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## Perchlorate Remediation Technologies



### ITRC Technical and Regulatory Guidance document: Remediation Technologies for Perchlorate Contamination in Water and Soil (PERC-2, 2008)

Sponsored by: Interstate Technology and Regulatory Council ([www.itrcweb.org](http://www.itrcweb.org))  
Hosted by: US EPA Clean Up Information Network ([www.cluin.org](http://www.cluin.org))

Perchlorate contamination exists in water and soil, and occurs widely throughout the United States. Public awareness and concern regarding perchlorate has increased in recent years. Perchlorate occurrence in drinking water and food supplies is a human health concern because it can interfere with iodide uptake by the thyroid gland and result in decreased thyroid hormone production. The ITRC Perchlorate Team was formed in 2004 to address technical issues associated with perchlorate. Many technologies are available to remediate perchlorate contamination, but only a few are commonly used.

This training introduces state regulators, environmental consultants, site owners, and community stakeholders to Remediation Technologies for Perchlorate Contamination in Water and Soil (PERC-2, 2008), created by ITRC's Perchlorate Team to assist reviewers in assessing the adequacy of perchlorate remediation projects. This course gives the student a background in the available remediation technologies to treat perchlorate contamination, discusses emerging technologies, and presents case studies of applications.

The first document produced by the ITRC Perchlorate Team, Perchlorate: Overview of Issues, Status, and Remedial Options (PERC-1, 2005), and associated Internet-based training provide regulators and other stakeholders a basic overview of a broad spectrum of information regarding perchlorate sources, sampling and analysis techniques, a discussion of risk issues, risk management strategies and regulatory status, and included a brief summary of remediation technologies. It is recommended that the registrant review the Perchlorate: Overview of Issues, Status, and Remedial Options (PERC-1, 2005) document and associated Internet-based training archive (available from [http://www.itrcweb.org/ibt.asp#Perchlorate\\_CurrentInfo](http://www.itrcweb.org/ibt.asp#Perchlorate_CurrentInfo)) for more information.

ITRC (Interstate Technology and Regulatory Council) [www.itrcweb.org](http://www.itrcweb.org)

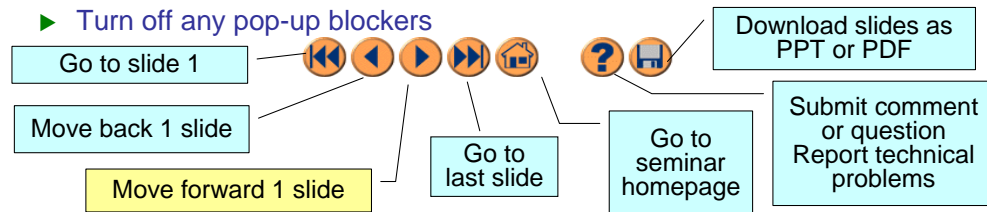
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ITRC Training Program: [training@itrcweb.org](mailto:training@itrcweb.org); Phone: 402-201-2419

## Housekeeping



- ▶ Course time is 2¼ hours
- ▶ Phone line participants
  - Do NOT put this call on hold
  - \*6 to mute; #6 to unmute
- ▶ Question & Answer breaks
  - Phone - unmute #6 to ask question out loud
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- ▶ Archives accessed for free <http://clu.in.org/live/archive/>



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## ITRC ([www.itrcweb.org](http://www.itrcweb.org)) – Shaping the Future of Regulatory Acceptance



### ► Host organization



### ► Network

- State regulators
  - All 50 states, PR, DC
- Federal partners



DOE DOD EPA

- ITRC Industry Affiliates Program



- Academia
- Community stakeholders

### ► Wide variety of topics

- Technologies
- Approaches
- Contaminants
- Sites

### ► Products

- Technical and regulatory guidance documents
- Internet-based and classroom training

The Interstate Technology and Regulatory Council (ITRC) is a state-led coalition of regulators, industry experts, citizen stakeholders, academia and federal partners that work to achieve regulatory acceptance of environmental technologies and innovative approaches. ITRC consists of all 50 states (and Puerto Rico and the District of Columbia) that work to break down barriers and reduce compliance costs, making it easier to use new technologies and helping states maximize resources. ITRC brings together a diverse mix of environmental experts and stakeholders from both the public and private sectors to broaden and deepen technical knowledge and advance the regulatory acceptance of environmental technologies. Together, we're building the environmental community's ability to expedite quality decision making while protecting human health and the environment. With our network of organizations and individuals throughout the environmental community, ITRC is a unique catalyst for dialogue between regulators and the regulated community.

For a state to be a member of ITRC their environmental agency must designate a State Point of Contact. To find out who your State POC is check out the "contacts" section at [www.itrcweb.org](http://www.itrcweb.org). Also, click on "membership" to learn how you can become a member of an ITRC Technical Team.

## ITRC Course Topics Planned for 2010 – More information at [www.itrcweb.org](http://www.itrcweb.org)



### Popular courses from 2009

- ▶ Decontamination and Decommissioning of Radiologically-Contaminated Facilities
- ▶ Enhanced Attenuation of Chlorinated Organics
- ▶ In Situ Bioremediation of Chlorinated Ethene - DNAPL Source Zones
- ▶ LNAPL Part 1: An Improved Understanding of LNAPL Behavior in the Subsurface
- ▶ LNAPL Part 2: LNAPL Characterization and Recoverability
- ▶ Perchlorate Remediation Technologies
- ▶ Performance-based Environmental Management
- ▶ Phytotechnologies
- ▶ Protocol for Use of Five Passive Samplers
- ▶ Quality Consideration for Munitions Response
- ▶ Determination/Application of Risk-Based Values
- ▶ Use of Risk Assessment in Management of Contaminated Sites

### New in 2010

- ▶ Use and Measurement of Mass Flux and Mass Discharge
- ▶ LNAPL Part 3: Evaluating LNAPL Remedial Technologies for Achieving Project Goals
- ▶ Mine Waste Treatment Technology Selection

**ITRC 2-day Classroom  
Training: Vapor  
Intrusion Pathway**

More details and schedules are available from [www.itrcweb.org](http://www.itrcweb.org) under "Internet-based Training" and "Classroom Training."

## Meet the ITRC Instructors



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**Rose Knox** is a Senior Environmental Engineer at the Massachusetts Department of Environmental Protection (MassDEP) in Boston. Rose has worked with the Bureau of Waste Site Cleanup's Policy and Program Development group since 2000. Her main duties include conducting technical analyses to support the development of policies and regulations under the Massachusetts Contingency Plan. Rose's recent projects include evaluating the impacts of the most prevalent sources of perchlorate contamination in environmental media in Massachusetts. These perchlorate sources include blasting agents, military munitions, fireworks, and hypochlorite (bleach) solutions. Rose recently completed a research study at the University of Massachusetts Dartmouth campus to evaluate the potential release of perchlorate to the environment as a result of a typical "community-type" fireworks display. As part of this study, Rose conducted groundwater modeling to evaluate the fate and transport of perchlorate in groundwater. Rose has been active in the ITRC since 2004 serving as a Perchlorate Team Member representing MassDEP. Prior to joining MassDEP, she was a principal engineer at a large environmental consulting firm responsible for feasibility studies and remedial design. Rose earned a bachelor's degree in civil engineering from Tufts University in Medford, Massachusetts in 1988. She earned a master's degree in environmental engineering from Tufts University in Medford, Massachusetts in 1991. Rose is certified as a Professional Engineer in Massachusetts.

**Bruce Robinson** is a Senior Hydrogeologist and ITRC Stakeholder from Tempe, Arizona managing a wide variety of projects from drinking water supply resource development to contaminant hydrogeology. Previously, he worked for the Gila River Indian Community Department of Environmental Quality in central Arizona for 7 years, Arizona Department of Environmental Quality, Superfund Section for 3 years and 10 years managing contaminant studies for Dames and Moore. Bruce's industry experience has focused on CERCLA and RCRA contaminant investigations for metals, chlorinated hydrocarbons and fuels. Bruce joined the ITRC in 2006 to participate in the Passive Sampling and Perchlorate Teams. He is active in field testing new passive sampling technologies for characterization of chlorinated hydrocarbon and perchlorate groundwater plumes. He has spent the last 7 years working on a complex site where a perchlorate plume from an abandoned manufacturing facility has commingled with multiple chlorinated hydrocarbon groundwater plumes. He has worked to expand the role of passive samplers in vertically characterizing contaminant stratification in aquifers. He has also been active in applying innovative analytical methods to the speciation of perchlorate. Bruce serves on the ITRC as a Stakeholder and has a long history of working with Community Advisory Boards (CABs) both as a regulator and as a consultant. He continues to advocate for regulators and private industry to get early input from community groups to build consensus and promote project efficiency and cost savings. As an ITRC Stakeholder, Bruce is interested in informing the public about the large number of sources of perchlorate not associated with the rocket propulsion industry. He believes that public education through organizations like the ITRC can lead to the implementation of best management practices that will limit the majority of anthropogenic perchlorate that is currently being released into the environment. Bruce earned a bachelor's in Geology from Ball State University in Muncie, Indiana in 1981 and is a registered geologist in the State of Arizona.

**Bob Barnwell** is a Geologist with the Alabama Department of Environmental Management (ADEM) located in Montgomery, Alabama. Since 2004, Bob has worked in the ADEM Water Division on CERCLA and RCRA projects at federal facilities located in Alabama. Bob provides geologic and hydrogeologic services for the environmental cleanup programs under the Defense and State Memorandum of Agreement. He is a state regulator for soil and groundwater investigations including site characterization, remedial alternatives, permitting, and risk assessments. His duties include oversight of perchlorate assessments at NASA and Department of Defense facilities. Investigations involve characterization and cleanup of perchlorate in soil and groundwater. Prior to ADEM, he worked for 16 years in the environmental consulting field conducting assessments throughout the country basing out of Washington, DC; Atlanta, GA; and Santa Fe, NM. Since 2005, Bob has contributed to ITRC as a team member representing the state of Alabama for ITRC's Perchlorate team. Bob earned a bachelor's degree in geology from Georgia Southern College in Statesboro, Georgia in 1988. He is certified as a Professional Geologist in Alabama and Georgia.

**Paul Hatzinger** is a senior scientist at the Princeton Research Center of Shaw Environmental in Lawrenceville, NJ. He joined Shaw in 2003 after working as a research scientist at Envirogen for 6 years. Paul's current areas of research focus on the development of in situ and ex situ bioremediation technologies for emerging contaminants and the use of isotopic methods to distinguish contaminant sources. He has been performing research on perchlorate biodegradation and bioremediation since 1999. Paul has served as the Principal Investigator on several research projects focused on perchlorate treatment, including three field demonstrations of in situ remedial approaches, and projects evaluating the use of stable isotopes to delineate natural from anthropogenic perchlorate in the environment. In addition, Paul works closely with the engineering group at Shaw that has designed and constructed 5 full-scale bioreactor systems for treatment of perchlorate in groundwater. He has authored more than 40 peer-reviewed research papers and book chapters, including several on perchlorate treatment and forensics. Paul has been a member of the ITRC Perchlorate team since inception. He earned a bachelor's degree in Biology and Environmental Science from St. Lawrence University in Canton, NY in 1986, and he holds both a master's degree (1991) and a doctoral degree (1996) in Environmental Toxicology from Cornell University in Ithaca, New York.

## What you will learn...



- ▶ Perchlorate remediation options
  - Perchlorate is pervasive in the environment
  - Regulators should be aware of the treatment options
- ▶ Training is based on the ITRC document: ***Remediation Technologies for Perchlorate Contamination in Water and Soil*** (PERC-2, 2008)



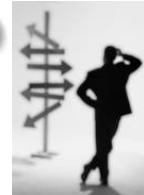
Public awareness and concern regarding perchlorate have increased over the last 10 years. The growing database of occurrence shows that perchlorate is detected in all media and found around the world, and the number of detections continue to increase as the perchlorate analytical techniques improve. We now understand that Perchlorate contamination is not an insignificant problem and we need to address.

The basis for this training is the ITRC Technical Regulatory Guidance Document: Remediation Technologies for Perchlorate Contamination in Water and Soil (PERC-2, 2008). Our purpose today is to conduct a review of technologies applicable to the remediation of perchlorate in groundwater and soil. In addition, the social, political and regulatory barriers to the use of these technologies will be discussed. The overall goal of the training is to provide industry, responsible parties, and state and federal environmental regulators with reliable guidance to help streamline the review and approval process for selecting and implementing perchlorate treatment technologies. Where possible, important regulatory issues to consider during site characterization, design, construction and monitoring are identified and discussed. For each technology presented today, we will provide a detailed description, discuss applicability, advantages and limitations and provide cost information. During the training today, the trainers will highlight various applications and potential complicating issues that may arise when implementing technologies at a site.



## Benefits to the Audience

- ▶ Understanding the treatment technologies for perchlorate remediation
- ▶ Assist with decision making
  - Save money
  - Save time
  - Improve quality of decisions
- ▶ Personal benefits
  - Improve job performance
  - Keep current
  - Add skills
  - Prepare to be proactive
  - Lead innovation

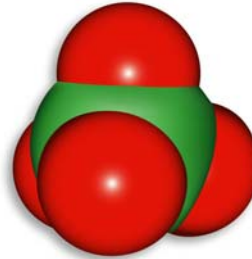


Perchlorate is a relatively new contaminant of concern and state and federal agencies and other stakeholders do not yet have the same level of experience and expertise to address perchlorate as other more conventional contaminants, such as petroleum and chlorinated solvents. Based on the experience gathered to date, this training will highlight the important elements to consider when evaluating perchlorate treatment technologies.



## Presentation Overview

- ▶ Overview/update
- ▶ Treatment selection considerations
- ▶ Categories of treatment technologies for groundwater and soil
- ▶ Groundwater treatment technologies
  - Physical
  - In situ and ex situ biological
- ▶ Soil treatment technologies
  - Thermal
  - In situ and ex situ biological
- ▶ Case study



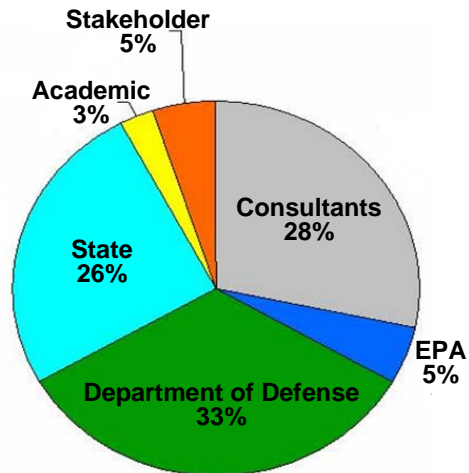
No associated notes.

## ITRC Perchlorate Team as of 2007



- ▶ Composition
- ▶ History
- ▶ Successes
- ▶ Products

- Perchlorate: Overview of Issues, Status, and Remedial Options (PERC-1, 2005)
- Remediation Technologies for Perchlorate Contamination in Water and Soil (PERC-2, 2008)
- Future Possibility: Best Management Practices Guidance Document



No associated notes.

## Brief Overview of Perchlorate



- ▶ Fate and transport
- ▶ Toxicity/exposure studies
- ▶ Regulatory status update
- ▶ Sources and occurrence

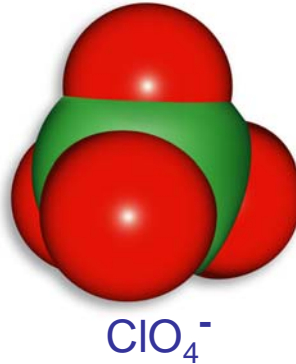


I will provide a brief overview of background information on perchlorate, including a discussion on chemical properties and fate and transport, updates on exposure studies and regulatory status, and summarize perchlorate sources, uses and occurrence. I recommend that you consult the first Overview document and associated training materials for background material not included in today's training course as the main focus of today's training is on the selection of perchlorate treatment technologies.

More information is available in the ITRC Perchlorate team's document "Perchlorate: Overview of Issues, Status, and Remedial Options" (PERC-1, 2005) available at [www.itrcweb.org](http://www.itrcweb.org) under "Guidance Documents" and "Perchlorate" and the associated Internet-based training course available from [www.itrcweb.org](http://www.itrcweb.org) under "Internet-based Training" and "Perchlorate"

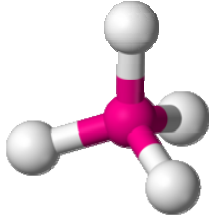
## What is Perchlorate?

- ▶ Inorganic chemical ion consisting of chlorine bonded to four oxygen atoms
- ▶ Usually found as the anion component of a salt, usually with one cation
  - Ammonium ( $\text{NH}_4\text{ClO}_4$ )
  - Sodium ( $\text{NaClO}_4$ )
  - Potassium ( $\text{KClO}_4$ )
- ▶ Also found in
  - Perchloric acid ( $\text{HClO}_4$ )



More information is available in the ITRC Perchlorate team's document "Perchlorate: Overview of Issues, Status, and Remedial Options" (PERC-1, 2005) available at [www.itrcweb.org](http://www.itrcweb.org) under "Guidance Documents" and "Perchlorate" and the associated Internet-based training course available from [www.itrcweb.org](http://www.itrcweb.org) under "Internet-based Training" and "Perchlorate"

## Why Do We Care About Perchlorate?



- ▶ Perchlorate
  - Soluble
  - Mobile
  - Stable



- ▶ Perchlorate in ground or surface water plumes
  - Extensive
  - Persistent



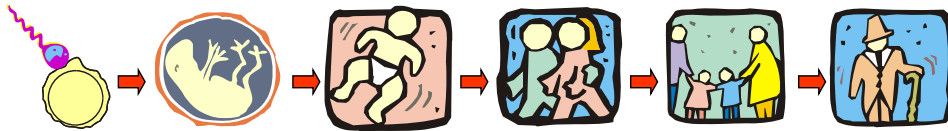
- ▶ Perchlorate can contaminate
  - Drinking water sources
  - Food supplies
- ▶ Presents a human health concern

More information is available in the ITRC Perchlorate team's document "Perchlorate: Overview of Issues, Status, and Remedial Options" (PERC-1, 2005) available at [www.itrcweb.org](http://www.itrcweb.org) under "Guidance Documents" and "Perchlorate" and the associated Internet-based training course available from [www.itrcweb.org](http://www.itrcweb.org) under "Internet-based Training" and "Perchlorate"

## Toxicity



- ▶ Perchlorate is **NOT** a known human carcinogen
- ▶ Perchlorate is one of several compounds that competitively interfere with iodide uptake in the thyroid
- ▶ Iodide is required for thyroid hormone production
- ▶ Thyroid hormones regulate human growth and development



More information is available in the ITRC Perchlorate team's document "Perchlorate: Overview of Issues, Status, and Remedial Options" (PERC-1, 2005) available at [www.itrcweb.org](http://www.itrcweb.org) under "Guidance Documents" and "Perchlorate" and the associated Internet-based training course available from [www.itrcweb.org](http://www.itrcweb.org) under "Internet-based Training" and "Perchlorate"

## Regulatory Status



- ▶ EPA adopted the National Research Council's RfD of 0.0007 mg/kg/day in February 2005

- EPA posted this value on the Integrated Risk Information System (IRIS)



- No current maximum contaminant level (MCL) for perchlorate, but EPA has begun the process to determine if an MCL should be established

No associated notes.



## Individual States Establish Cleanup Standards and Health-based Goals



- ▶ Promulgated a drinking water Maximum Contaminant Level (MCL)
  - 2 ppb – Massachusetts in 2006
  - 6 ppb – California in 2007
- ▶ Adopted EPA's advisory level as a cleanup standard
  - 18 ppb – Nevada
- ▶ Some states established their own health-based goals
  - 4 ppb – Vermont
  - 5 ppb – New Jersey
  - 11 ppb – Kansas
  - 14 ppb – Arizona
  - 17 ppb – Texas

Massachusetts promulgated a drinking water MCL of 2 ppb in 2006.

California promulgated a drinking water MCL of 6 ppb in 2007.

Nevada adopted EPA's advisory level of 18 ppb as a cleanup standard.

Some states established their own health-based goals

## Sources and Uses of Perchlorate



Naturally occurring

Widely manufactured



- Knowing sources and uses guides perchlorate investigations as we will discuss in the case study

More information is available in the ITRC Perchlorate team's document "Perchlorate: Overview of Issues, Status, and Remedial Options" (PERC-1, 2005) available at [www.itrcweb.org](http://www.itrcweb.org) under "Guidance Documents" and "Perchlorate" and the associated Internet-based training course available from [www.itrcweb.org](http://www.itrcweb.org) under "Internet-based Training" and "Perchlorate"

## Uses of Perchlorate



► Prior to WWII

- Fireworks
- Flares



► After WWII, additional uses

- Oxidizing agent for solid propellant rockets and missiles



More information is available in the ITRC Perchlorate team's document "Perchlorate: Overview of Issues, Status, and Remedial Options" (PERC-1, 2005) available at [www.itrcweb.org](http://www.itrcweb.org) under "Guidance Documents" and "Perchlorate" and the associated Internet-based training course available from [www.itrcweb.org](http://www.itrcweb.org) under "Internet-based Training" and "Perchlorate"

## Perchlorate Releases – Past Practices

- ▶ Disposal of solid propellant, explosives, and munitions
  - Open burn and open detonation
  - Hydraulic wash out (hog-out)
- ▶ Manufacturing practices
  - Wastewater storage
  - Disposal and storage practices
  - Testing



More information is available in the ITRC Perchlorate team's document "Perchlorate: Overview of Issues, Status, and Remedial Options" (PERC-1, 2005) available at [www.itrcweb.org](http://www.itrcweb.org) under "Guidance Documents" and "Perchlorate" and the associated Internet-based training course available from [www.itrcweb.org](http://www.itrcweb.org) under "Internet-based Training" and "Perchlorate"

## Potential Perchlorate Releases



- ▶ Fireworks
- ▶ Explosives use, such as blasting sites
- ▶ Impurities in agricultural chemicals
- ▶ Sodium hypochlorite used in water and wastewater treatment
- ▶ Sodium chlorate manufacture and use



More information is available in the ITRC Perchlorate team's document "Perchlorate: Overview of Issues, Status, and Remedial Options" (PERC-1, 2005) available at [www.itrcweb.org](http://www.itrcweb.org) under "Guidance Documents" and "Perchlorate" and the associated Internet-based training course available from [www.itrcweb.org](http://www.itrcweb.org) under "Internet-based Training" and "Perchlorate"

## Detecting Perchlorate in the Environment



- ▶ Improved analytical methodologies resulted in increased detection
  - 1997
    - 4 ppb quantitation level
  - Today
    - 1 ppb and lower quantitation level



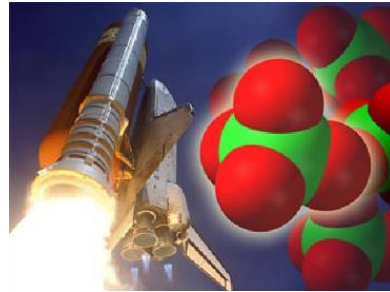
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## Feasibility Study Process – Selecting Alternatives



### Developing and screening alternatives

- ▶ Establish remedial action objectives
- ▶ Develop a response action that will accomplish the remedial action objective
- ▶ Identify and screen appropriate technologies
- ▶ Select representative process options
- ▶ Reevaluate data needs
- ▶ Develop alternatives



Remedial Action Objective - This is your specific goal for how to accomplish cleanup and protection of the environment

Response actions – Are selected to satisfy the remedial action objectives and relate to the basic method of protection such as containment or treatment.

Screening Technologies - includes a review of the site characterization data to determine if there are technologies on the list that are not effective (technical implementability).

Technical Process Option – Refers to a specific alternative process within a technology family

Reevaluate data needs – To determine if enough information is available to select alternatives

The selection process of the appropriate remedy for perchlorate is similar to that for other contaminants, in that it requires in-depth knowledge of the following (source; Harry Van Den Berg paper):

- Stratigraphy
- Depth to groundwater
- Hydraulic conductivities and gradients of water-bearing zones
- Groundwater flow and contaminant transport
- Perchlorate distribution in both source areas and underlying aquifer(s)
- Geochemistry (specifically manganese [Mn], iron [Fe], dissolved oxygen, oxidation/reduction potential, pH, and major anions [nitrate, sulfate, bicarbonate, chloride])
- Presence of other contaminants, which may require additional treatment before or after perchlorate removal
- Regulatory requirements/action levels
- Land use, which may impact the feasibility of installing treatment system infrastructure
- Available discharge options and requirements, which may impact the viability of hydraulic containment or remedial alternatives relying on pump-and-treat.



## Developing Remedial Action Objectives



- ▶ Initial (fundamental) considerations
  - Establish remedial objective
  - Numerical cleanup standards
  - Remediation time frame
  - Evaluate ex situ versus in situ treatment



*Keep in mind! – duration of treatment is directly proportional to ultimate remedy cost.*

No associated notes.

## Remedial Action Categories



- ▶ No further action
- ▶ Land use controls
- ▶ Engineering controls (containment)
- ▶ In situ mass removal
- ▶ Ex situ mass removal



The remedial action categories are.....

The No-Action alternative is used as a baseline to compare other alternatives. Measures such as fencing or monitored natural attenuation are not No-Action alternatives.

Examples of Land Use Controls are

**DEUR:** Declaration of Environmental Use Restriction. A restrictive land use covenant that is required when a property owner elects to use an institutional (i.e., administrative) control or engineering (i.e., physical) control as a means to meet remediation goals. The DEUR runs with and burdens the land, and requires maintenance of any institutional or engineering controls.

**VEMUR:** Voluntary Environmental Mitigation Use Restriction. A restrictive land use covenant that, prior to July 18, 2000, was required when a property owner elected to remediate the property to non-residential uses. Effective July 18, 2000, the DEUR replaced the VEMUR as a restrictive use covenant.

## Federal Regulatory Requirements



- ▶ EPA, 1968 National Oil and Hazardous Substances Contingency Plan (NCP)
  - Establishes national goal and expectations for the environment
- ▶ Goals and expectations codified in Superfund regulations. Superfund defines
  - Feasibility study (FS) process
  - Setting Remedial Action Objectives (RAO)
  - Remedy selection process



The Comprehensive Environmental Response, Compensation and Liability Act of 1980, known as Superfund, was enacted to address abandoned hazardous waste sites in the U.S. The law has subsequently been amended, by the Superfund Amendments and Reauthorization Act of 1986 (SARA), and the Small Business Liability Relief and Brownfields Revitalization Act of 2002.

For more information you can go to <http://www.epa.gov/oilspill/ncpover.htm>  
<http://www.epa.gov/superfund>

## Regional Regulatory Considerations



- ▶ Research municipal, county, Tribal and State ARARs
- ▶ Develop matrix of all ARARs (regional and federal)
- ▶ Evaluate organizational priorities
  - Some state programs will have precedence
- ▶ Use your state's environmental agency as a resource as they will have completed this task for other projects



- 1) Be comprehensive in your evaluation of potential applicable or relevant and appropriate requirements. Good guidance on the ARAR process can be found at <http://www.epa.gov/superfund/policy/remedy/sfremedy/arars/overview.htm>.
- 2) Developing a matrix of ARARs will assist in managing the task and evaluating precedence.
- 3) If the State or Tribal Community has a delegated program from the EPA those requirements will have precedence over other similar regulations.
- 4) Do not overlook your State environmental agency as a source for compiling ARARs.

## Regulatory Issues Associated with Technology



### Example: Tronox Fluidized-bed Reactor (FBR) Permit Requirements, Henderson, Nevada

- ▶ Water appropriations permit
- ▶ National Pollutant Discharge Elimination System (NPDES) permit
- ▶ Rolling stock permit
- ▶ Air permit
- ▶ Bureau of Alcohol, Tobacco and Firearms (BATF) tax reporting permit
- ▶ Sludge produced
- ▶ Spent resin



Here is a specific example of the permits necessary for a fluidized bed reactor site in Henderson Nevada.

Permits that may typically be required include:

NPDES: Treated water discharge

UIC: Injection of amendments for in situ bioremediation

Air Permits: Volatile and dust permits associated with storage of amendments for treatment systems

RCRA: Waste such as spent resin

## Stakeholder Issues and Concerns



### Stakeholder issues related to remedy selection

- ▶ Demonstrate respect and include stakeholders early in the process
- ▶ Educate stakeholders on engineering of remedies so they make wise decisions
- ▶ Be clear how remedy will impact stakeholder
  - Noise, traffic, air-water-soil quality, and property value
- ▶ Remediation time frame
- ▶ Cleanup goal



- 1) Stakeholders should be incorporated into the project early in the Remedial Investigation. It is important to expose the public to the details of the site investigation including size, extent, type of constituents and the fate and transport. This information is essential to the stakeholder assisting in the remedy selection process.
- 2) Stakeholders will be concerned about how their lives may be impacted (noise, safety, traffic, exposure to contaminants and affect on property values).
- 3) Stakeholders will want to be included in deciding cleanup goals and remediation time frames. These issues are fundamental to determining the cost and life cycle of the site remediation.

## Remediation Technologies



### Physical Processes



### Biological Processes

#### ▶ Water

- Physical
  - Ion exchange or carbon
- (Q&A break)
- In situ biological
  - Carbon source and amendments
- Ex situ biological
  - Bioreactors

#### ▶ Soil

- In situ biological
- Ex situ biological
  - Composting
- Thermal
  - Incineration

#### ▶ Phytoremediation

- Roots

There are perchlorate remediation technologies that utilize **physical** and **biological** processes. Many of these technologies were developed in the past for other purposes, such as in water treatment. Customized to address perchlorate issues.

The remedial technologies focus on groundwater, surface water, drinking water, and/or soil that have been impacted by perchlorate.

Physical processes for water

- primarily ion exchange,
- tailored granular activated carbon adsorption,
- reverse osmosis, and
- innovative and emerging technologies.

Biological processes for water

- In situ technologies for groundwater to help understand the environment necessary for optimal biodegradation.
- Ex situ technologies for water by means of bioreactors (stirred-tank, fluidized bed, or packed bed reactors).

Treatment technologies for soil.

- In situ bioremediation (get amendments in the soil),
- Ex situ bio (composting), and
- Thermal treatment (incineration).

Phytoremediation to degrade perchlorate not just have uptake.

- Rhizodegradation
- Phytoaccumulation
- Phytodegradation

• More detailed information can be found in Remediation Technologies for Perchlorate Contamination in Water and Soil (PERC-2, 2008) at [www.itrcweb.org](http://www.itrcweb.org) under "Guidance Documents" and "Perchlorate"



## Physical Processes for Water



- ▶ Ion exchange
- ▶ Carbon
- ▶ Reverse osmosis
- ▶ Innovative and emerging technologies



**Perchlorate on eBay and Mars**



Physical treatment processes are technologies that remove perchlorate from impacted water without altering its chemical composition. Some technologies are proven and commercially available while others are still in the research and development phase.

Ion exchange is the most widely used physical technology, therefore, will be further discussed on a handful of upcoming slides. Carbon adsorption is also at full scale and will have a couple of slides.

A discussion on the remaining physical technologies will be brief, refer to the ITRC Remediation Technologies for Perchlorate Contamination in Water and Soil (PERC-2, 2008).

Potassium perchlorate on eBay indicating how readily available it is, even to the public. Since the widespread occurrence of perchlorate is becoming more evident and health concerns have been identified, a variety of remedial technologies is essential.

## Ion Exchange Systems

Ion exchange (IX) is the most proven and widely-accepted physical process technology to meet existing perchlorate-treatment goals



**Single-use system**

San, Bernardino, CA



**Regenerable system**

La Puente, CA

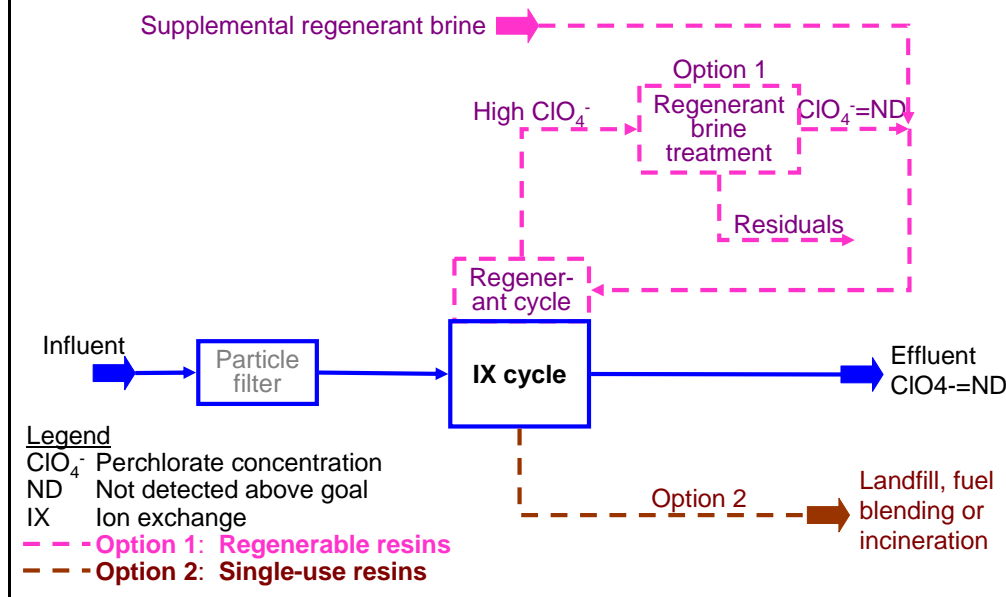
Various systems listed in Table 5-3 in the ITRC tech-reg document, **Remediation Technologies for Perchlorate Contamination in Water and Soil (PERC-2, 2008)**

Ion exchange is the most proven and widely-accepted physical process technology to meet existing perchlorate-treatment goals. See Table 5-3 in the ITRC tech-reg document "Remediation Technologies for Perchlorate" for some system specific info like influent/effluent concentrations.

During ion exchange, perchlorate, which is a negatively charged ion (the anion), is exchanged with another anion, typically chloride. Many different types of ion exchange products prepared as resins are commercially available. When perchlorate-impacted water flows through the resin, perchlorate anions attach to the resin and release bound chloride ions.

Ion exchange systems can be operated as single-use systems with disposable resins or as regenerable systems with reusable resins.

## Ion Exchange



**Single use system**, contaminated water is pumped through one or more vessels (or columns) that hold the resin where ion exchange takes place. A vessel/column can contain millions of small resin beads that form the resin bed. Multiple columns are often run in series (lead-lag configurations) to ensure that water exiting the process is adequately treated and breakthrough does not occur. Over time, the resin becomes saturated with perchlorate and competing ions, reaching its adsorption capacity thus allowing breakthrough (perchlorate is passing through). The resin bed is then taken out of service and the resin must be disposed of (e.g. incineration) and fresh resin is brought online to ensure ongoing removal efficiency.

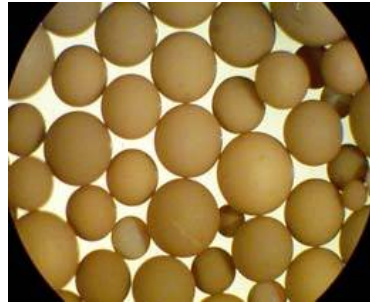
Single-use systems are primarily used due to the increase in efficiency of single-use perchlorate-selective resins.

**Regenerable system**, the ion exchange capacity of resins is progressively exhausted, then the column is taken off-line so that the resin can be regenerated using a regenerant solution to displace the adsorbed perchlorate ions (like you are washing it). There are two types of regenerable system designs: a fixed-bed system and a moving bed system.

Regenerable systems have not been as successful as single-use systems due to the brine issue during regeneration.

## Ion Exchange Resins

- ▶ Selectivity for perchlorate
- ▶ Single use resins
  - Strong base
  - Bifunctional (Biquat)
  - Resin disposal
- ▶ Regenerable resins
  - Weak and strong base
  - Regenerant
  - Brine disposal



Resin beads



Get the perchlorate-selective resin

In resins, you have anion exchangers (perchlorate), strong and weak base resins. Strong base anion resins are highly ionized and can be used over the entire pH range, weak base resins are more sensitive to pH. Resins have an order of preference for exchanges that first swap out for nitrates, then perchlorate, down to sulfates.

Single-Use Resins are disposable and primarily strong base. Newer resin designs take advantage of an even greater selectivity for perchlorate, making it possible to operate the ion exchange systems for a longer period of time. Use and disposal of single-use resins avoids the difficulties and liabilities associated with the perchlorate-laden waste streams that are produced during resin regeneration.

The Oak Ridge National laboratory (ORNL) developed a new class of bifunctional anion exchange resins, which are highly selective for sorption of perchlorate from contaminated groundwater or surface water. Trademarked as **BiQuat**, this resin is particularly effective in removing trace quantities of perchlorate in groundwater while also managing large volumes. The treatment process does not involve the addition or removal of unwanted organic or inorganic compounds or nutrients in the water because of the high selectivity of the bifunctional resins.

As ion exchange is not a destructive process, perchlorate-laden spent resin produced from single use systems requires proper handling and disposal, which must be considered in system design. The resins are typically sent to an approved landfill or incinerated (waste-energy). Also, a technology has been tested to regenerate single-use resins.

Regenerable Resins are reusable but produce a brine that requires disposal. These can be weak or strong base resins.

- The weak base perchlorate-selective anion resins, unlike strong base anion resins, have functional groups dependent on pH. At low pH (<7), the functional groups are ionized and able to exchange anions.

- Pretreatment step to lower pH prior to ion exchange
  - Post-treatment to restore the pH

Once the resin is spent, regeneration is accomplished by increasing the pH (>7) and

## Ion Exchange – Summary

- ▶ **Municipal drinking water supply**
  - Systems operating at full scale
  - Regulatory acceptance by meeting goals
  - Other technologies limited (certifications or technically impracticable)
- ▶ **Design considerations**
  - Cleanup goal
  - Water quality (competing anions)
  - Perchlorate concentrations
- ▶ **Single use or regenerable system**
  - Resin selection
  - Disposal options
  - Costs (capital upfront or O&M backend)



**Ion exchange is the key to drinking water**

**Municipal drinking water supply** impacted with perchlorate, IX is the key technology working today.

- The single-use system is the main IX technology. They are in full-scale operation at sites in Arizona, California, Massachusetts, and Texas.
- Regulatory acceptance and the cleanup goals are being achieved.
- Other technologies at full scale like GAC or biological are not being used for drinking water applications. These technologies have processes not yet certified for drinking water use. Bio does seem more viable for treating impacted groundwater not discharged for public drinking.

### Design Considerations

- Regulatory cleanup goal, defining the objective.
- Understanding the impact of competing anions on resin capacity is essential for reliable performance. System design should allow for expected seasonal changes in water quality. High total dissolved solids needs more O&M.
- Treats a range of perchlorate concentrations. A system will require more resin O&M when the concentrations > 100 ppb.

### Single or regenerable

- Perchlorate selective resins make systems more efficient. This is a key reason for using single-use systems as well as the fact that resin prices have fallen significantly during the past several years. Better selective resins remove perchlorate more efficiently, saving time and money.
- Single-use resins require disposal. Regenerable resins create a brine. The brine waste and spent regenerant solution require disposal.
- Capital costs for system design, installation, and operation and maintenance are dependant on site conditions and cleanup goals. You will spend less capital costs on a single-use system (less mechanics) but spend more replacing spent resin.

## Granular Activated Carbon (GAC)



- ▶ GAC
  - Adsorption
  - Polishing
  - Regeneration
  
- ▶ Tailored GAC (T-GAC)
  - Perchlorate selective
  - Preload
  - IX process



Three vessels at Fontana, CA site

Granular carbon is manufactured from high-carbon-content materials such as coal, wood, or coconut shells.

- Activating (heating) carbon material to form (GAC) will produce more surface area for contaminants to adsorb. Part of the surface area of each standard (virgin) GAC particle is positively charged. This surface area attracts negatively charged contaminants, such as perchlorate. However, because the positively charged surface area of standard carbon is limited; using standard GAC is not effective in removing high concentrations of perchlorate from groundwater.
- Good at polishing to address low perchlorate levels.
- Thermal or chemical regeneration

Tailored GAC (T-GAC) - adsorptive capacity may be enhanced through coating the surface with a thin layer of a surface-active substance. There is more surface area to utilize (more of the pore space) and the enhancement (monomers, polymers, etc.) used as a coating serve as an ion exchange type process where the perchlorate is adsorbed and chloride is released.

- Preload a surfactant with iron-oxalic acid
- Surfactant works like ion exchange
- Capture any surfactant that desorbs from the T-GAC onto polishing GAC
- Thermal or sodium borohydride regeneration treatment of T-GAC

## Granular Activated Carbon Summary



### ► Advantages

- A proven technology but full scale limited
- Carbon can be regenerated
- Tailored to be perchlorate selective
- Treatment train for co-contaminants



### ► Disadvantages

- Less effective at high concentrations
- Not a complete destruction process
- Water quality (temperature, pH, etc.)
- Pretreatment and backwashing
- Tailoring agent needs drinking water certification
- Tailoring targets perchlorate but limits co-contaminants

#### Advantages

A proven technology with supporting data that has been placed in full-scale operation.

The carbon material can be regenerated for reuse. Thermal regeneration or destruction destroys the perchlorate ion – no brine/resin toxic waste to manage as with IX systems.

Tailoring for perchlorate selectivity

Treats VOCs and explosives

#### Disadvantages

Less effective when perchlorate concentrations are high (>100 ppb)

Not destructive, carbon regeneration does produce waste concerns.

Water quality effects efficiency and can cause quicker breakthrough (temp, pH, and total dissolved solids).

The presence of competing ions (such as nitrate and sulfate) and higher concentrations of perchlorate will result in faster breakthrough times for perchlorate, driving up O&M costs

Pretreatment and backwash requirements

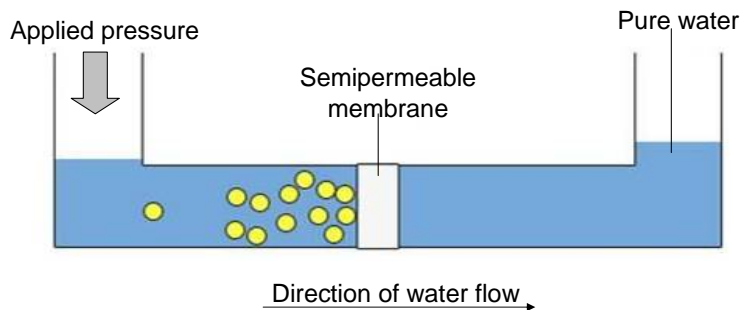
Tailoring helps adsorb perchlorate but minimizes adsorption of other contaminants



## Membrane Filtration

### ► Reverse Osmosis (RO)

- Filtration under high pressure
- Home Systems (Point of Use)
- Pretreatment or polish usage
- Perchlorate-laden brine



#### Bench scale testing for municipal systems

Reverse osmosis (RO), also known as hyperfiltration, is a membrane filtration technology where water is demineralized using a semi-permeable membrane operating at high pressure. RO has long been used to remove ions from drinking-water supplies.

- Water containing perchlorate is driven under high pressure through a semi-permeable membrane that does not allow contaminants with a molecular size greater than the membrane cut-off size to pass. Purified water passes through the RO membrane into a fresh-water section leaving a perchlorate-laden brine solution.
- Home systems available. There is a national standard (NSF/ANSI Standard 58) that covers reverse osmosis systems for perchlorate (130 ppb perchlorate to 4 ppb or less in the treated water).
- High energy and maintenance requirements
- Good as pretreatment or polish on big systems
- The brine needs proper disposal

## Other Innovative and Emerging Technologies



- ▶ Nanofiltration
- ▶ Electrodialysis
- ▶ Capacitive Deionization
- ▶ Electrolysis
- ▶ Ultraviolet Laser Reduction
- ▶ Zero-Valent Iron (ZVI) Reduction
- ▶ Nanoscale Bimetallic Particles
- ▶ Titanium Reduction
- ▶ Hydrogen Gas Membrane



Other innovative and emerging technologies are primarily bench-scale (laboratory) studies.

Nanofiltration uses membranes to preferentially separate fluids or ions under low pressure.

- Not as fine a filtration process as RO,
- Does not require as much energy as RO.
- Membrane with a pore size in the range of approximately 0.0001 to 0.005 microns

Electrodialysis is a type of membrane treatment technology that uses an electrical current to effect separation (electrodialysis cell).

- The cell consists of a feed (diluate) compartment and a concentrate (brine) compartment formed by an anion exchange membrane.
- Water is fed through a series of these cells called stacks where the electrical current and membranes work to separate.
- Historically been the desalination of brackish water or seawater as an alternative to RO
- Fouling problems decrease the efficiency
- Pretreatment required

Capacitive deionization is an electrochemical technology primarily for desalinating brackish water like the electrodialysis, but can also be used to remove perchlorate ions.

- Separates ions from solution using an electric field applied between electrodes rather than a membrane.
- The negative electrode attracts positively charged ions (cations) such as calcium, magnesium, and sodium, while the positively charged electrode attracts negative ions (anions) such as perchlorate, chloride, nitrate and silica.
- This technology, patented in 1995 by Lawrence Livermore National Laboratory (LLNL)

Electrolysis is the process of decomposing an electrolyte solution into positive and negative ions using electricity. During the process, electricity splits up some of the water being treated into its atomic parts (hydrolysis). Perchlorate is reduced at the cathode.

Ultraviolet (UV) Laser Reduction uses photons that can provide the activation energy necessary for some molecules in water solution, such as perchlorate, to react. The rate of perchlorate reduction has been shown to be a function of the UV light intensity, as well as the concentration of electron donors (iron).

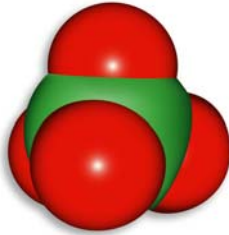
ZVI w/UV. Tests have shown that perchlorate can be reduced by metallic iron, and furthermore that UV light can accelerate the reaction rate to levels that could make the process viable for practical applications.

Nanoscale bimetal particles have large surface areas and high surface reactivity. Provides enormous flexibility for in situ applications.

Titanium ions reduce perchlorate ions in acidic aqueous solutions, but that the reaction is quite slow. This process may be suitable for perchlorate destruction in conditions of high acidity and/or high salt concentrations for which biological remediation is not feasible.

Hydrogen gas membranes works to filter perchlorate from water. Catalysts are incorporated into membrane for deployment in a continuous flow reactor.

## Questions & Answers



? Questions ?


? Questions ?



No associated notes.

## Remediation Technologies (continued)

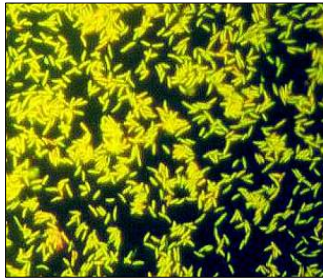


- ▶ Water
  - Physical
    - Ion exchange or carbon
  - (Q&A break)
  - ▶  • In situ biological
    - Carbon source and amendments
  - Ex situ biological
    - Bioreactors
- ▶ Soil
  - In situ biological
  - Ex situ biological
    - Composting
  - Thermal
    - Incineration
- ▶ Phytoremediation
  - Roots

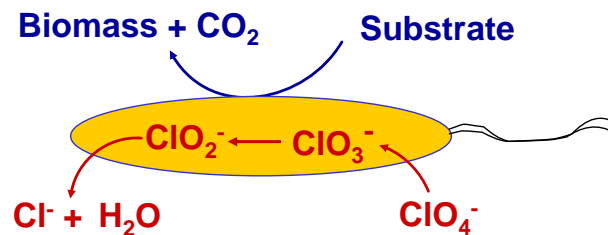
No associated notes.

## Perchlorate Biodegradation

- ▶ Perchlorate-reducing bacteria are common in nature and widely distributed
- ▶ Perchlorate is utilized as a terminal electron acceptor
- ▶ Perchlorate is reduced completely to chloride ion and water
- ▶ Many different substrates (electron donors) support growth of perchlorate-reducing bacteria



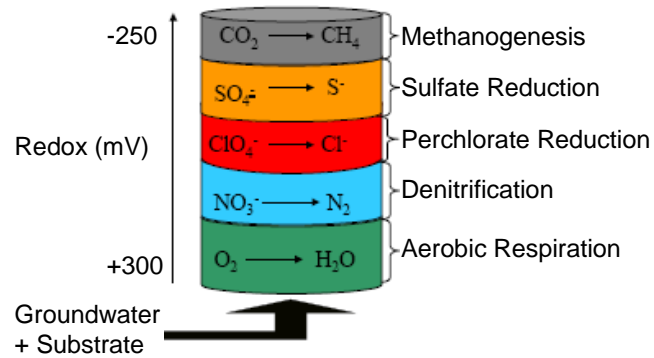
*Azospira suillum* JPLRND



No associated notes.

## Perchlorate Biodegradation (continued)

- Perchlorate biodegradation occurs under mildly reducing conditions, after denitrification but before sulfate reduction



No associated notes.

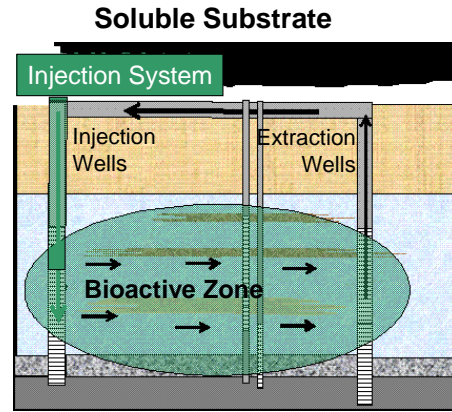
## In Situ Bioremediation

- ▶ *In situ* bioremediation usually entails adding a suitable carbon substrate (i.e., electron donor) to stimulate indigenous perchlorate-reducing bacteria
- ▶ Bioaugmentation is rarely necessary
- ▶ Amendment strategies
  - Mobile amendment systems
    - Soluble substrate addition with groundwater recirculation for mixing
  - Fixed biobarriers
    - Slow release substrates emplaced via injection or in trenches to create reactive barriers

No associated notes.

## Mobile Amendment Systems: Groundwater Recirculation Systems

- ▶ Soluble substrates
  - Examples: sodium lactate, benzoic acid, citric acid, ethanol
- ▶ Active mixing
  - Continuous or semi-continuous pumping to enhance mixing of substrate with groundwater
- ▶ System design: Source treatment or cutoff barrier
- ▶ Several field tests complete
- ▶ One full-scale system
  - AMPAC (former PEPCON Site), Henderson, NV



No associated notes.

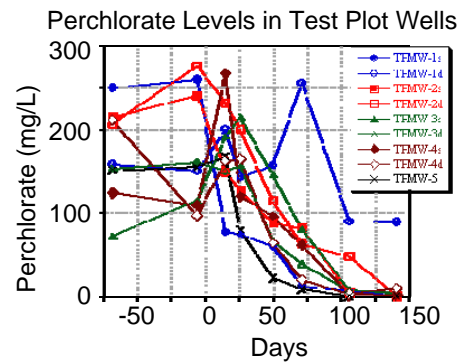
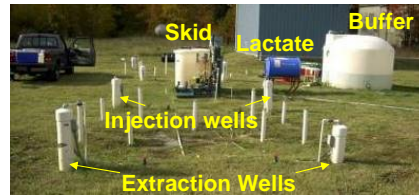


## Mobile Amendment Field Demo



### Indian Head Division Naval Surface Warfare Center, Maryland

- ▶ Source area (hog-out)
  - Shallow groundwater (6 ft)
  - High perchlorate (50-250 mg/L)
  - Low pH
- ▶ Intermittent pumping (~ 1 GPM)
  - Sodium lactate
  - Carbonate buffer
- ▶ Results
  - > 95% perchlorate removal in 8/9 wells in 15 weeks



No associated notes.

## Mobile Amendment: Full Scale



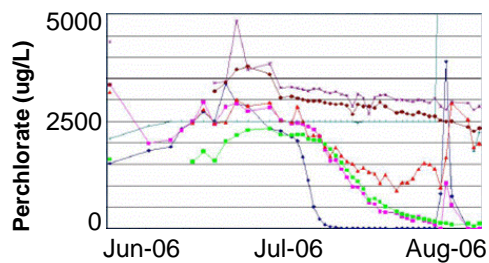
### AMPAC (former PEPCON site), Henderson, Nevada

#### ► Cutoff barrier

- ~ 250-350 gallons per minute (GPM) flow
- 10-12 mg/L perchlorate
- Continuous pumping
- 9 extraction wells
- Sodium benzoate
- Chlorine dioxide as biocide



See  
Appendix A,  
p. A-21-28



PEPCON site operated from 1958 – 1988. Groundwater plume running north for ~ 2 miles toward the Las Vegas Wash. Perchlorate down to 350' with concentrations ranging from ~ 600 ppm in source area to 1 ppm at toe of plume. Installed completed in late 2006. 9 extraction wells convey water to a plant where it is amended with sodium benzoate as an electron donor (chlorine dioxide as a biofouling agent) then reinjected in a series of 6 wells. The intended flow is 250-350 gpm, and the system is treating ~ 10-12 mg/L perchlorate (~ 40-50 lbs perchlorate per day). See early results in wells closest to the system – downgradient. Biofouling of the injection wells is a significant O&M concern for this system and all active in situ systems.

## Fixed Biobarriers

- ▶ Slow release substrates
  - Examples: vegetable oil, emulsified vegetable oil, hydrogen-release compound (HRC), cheese whey, compost
- ▶ No pumping
  - Rely on natural gradient
- ▶ System design: source treatment or cutoff barrier
  - Trench systems
  - Direct substrate injection
- ▶ Several field tests complete
- ▶ One full-scale system
  - Naval Weapons Industrial Reserve Plant, McGregor, Texas



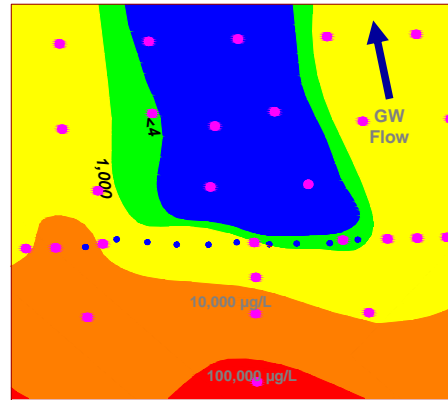
No associated notes.

## Fixed Biobarrier Case Study



### Emulsified Oil Injection; Aerospace Site, Elkton, Maryland

- ▶ Source area (impoundment)
  - Shallow alluvium (10-20 ft)
  - Perchlorate ~ 1-10 mg/L
  - Neutral pH
  - Groundwater flow ~ 80 – 150 ft/yr
- ▶ Barrier design (50 ft pilot)
  - Direct EOS Injection
  - 10 points; 5 ft on center
  - 11 gal EOS; 165 gal chase per well
- ▶ Results
  - < 4 ug/L downgradient of barrier in 6 months



Perchlorate in groundwater 6 months after EOS injection

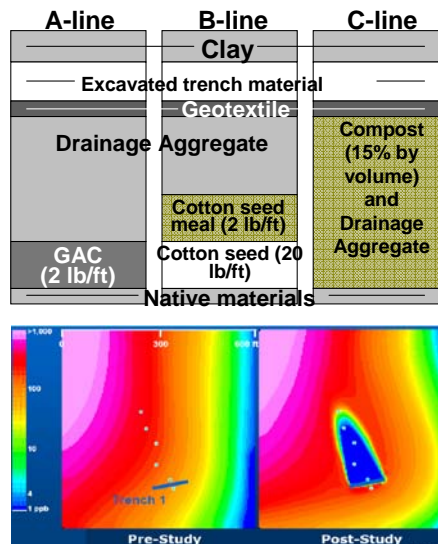
No associated notes.

## Fixed Biobarrier: Full Scale

### Trench Barrier System: Naval Weapons Industrial Reserve Plant, McGregor, Texas

See Appendix A,  
p. A-31-38

- ▶ Several permeable reactive barriers
  - > 12,000 ft total length
  - Differing designs; 25 feet deep
  - Filled with mushroom compost, wood chips, meal, aggregate
  - Lines for acetate addition
- ▶ Results
  - Significant reductions in downgradient perchlorate



Several trench designs were tested to cutoff a shallow perchlorate plume beginning in 1999. Approximately 4,000 ft of trenches were subsequently installed in Area S in 2003. Filled with 4,800 tons of drainage aggregate, mushroom compost, soybean oil saturated wood chips. Included subsurface piping for later substrate addition if necessary. Based on early success, another 9,000 ft was installed in 2005.

## In Situ Bioremediation: Strengths and Limitations



### ► Advantages

- Lower capital costs
- Destruction of contaminants *in situ*
- Perchlorate-reducing bacteria are naturally occurring
- Can potentially treat co-contaminants
- Many different system configurations

### ► Disadvantages

- Secondary water quality considerations
  - Mobilization of metals
  - Methane and sulfide generation
- Biofouling of active systems

No associated notes.

## Ex Situ Bioremediation

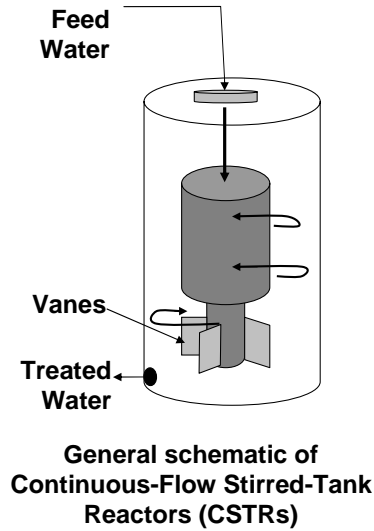
- ▶ Bioreactor designs for groundwater and wastewater
  - Continuous-flow stirred-tank reactors (CSTRs)
  - Fluidized-bed reactors (FBRs)
  - Packed-bed reactors (PBRs)



No associated notes.

## Continuous-Flow Stirred-Tank Reactors (CSTRs)

- ▶ Suspended-growth reactor with continuous influent and effluent flow
- ▶ Most commonly applied to the treatment of high industrial wastewaters
- ▶ Generally best suited for low-flow, high-strength waste streams
- ▶ Can treat some co-contaminants, such as nitrate and RDX
- ▶ Two full-scale systems installed



No associated notes.



## Full-Scale Continuous-Flow Stirred-Tank Reactor (CSTR) at Hodgdon Powder



### Pyrodex Plant in Herington, Kansas

- ▶ Gunpowder manufacturing
  - Perchlorate >3000 mg/L
  - Nitrate >2000 mg/L
  - 3 gpm flow rate
  - Substrate-desugared molasses
- ▶ Effluent discharge to Publicly Owned Treatment Work (POTW)
  - Inoculated April, 2003
  - Regulatory Permit <100 ug/L
  - < MDL (20 ug/L)

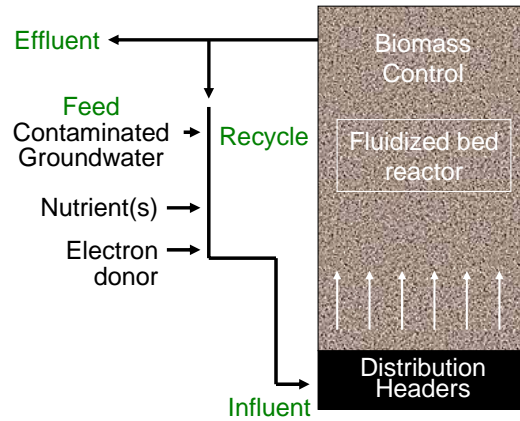


**Dual-Phase Continuous-Flow Stirred-Tank Reactor (CSTR) system at Pyrodex Plant, Herington, KS**

Two 2500 gal reactors with a residence time of 8-30 hrs to treat perchlorate. Treated greater than 2M gals since installation in 2003.

## Fluidized-bed Reactors (FBRs)

- ▶ Uses solid media, often sand or granular activated carbon to support microbial biofilms
- ▶ Applicable for wide range of perchlorate concentrations (10 ppb to > 500 ppm)
- ▶ Can treat some co-contaminants, such as nitrate, chlorate and RDX
- ▶ Permittable for drinking water treatment in California
- ▶ 5 full-scale systems in operation (16 reactors total)



General flow schematic of  
a Fluidized Bed Reactor (FBR)

No associated notes.

## Full-scale Fluidized Bed Reactor System in Henderson, Nevada



- ▶ 9 reactors total
- ▶ Ethanol used as electron donor
- ▶ Operational since 2004
- ▶ Treating perchlorate
  - From ~250 mg/L
  - To < 4 ug/L
- ▶ 1,000 gallons per minute (GPM) flow
- ▶ Treats
  - ~ 400 tons perchlorate per year
- ▶ Discharge to Las Vegas Wash



Fluidized Bed Reactor (FBR)  
System in Henderson, Nevada

This system, which was installed in 2004, currently consists of nine 14'-diameter fluidized bed reactors. The reactors are ~ 26' tall. The ethanol (electron donor) tank is visible in the foreground. The first bank of vessels consists of four of the FBRs (vessels 1,3,4,6 from the left) and two conical biomass separators (vessels 2 and 4, respectively).

## Packed-bed Reactors (PBRs)

- ▶ Fixed-film bioreactor that uses a solid media to support biodegradative organisms
- ▶ No full-scale PBRs, but pilot testing has shown that this reactor design can effectively remove perchlorate and nitrate in groundwater
- ▶ Permittable for drinking water treatment in California



Pilot-Scale PBR Tested at  
Redlands, California

This pilot-scale system was tested in Redlands, CA. It consists of an upflow PBR packed with porous plastic media. The dimensions of the reactor are ~ 6' tall x 2' wide x 1' deep. The groundwater flow rate of the pilot system is ~ 1 GPM.

## Example of Treatment Costs

- ▶ As perchlorate concentration increases, ion exchange becomes appreciably more expensive than biological treatment
- ▶ Site-specific costing is necessary

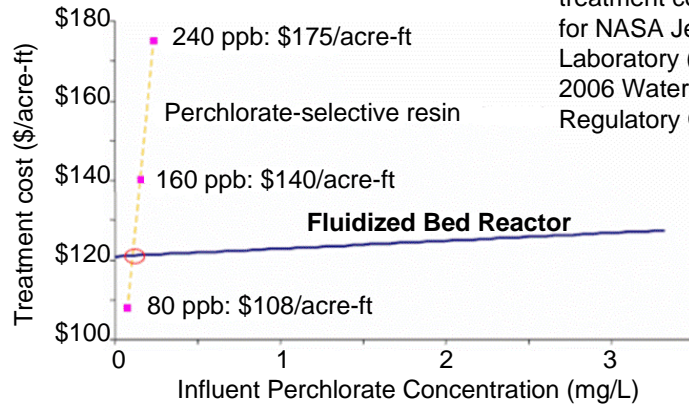


Figure 3.2 Estimated treatment cost comparison for NASA Jet Propulsion Laboratory (JPL). From 2006 Water Quality/Regulatory Conference

No associated notes.

## Summary – Bioremediation of Water



- ▶ Full-scale technologies are available for *in situ* and *ex situ* perchlorate bioremediation
- ▶ A variety of considerations are involved in selecting a bioremediation technology
  - Plume or wastewater characteristics
  - Remedial objectives
  - Water use and reuse
  - Cost

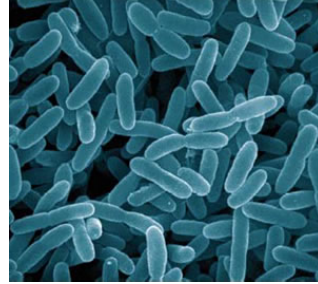


No associated notes.

## Biological Treatment of Soil



- ▶ Source area treatment
  - Site investigation
  
- ▶ Microbial technologies
  - In situ and ex situ approaches
  - All rely on microbially mediated perchlorate reduction
    - Requires anaerobic conditions
  - Both require “effective” delivery of substrate/donor and possibly other amendments



***Dechloromonas***  
strain of perchlorate  
reducing proteobacteria

Perchlorate degraders are widespread in soils and the process appears to occur under a wide range of environmental conditions. Perchlorate remaining in the vadose zone may represent a major continuing source of perchlorate to the groundwater, therefore source area treatment may be warranted. Need a good site characterization to identify the source. Due to its affinity to soil particles, delineation should be checked to the water table, not just to non-detect.

Similar to in situ bio for groundwater – need a mildly reducing (anaerobic) environment, substrate delivery, substrate selection, nutrient balance and, microcosm studies all important.

There are in situ and ex situ approaches, delivery of donor and amendments to the source area is a key.

## In Situ Microbial Approaches



### Surface amendment strategies

#### ► Liquid amendments

- Ethanol, acetate, molasses, or mushroom compost “tea”
- Sprinkler irrigation injection or infiltration gallery

#### ► Solid amendments

- Manures
- Surface spreading with irrigation/precipitation infiltration
- In situ soil mixing



Aerojet (Cavitt Ranch)  
California

In situ treatment at the surface addresses hot spots.

Liquid amendments – At the Aerojet facility in California, soil-washing with an anaerobic slurry was made using saturated soils and a variety of electron donors – ethanol, manure, food waste, vinegar and molasses.

Solid amendments can be applied but then must be mixed in and watered. Solid amendments at Aerojet included manure overlays and calcium magnesium acetate. This anaerobic composting was used at perchlorate hot spots. Compost was later tilled into soil to enhance perchlorate destruction at the surface.

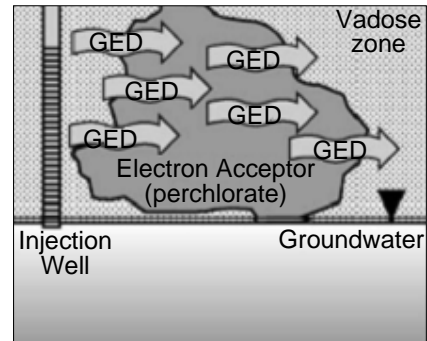


## In Situ Microbial Approaches (continued)



### Subsurface amendment strategies

- ▶ Liquid/solid amendments
  - Ethanol, acetate, molasses
- ▶ Gas-phase amendments
  - Anaerobic bioventing
  - Gas injection



Gaseous Electron Donor (GED) Injection

Perchlorate in the deeper vadose zone. Electron donors directly applied to the vadose zone. Liquid and gaseous delivery systems offer the two general approaches of supplying donors to the vadose zone.

Liquid and solid amendments are mixed in with surface soils (0 – 3 feet) as discussed in the previous slide. Once mixed they can be mobilized with water to greater depths to stimulate perchlorate biodegradation. The liquid nutrient amendments generally perform better at sites where the contamination is deep or the clay content is high. The type and amount of soil amendments, clay content, field capacity, and water application rate determine the biodegradation rate of perchlorate.

Gas-phase amendments, anaerobic bioventing can disperse further into the unsaturated materials than liquids. However, gaseous injection may cause soils to lose moisture to levels that do not support biodegradation.

Carrier gases like nitrogen or hydrogen can be amended with a donor and injected into the soil to flush oxygen and enhance anaerobic conditions. Radius of influence is a key.

## Ex Situ Microbial Approaches



- Composting – ex situ soil treatment through bulking and organic amendment to allow thermophilic microbial activity



Longhorn Army Ammunition Plant  
Texas



Former Munitions Facility  
California

Ex situ treatment through thermophilic activity (composting – organisms growing at high temperatures).

Soils can be excavated and screened to remove rock and debris. Soil is then mixed with water and amendments in treatment or containment cells. Then indigenous anaerobic bacteria reduce the perchlorate to chloride. Treatment can continue in a controlled environment. Water is added, soils tilled, and samples collected for data.

At the Longhorn Ammunition Plant in Texas, cells were divided to test various nutrient amendments including cow manure, chicken manure, methanol, ethanol, acetate, molasses, and cotton gin waste. The McGregor Naval Weapons Plant near Waco, Texas used citric acid (carbon source), nitrate and phosphate-fertilizers (micronutrients), and soda-ash (buffer).

## Thermal Treatment



- ▶ Ex situ
- ▶ Destructive process through incineration
- ▶ Temperature range
  - ~600 -1100°F
- ▶ Treated soil may be suitable for placement back on site



Massachusetts Military Reservation

The thermal desorption system uses heat to separate contaminants from the soil and then thermally destroys them.

- Rocks and other debris are removed
- Soil is fed into a rotating drum and heated to between 600 and 1,100°F.

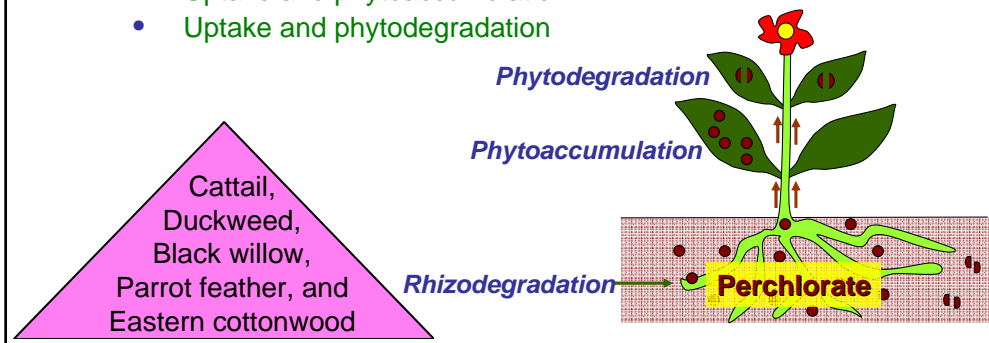
These high temperatures dry the soil, burn off any organic material and drive off contaminants from the soil, so that they are caught in the exhaust or off-gas.

The main advantage is complete destruction of perchlorate and it treats co-contaminants as well. A disadvantage would be the high temperature and energy requirements.

Massachusetts Military Reservation (MMR) ran a system for about three years. Approximately 60,000 tons of soil were treated from 100 mg/kg to below remediation goal of 4 ug/kg during full-scale operation.

## Phytoremediation

- ▶ Relies on the activity of plants and root zone bacteria, directly or indirectly, to remove/degrade the perchlorate
- ▶ Predominant mechanisms for phytoremediation in order of importance
  - Rhizodegradation
  - Uptake and phytoaccumulation
  - Uptake and phytodegradation



Phytoremediation, this is a treatment technology that uses natural plant processes and microorganisms associated with the root system to remove, contain, or degrade perchlorate in soil, sediment, and water. Use of plants and their root zone associated microorganisms can either sequester or degrade contaminants or a combination of the two processes.

The main mechanism is rhizodegradation, at the roots.

- Biostimulate root zone of plants to enhance rapid rhizodegradation of perchlorate, accelerate cleanup, and minimize plant uptake of perchlorate into the leaf tissues. The root system acts like a bioreactor.
- Enhancement achieved by providing carbon and electron donors to the root zone at planting or during the operation and maintenance phase.
- No secondary waste production if phytoremediation is engineered to enhance rhizodegradation.

Because uptake and phytodegradation is a slower process, it poses ecological risk resulting from the phytoaccumulation of the perchlorate taken up and transported mainly to plant leaves.

Phytoaccumulation has led to health concerns regarding perchlorate levels in lettuce and other food crops irrigated with perchlorate-contaminated water. The occurrence of perchlorate in dairy milk is due in part to cows feeding on grass grown on perchlorate-contaminated soils and/or water.

Plants tested that have shown effectiveness:

- Cattail
- Duckweed
- Black willow
- Parrot feather, and
- Eastern cottonwood

## Phytoremediation Strengths and Limitations



### ► Advantages

- Costs
- High public acceptance
- Controlled environment
- Treat co-contaminants
- Other land use goals

### ► Disadvantages

- Depth and climate
- Slow process
- Accumulation
- Ecological risk
- Regulatory acceptance



Various plants have been tested for effectiveness. However, there has been concern on how far down phytoremediation can be effective since root systems don't go very deep.

Testing has been done where deeper groundwater can be pumped and used to water plants in designed systems. In a controlled area (like a constructed wetland), water can be applied at a proper rate for roots to utilize and work on the degradation process.

### Advantages

Low cost. Phytotechnologies generally compare well with costs for aboveground treatment technologies,

High public acceptance,

Controlled environment through constructed wetlands.

No secondary waste production if phytoremediation is engineered to enhance rhizodegradation,

Can also treat other common co-contaminants, such as VOCs and explosives

Wetland banks and site improvements

### Disadvantages

Depth and climate restrictions, plant growth can be impacted, so you need a variety during the treatment period

Potential for transfer of contaminants from soil and groundwater into the food chain, an ecological risk until degraded.

Relatively slow process - if phytoremediation is not engineered to achieve rhizodegradation enhancement directly impacts sustainability and time-effective risk mitigation,

Regulatory acceptance – still a new technology without cost and performance data. Difficult for site managers to select and obtain approval for phytoremediation of perchlorate.

See other ITRC documents that address phytoremediation and wetland construction available at [www.itrcweb.org](http://www.itrcweb.org) under "Guidance Documents."

## Case Study: The Merrimack River

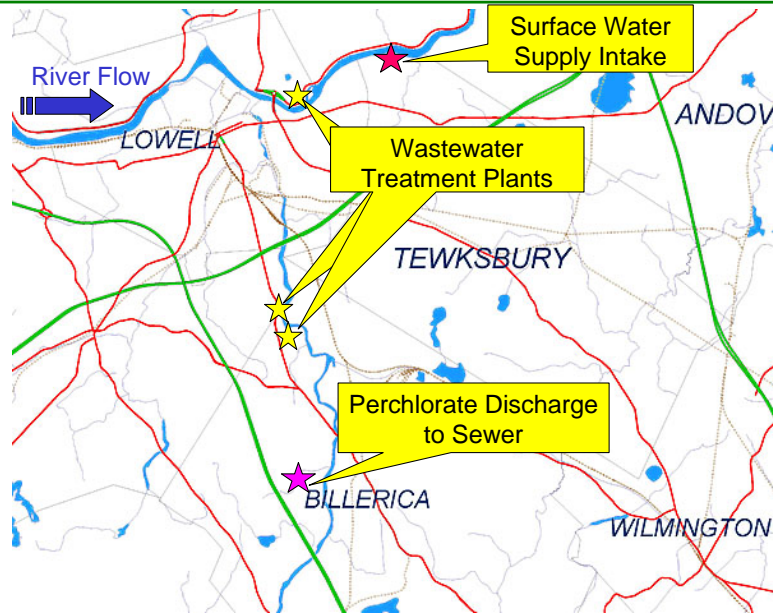


- ▶ Hits greater than 1  $\mu\text{g/L}$  in surface water supply (Tewksbury)
- ▶ Massachusetts Department of Environmental Protection conducted source investigation
  - Ambient sampling of Merrimack and Concord rivers
  - Influent, process, and effluent sampling of wastewater treatment plants
  - Mapping and sampling of sites, facilities and other sources along the rivers
  - Concurrent sampling using IC and LC/MS/MS



No associated notes.

## Merrimack River Overview Map



No associated notes.

## Merrimack River – Results

- ▶ Source identified as perchloric acid used for manufacturing surgical and medical instruments
- ▶ Batch process explains data variability
- ▶ Pretreating wastewater using ion exchange



No associated notes.



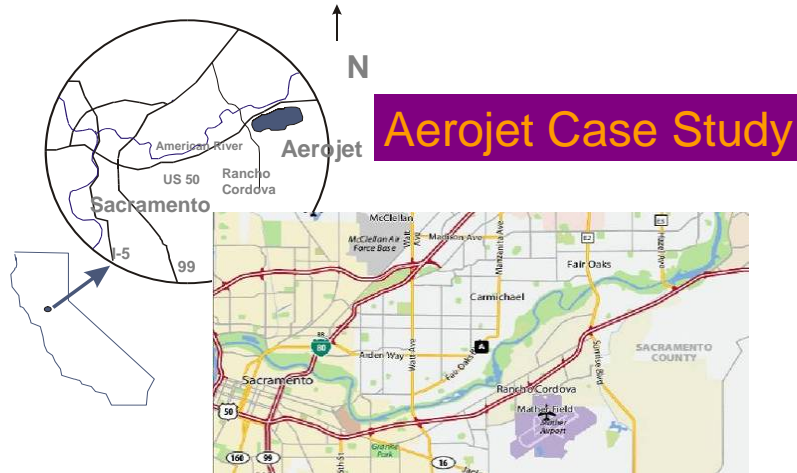
## Case Study: Aerojet Sacramento Site, Rancho Cordova, California



The Aerojet Case Study can be found in Appendix A of the Remediation Technologies for Perchlorate Contamination in Water and Soil (PERC-2, 2008) Tech-Reg Document, approximately page 164 of the PDF.

This is an interesting photo of the ground surface at the Aerojet site showing the topography left after surface gold mining at the turn of the century.

## Aerojet Location



- Aerojet is in northern California east of Sacramento in Rancho Cordova. Aerojet is east of the airport shown here and generally south of the American River shown on the map.

## Aerojet Historical Remediation Overview



- 1982 Begin TCE groundwater remediation
- 1995 Perchlorate provisional reference dose 4-18 ug/l
- 1995 Perchlorate detected off-site at 6000 ug/l
- 1996 Aerojet required to include perchlorate removal and evaluate extent of off-site perchlorate



This photo provides a rare glimpse on how a jet propelled rocket engine is test fired.

In 1982 Aerojet began remediation of TCE at the site using pump and treat technology. Following treatment the water was re-injected downgradient of the plume to create a hydraulic barrier to contaminant transport. At the time the system was designed the perchlorate concentration in the treatment effluent was not known to be a problem.

In 1995 EPA established a provisional reference dose for perchlorate of approximately 4-18 ug/l in drinking water. At that time the analytical detection limit for perchlorate was only 400 ug/l. The resulting discrepancy between reference dose and detection limit fueled subsequent refinement in the analytical method. Today a GCMS/MS method can provide a quantitative detection of as low as 0.94 ug/l.

Also in 1995 Aerojet detected perchlorate downgradient from the groundwater injection field at approximately 8000 ug/l.

Subsequently in 1996 the Regional Water Quality Control Board requested that Aerojet investigate the extent of the off-site plume and remediate perchlorate in groundwater.

## Aerojet Background



- ▶ 13,000 acre site
- ▶ Former gold mine removed 100 feet of cover disturbing clay cover
- ▶ Groundwater depth 10 to 100 feet with radial flow due to bedrock
- ▶ High quality low total dissolved solids (TDS) and metals aquifer local drinking water supply (300-600 feet bgs)

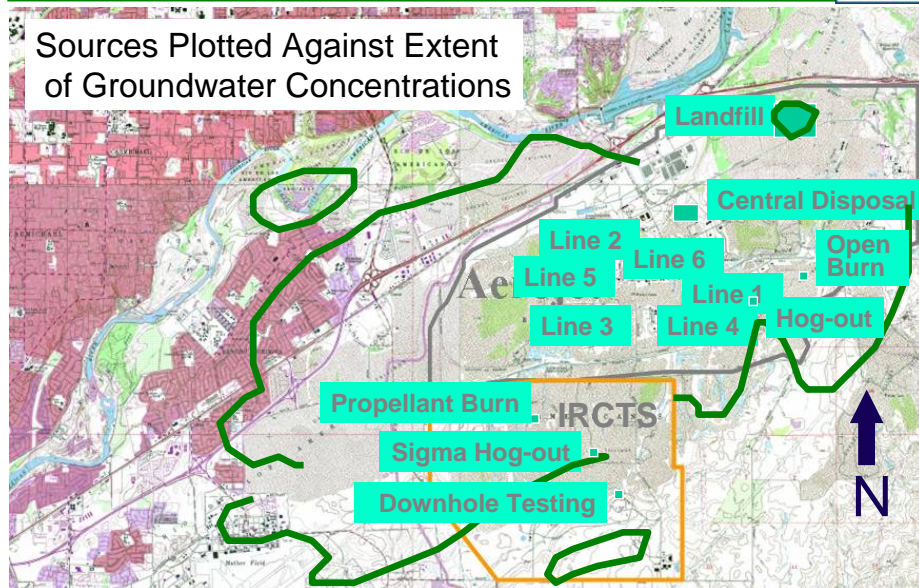


Groundwater in the area of Aerojet is of high quality and the mountain front to the east of Aerojet creates an important recharge corridor for the regional aquifer. Due to the shallow bedrock at the eastern edge of the property there is groundwater at 10-feet below the ground surface. As you move west across the 13000 acre property the depth to bedrock and groundwater increases till groundwater on the western portion of the property is 100-feet. The bedrock subsurface causes groundwater to flow radially across the site with north south and westerly components.

## Aerojet Background (continued)



Sources Plotted Against Extent of Groundwater Concentrations



The horizontal extent of perchlorate concentrations within the project area are shown as green contours. Along the southern extent of the map you can see the former 400 acre McDonnell Douglas parcel (IRCTS) and the former Downhole Testing Facility.

Manufacturing areas are called manufacturing “lines” and are shown here as the line number. These areas of manufacturing included the use of solvents and water to clean casings, toolings and wash down of the facilities. Water and spent solvents from the process went into those swails created by the former gold mining process. These unlined ponds were located across the site.

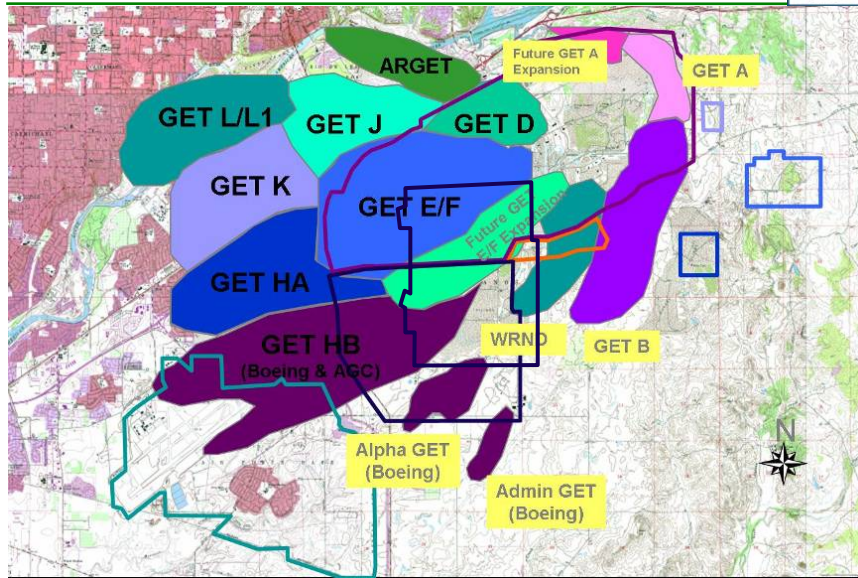
Hog Out Facilities are locations where a water knife was used to safely remove unused perchlorate from missile casings. This is the largest source of perchlorate at Aerojet reaching 100,000 ug/l in groundwater.

**Propellant and open burn locations** were locations where waste accelerant was stockpiled and burned for disposal. Over time precipitation has caused migration of the perchlorate through the vadose zone and into the groundwater.

**There were four** landfills at the site containing up to 26,000 ug/l of perchlorate in groundwater. This perchlorate was leached from card board boxes used to transport and store perchlorate stock.



## Aerojet Groundwater Extraction Treatment (GET) Areas



The distribution of Groundwater Extraction Treatment areas (GETs) are shown on this map. Each GET represents a separate treatment system. As you can see from the distribution of the capture zones for each GET, there is radial groundwater flow across the site.

Groundwater remediation as of March 2008 is as follows:

- 83 billion gallons treated to date
- Current flow 13,000 gallons per minute (gpm).
- Estimated Future Flow – 20,000 gpm
- 150 lbs chemicals removed daily
- Over 730,000 lbs removed to date

## Aerojet Overview Groundwater Remediation



- 1982 Aerojet Commences Air Stripper Groundwater Remediation (for TCE)
- 1996 Fluidized Bed Reactor Pilot Test Groundwater Extraction Treatment (GET) F
- 1998 Fluidized Bed Reactor with Ultraviolet Treatment of groundwater added GET E/F – 4 Reactors with 5,000 GPM capacity
- 1998 Ion Exchange Resin Treatment used at GET B and D and off-site at GETs H, J, and K. These lower flow, lower concentration locations make resin more cost competitive
- 2000-2007 In situ bioremediation field studies using various designs including soluble mobile amendments (ethanol, citric acid) and permeable reactive barriers



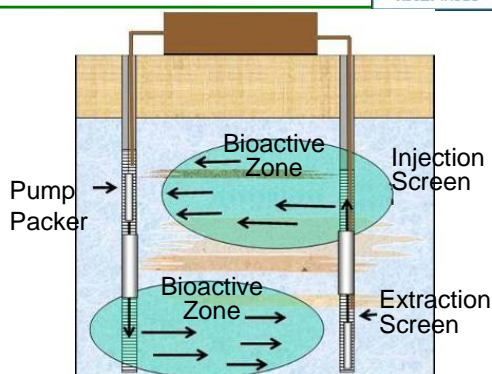
The Fluidized Bed Reactor - Groundwater extracted through 21 wells is diverted to a system employing four 14-foot-diameter, 22-foot-high bioreactors operating in parallel. Each reactor contains 44,000 pounds of carbon substrate to which ethanol is added as an electron donor. The Fluidized Bed Reactors are equipped with a bed-cleaning eductor system that typically adjusts the reactor bed height once each day. Retention time within each reactor averages 12 minutes. The system currently operates at a rate of approximately 5,000 gallons per minute and has demonstrated the capability to treat up to 6000 gallons per minute and is capable of reducing an influent concentration of 8000 ug/l to less than the 4 ug/l detection limit.

The ion exchange system located at GET D is the second largest treatment system on the site. This system includes twelve 48-inch-diameter ion exchange vessels arranged in two parallel banks of six (Figure 3), which allows for operation of a two-stage "lead/lag" treatment process operating at a rate of 980 gpm. Each vessel contains 60 cubic feet of a "once-through" gel anion resin targeting perchlorate removal. This site and the offsite GET locations have much lower concentrations of perchlorate than the area remediated by the fluidized bed reactor making utilization of ion exchange effective.

## 76 Current Pilot Studies – In Situ Bioremediation of Perchlorate in Groundwater



- ▶ Horizontal flow treatment wells – pilot test just completed (ESTCP)
- ▶ Citric acid as electron donor
- ▶ Chlorine dioxide for biofouling control
- ▶ Perchlorate reduced by >95% in shallow wells and in deep downgradient wells
- ▶ Attempt to minimize secondary groundwater impacts by tight control of electron donor addition (e.g., mobilization iron and manganese)



Perchlorate in shallow downgradient monitoring wells during Aerojet HFTW demonstration.

The pilot treatment system at the Environmental Security Technology Certification Program (ESTCP) project creates a biologically reactive zone in groundwater utilizing horizontal flow treatment wells. The process demonstrates a 95% reduction in perchlorate and has seen success at controlling the mobilization of iron and manganese. It appears that controlling the oxygen reducing potential is key to limiting mobilization.



## Remediation of Perchlorate in Soils



- ▶ Cavitt Ranch – 2001
  - Burn and disposal area
    - Composting and direct application
  - Calcium magnesium acetate (CMA)
  - Ex situ composting – rapid reduction (\$65 yd<sup>3</sup>)
- ▶ Hog-out area – 2006 ongoing
  - Vadose zone and shallow groundwater
    - Biologic treatment
  - Idea: biologically active zone below the water table
  - Flushing citric acid (electron donor) and dehydrated bacteria



Ten Cavitt Ranch locations with high levels of perchlorate ranging from 50 to 11,000 mg/kg were remediated by excavating the soil, amending the soil with cow manure and calcium magnesium acetate and then returning it to the excavation where it was covered with a 6-12 inch layer of composted cow manure. The Cavitt Ranch soil remediation activity was expanded by Aerojet in 2001. Cost is competitive at \$65 per cubic yard and it worked very well in the relatively shallow soil situations underlain by bedrock. A deeper vadose zone pilot study utilizing a similar technique was not as successful.

Aerojet conducted a pilot test at the former propellant hog-out facility to determine the feasibility of using a radial biobarrier to biodegrade perchlorate in both the 30-foot vadose zone and shallow groundwater. Groundwater was extracted and potassium oleate added as an electron donor. The water was then returned to the former hog-out impoundments where it leached perchlorate through the vadose zone and into the groundwater. The perchlorate was then pulled through the biologically active zone and degraded. The process was later modified to include bacterial inoculation.

## Summary of Today's Training Topics



- ▶ Overview/update
- ▶ Treatment selection considerations
- ▶ Categories of treatment technologies for groundwater and soil
- ▶ Groundwater treatment technologies
  - Physical
  - In situ and ex situ biological
- ▶ Soil treatment technologies
  - Thermal
  - In situ and ex situ biological
- ▶ Regulatory and permitting
- ▶ Case study



Well, in conclusion I would like to point out the success stories that are demonstrated today. The Henderson Site, the Aerojet Site and the Indian Head Mass Pilot Study all have had a greater than 90% reduction in perchlorate. This result is a wonderful example of how people in the industry have stepped up to the plate and rapidly developed treatment technologies. Additionally, I think this training clearly points out how widespread and pervasive perchlorate concentrations are in both soils and groundwater. Clearly this is not just a defense and aerospace issue, but one that even affects public utilities using sodium hypochloride to disinfect drinking water.

## Thank You for Participating



- ▶ 2nd question and answer break
- ▶ Links to additional resources
  - <http://www.clu-in.org/conf/itrc/perremtech/resource.cfm>
- ▶ Feedback form – *please complete*
  - <http://www.clu-in.org/conf/itrc/perremtech/feedback.cfm>

Need confirmation of your participation today?

Fill out the feedback form and check box for confirmation email.

Links to additional resources:

<http://www.clu-in.org/conf/itrc/perremtech/resource.cfm>

Your feedback is important – please fill out the form at:

<http://www.clu-in.org/conf/itrc/perremtech/feedback.cfm>

### The benefits that ITRC offers to state regulators and technology developers, vendors, and consultants include:

- ✓ Helping regulators build their knowledge base and raise their confidence about new environmental technologies
- ✓ Helping regulators save time and money when evaluating environmental technologies
- ✓ Guiding technology developers in the collection of performance data to satisfy the requirements of multiple states
- ✓ Helping technology vendors avoid the time and expense of conducting duplicative and costly demonstrations
- ✓ Providing a reliable network among members of the environmental community to focus on innovative environmental technologies

### How you can get involved with ITRC:

- ✓ Join an ITRC Team – with just 10% of your time you can have a positive impact on the regulatory process and acceptance of innovative technologies and approaches
- ✓ Sponsor ITRC's technical team and other activities
- ✓ Use ITRC products and attend training courses
- ✓ Submit proposals for new technical teams and projects