>Site</th>
<th>Toxicity Result</th>
</tr>
</thead>
</table>
| GET A | • 10 of 11 Cl₂/UV AOP samples resulted in 0% C. dubia mortality  
• 1 out of 11 Cl₂/UV AOP samples resulted in 10% C. dubia mortality |
| GET J | • All Cl₂/UV AOP samples resulted in 0% C. dubia mortality |

- Control samples from both GET A and GET J resulted in 0% C. dubia mortality
- Previous tests on GET A water treated with Cl₂/UV AOP verified that no trihalomethanes or haloacetic acids were produced during treatment
- Combined, these results are consistent with pilot data from other locations indicating that the use Cl₂/UV AOP to treat water will not result in a negative impact on water quality
## Economic Comparison of Cl₂/UV and H₂O₂/UV AOP

*Treatment and cost parameters used in economic analysis*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Assumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Price of NaCl salt</td>
<td>$0.17/lb</td>
</tr>
<tr>
<td>Price of 50% aqueous H₂O₂</td>
<td>$4.50/gallon</td>
</tr>
<tr>
<td>Price of energy</td>
<td>$0.105/kWh</td>
</tr>
<tr>
<td>H₂O₂ dose required at GET A</td>
<td>7.4 mg/L</td>
</tr>
<tr>
<td>FAC dose required at GET A</td>
<td>2.5 mg/L</td>
</tr>
<tr>
<td>Water flow at GET A</td>
<td>416 gal/min</td>
</tr>
<tr>
<td>H₂O₂ dose required at GET J</td>
<td>7.4 mg/L</td>
</tr>
<tr>
<td>FAC dose required at GET J</td>
<td>3 mg/L</td>
</tr>
<tr>
<td>Water flow at GET J</td>
<td>3817 gal/min</td>
</tr>
<tr>
<td>Carbon cost for GAC filters at GET J</td>
<td>$1.50/lb</td>
</tr>
</tbody>
</table>
Cost Comparison: GET A

*Use of Cl₂/UV AOP at GET A could result in an annual savings of $10,800*

Both lower chemical cost and chemical usage drove projected treatment cost reduction.

Annual chemical cost savings is moderate, but relevant if scaled across wells.

Impact of UV energy use not explored in this pilot.
Cost Comparison: GET J

*Use of Cl₂/UV AOP at GET J could result in an annual savings of $74,200*

Complete VOC removal at GET J with Cl₂/UV AOP requires slightly increased carbon usage.

Combined costs of Cl₂/UV AOP and carbon filtration are significantly lower than the H₂O₂/UV AOP option.

- Acidification could also be used to enhanced VOC removal, but would not be cost competitive with increased carbon recharging.
Conclusions

- Cl₂/UV AOP was successfully utilized at GET A to achieve TCE removal goals.
- Cl₂/UV AOP combined with in-place carbon filtration was successfully utilized at GET J to achieve TCE removal goals.
- Water treated with Cl₂/UV AOP was found to be non-toxic towards C. dubia.
- Cl₂/UV AOP was found to be significantly less expensive in terms of chemical costs as compared to H₂O₂/UV AOP.
Acknowledgements

Collaborators

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