Perchlorate Treatment Technologies

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Agenda

- Introduction
- Perchlorate chemistry
- Perchlorate treatment technologies (overview)
- Technology applicability
- Technology advantages/disadvantages
- In-situ Bioremediation
Perchlorate Chemistry

- **Highest Oxidized Form of Chlorine** - $\text{ClO}_4^-$

- **Redox Paradox:**
  - Strong Oxidizer, but not very reactive in groundwater
  - High Activation Energy Required

- **Bad News:** Abiotic Reduction Only Under Extreme Conditions

- **Good News:** Can Be Readily Reduced Biologically
**Perchlorate Treatment Technologies**

**Ex-Situ**
- Ion Exchange
- (Fluidized Bed) Bioreactor
- Membrane Technologies (e.g. Reverse Osmosis)

**In-Situ**
- Enhanced Biological Reduction
- Monitored Natural Attenuation
- Soil Flushing
Hypothetical Site Model

- WATER SUPPLY WELL
- FORMER PERCHLORATE SOURCE
- ZONE 1
- ZONE 2
- ZONE 3
- ZONE 4
- VADOSE ZONE
- LOCAL GROUNDWATER (NON-POTABLE)
- AQUIFARD
- DRINKING WATER AQUIFER

[Diagram showing underground layers and zones]
### Treatment Technology Applicability

<table>
<thead>
<tr>
<th>Impact Zone</th>
<th>Description</th>
<th>Typical Technologies/Options</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 1</td>
<td>Vadose Zone (Soils)</td>
<td>Excavation and Treatment/Disposal, In-situ Bioremediation, Soil Flushing</td>
</tr>
<tr>
<td>Zone 2</td>
<td>Groundwater with High [ClO₄⁻]</td>
<td>In-situ Bioremediation, Pump and Treat/Flush, Hydraulic Containment, Natural Attenuation</td>
</tr>
<tr>
<td>Zone 3</td>
<td>Groundwater with Low [ClO₄⁻]</td>
<td>In-situ Biobarrier, Hydraulic Containment, Natural Attenuation</td>
</tr>
<tr>
<td>Zone 4</td>
<td>Impacted Potable Supply Well</td>
<td>Wellhead Treatment, Blending (Low Impacts Only), Shut Down</td>
</tr>
</tbody>
</table>
## Ex-situ Ion Exchange Treatment

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Full-scale operations in LA Area</td>
<td>- Perchlorate removed but not destroyed</td>
</tr>
<tr>
<td>- System can remove perchlorate to &lt;2.5µg/l or possibly lower</td>
<td>- Other large anions (sulfate, nitrates) are removed and need to be addressed further.</td>
</tr>
<tr>
<td>- Operation is fully automatic</td>
<td>- Resin to be disposed or regenerated</td>
</tr>
<tr>
<td>- Nitrates and nitrites present in the groundwater are removed simultaneously</td>
<td>- Full-scale application of catalytic destruction unit is unproven</td>
</tr>
<tr>
<td>- Does not add TSS and TOC</td>
<td></td>
</tr>
</tbody>
</table>

The table above lists the advantages and disadvantages of ex-situ ion exchange treatment.
### Ex-situ Biological Treatment

**Advantages**
- Can remove perchlorate to <4 µg/l
- Perchlorate is broken down into harmless compounds
- Nitrates and nitrites are degraded simultaneously

**Disadvantages**
- Regulatory/Community Concerns for potable use of discharge
- Potential upset due to toxic compounds
- Post treatment (filtration and disinfection), necessary for drinking water applications
- System is not packaged/large footprint
- High operator attention required
- Discharge may contain TOC
- Cold weather can reduce efficiency
- Reduction of sulfates may generate hydrogen sulfide (H₂S).
**In-Situ Biological Treatment of Perchlorate**

**Advantages**
- Eliminates need for (large) aboveground treatment plant
- Demonstrated at several sites to treat perchlorate
- May improve secondary water quality (reducing nitrates and nitrites)
- Moderate capital cost
- Moderate operating costs
- Perchlorate is completely broken down into harmless compounds

**Disadvantages**
- May require dense extraction/injection well field
- No long-term full-scale application data
- Possible mobilization of metals (iron and manganese)
- Possible sulfide formation
- Capital cost highly sensitive to hydrogeology
- Possible need for periodic rehabilitation of injection wells
- Potential upset by compounds that are toxic to bacteria
Degradation Processes Redox Potential

Groundwater + Substrate

$\text{ORP (mV)}$

+800

-250

- $O_2 \rightarrow H_2O$
- $NO_3^- \rightarrow N_2$
- $ClO_4^- \rightarrow Cl^-$
- $SO_4^{2-} \rightarrow HS^-$
- $CCl_4 \rightarrow Cl^-$
- $CO_2 \rightarrow CH_4$

- Aerobic Respiration
- Denitrification
- Perchlorate Reduction
- Sulfate Reduction
- Reductive Dechlorination
- Methanogenesis
**Perchlorate Reduction Pathway**

\[ \text{ClO}_4^- \rightarrow \text{ClO}_3^- \rightarrow \text{ClO}_2^- \rightarrow \text{Cl}^- + \text{O}_2 \]

**Perchlorate** | **Chlorate** | **Chlorite** | **Chloride**
---|---|---|---
Oxidation State: | (+7) | (+5) | (+3) | (-1)

\[ \text{CH}_2\text{O} \rightarrow \text{CO}_2 \rightarrow \text{H}_2\text{O} \]

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**Perchlorate Reduction Pathway**

- **Perchlorate** \( \text{ClO}_4^- \)
- **Chlorate** \( \text{ClO}_3^- \)
- **Chlorite** \( \text{ClO}_2^- \)
- **Chloride** \( \text{Cl}^- \)

**Oxidation State:**
- Perchlorate: (+7)
- Chlorate: (+5)
- Chlorite: (+3)
- Chloride: (-1)

\[ \text{CO}_2, \text{H}_2\text{O} \rightarrow \text{CO}_2, \text{H}_2\text{O} \rightarrow \text{CO}_2, \text{H}_2\text{O} \]
## In-situ Bioremediation Analytes

<table>
<thead>
<tr>
<th>Primary Analytes</th>
<th>Reason for Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Dissolved Oxygen</td>
<td>DO affects electron donor demand $O_2$</td>
</tr>
<tr>
<td>pH</td>
<td>6.5-7.5</td>
</tr>
<tr>
<td>ORP</td>
<td>0-100 mV range</td>
</tr>
<tr>
<td>Total Organic Carbon</td>
<td>May serve as electron donor</td>
</tr>
<tr>
<td>Nitrate + Nitrite</td>
<td>Nitrate and nitrite affect electron donor demand</td>
</tr>
<tr>
<td>$NO_3^- + NO_2^-$</td>
<td></td>
</tr>
<tr>
<td>Chlorate (ClO$_3^-$)</td>
<td>Degradation product</td>
</tr>
<tr>
<td>Chlorite (CLO$_2^-$)</td>
<td>Degradation product</td>
</tr>
<tr>
<td>Chloride Cl$^-$</td>
<td>Degradation product may be masked by high background (Cl$^-$)</td>
</tr>
</tbody>
</table>
Important Variables

- Stratigraphy
- Hydraulic Conductivity
- Storativity
- Groundwater Flow and Transport
- Perchlorate Distribution
- General Minerals Analysis
**In-situ Bioremediation of Perchlorate**

- *In-situ bioremediation of perchlorate is an emerging technology*

- **Laboratory-scale studies, R&D**
  - Penn State University, Southern Illinois University, Envirogen, GeoSyntec

- **Field Demonstrations**
  - Aerojet Superfund Site (CA)
  - Edwards AFB (CA)

- **Biobarrier (immobile C source)**
  - NWIRP (McGregor, TX)
Ex-situ Bioremediation of Perchlorate

Ex-situ Bioremediation of perchlorate is a proven technology:

- Aerojet (N. CA)
  - 4 full-scale bioreactors operating since 1998
  - 2,500 µg/L consistently reduced to <4 µg/L
- San Gabriel Superfund Site (CA)
- Tyndall AFB (FL)
- Thiokol (UT)
- Longhorn Ammunition Plant (TX)
- NWIRP (McGregor, TX)
Technology Status of In-Situ Bioremediation of Perchlorate

- Numerous potentially suitable electron donors (compost, mulch, vegetable oil, sugars, alcohols, lactate, acetate, etc.)
- Implementable through recirculation cells or in biobarriers
- Few in-situ field applications have been completed, but numerous studies are underway
- Will require site-specific treatability testing and pilot-scale field demonstration