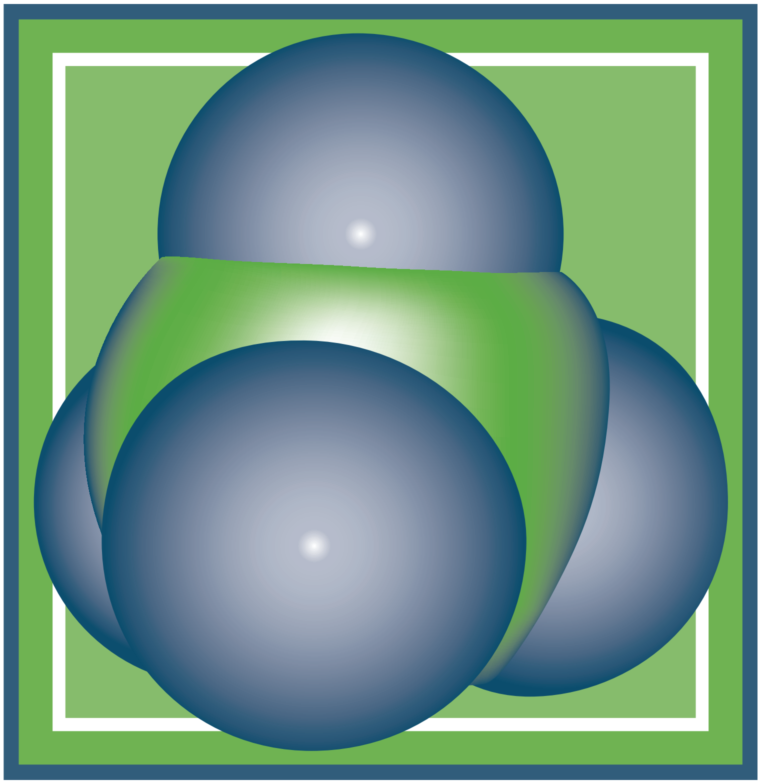
Technical/Regulatory Guidance

Remediation Technologies for Perchlorate Contamination in Water and Soil



March 2008

Prepared by
The Interstate Technology & Regulatory Council
Perchlorate Team

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EXECUTIVE SUMMARY

Perchlorate, an anion, consists of one chlorine atom bonded to four oxygen atoms (ClO_4^-) and is both naturally occurring and manmade. Highly soluble and mobile in water, perchlorate is generally very stable in the dissolved state. Most of the attention focused on perchlorate has concerned its presence in groundwater and surface water. However, perchlorate can also be found in soil and vegetation and has entered the human and environmental food chains. 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.

Past management practices were not concerned with the release of perchlorate to the environment because it was not recognized or regarded as a contaminant of concern. Widespread perchlorate presence in the United States was observed after the spring of 1997 when an analytical method was developed with a quantitation level of 4 parts per billion. Subsequent advances in analytical chemistry have proven perchlorate to be more widespread in the environment than previously thought. Chapter 1 provides an overview of perchlorate issues.

The success or failure of a treatment technology often depends on having a complete understanding of the nature and extent of the release. Site investigators start with a conceptual site model, which is gradually refined through sampling and other investigative techniques. Chapter 2 discusses this and other site evaluation issues.

A variety of remediation technologies are currently commercially available and are being used for perchlorate remediation. Most of these remediation technologies fall into two broad categories: physical and biological treatment processes. Chapter 3 discusses considerations for the selection of a particular remedy.

Perchlorate remediation system installation and operation could involve various local, state, and federal government departments. These entities might require compliance to various rules or permits that directly or indirectly involve the operation of planned remedial systems. Information regarding compliance with local, state, federal or tribal regulations to install and operate a perchlorate treatment system should be researched and obtained at the outset of a project to prevent unforeseen delays to treatment projects. Chapter 4 discusses regulatory considerations.

Physical treatment processes remove perchlorate from impacted media but do not alter its chemical composition. Considerable progress has been made in developing innovative physical processes for removing perchlorate from drinking water, groundwater, and surface water. Some technologies are proven and commercially available, while others are still in the research and development phase. Chapter 5 discusses physical processes for treatment of perchlorate-impacted water, including ion exchange, granular activated carbon, reverse osmosis, nanofiltration/ultrafiltration, electrodialysis, capacitive deionization, and electrolysis.

Ion exchange, the most proven and widely accepted physical process technology for perchlorate treatment, is a process by which ions of a given species are displaced from an insoluble exchange material by ions of a different species in solution. Perchlorate selective ion exchange targets perchlorate using conventional ion exchange resin beds with specially designed resins that preferentially remove perchlorate anions.

Biological degradation of perchlorate involves reducing bacteria, which are widespread in the environment. Perchlorate-reducing bacteria have the ability to grow in either the presence or absence of air, provided proper nutrients are available in the environment. Both in situ and ex situ biological treatment systems have been applied at full scale to treat perchlorate. Chapters 6 and 7, respectively, discuss in situ and ex situ bioremediation technologies for perchlorate in water.

Soil impacted with perchlorate can be treated using in situ bioremediation, ex situ bioremediation, and ex situ thermal treatment. Shallow soil can generally be treated in place or excavated and treated on site by bioremediation methods such as composting or intrinsic bioremediation. Excavated soils may also be treated using thermal desorption. Chapter 8 discusses remediation technologies for soil. Phytoremediation shows promise to treat both vadose zone soils and groundwater. Chapter 9 discusses phytoremediation and constructed wetlands. Cost-effective treatment of deeper occurrences represents an important challenge.

Most environmental sites affect local communities at some level. The federal government, states, and sovereign tribal nations regulate and/or mandate the participation of stakeholders in the investigation and remediation process. Remediation concerns common to all stakeholders typically relate to health issues, economic or monetary issues, inconvenience, and natural resource issues. Chapter 10 discusses stakeholder issues such as these.

Chapter 11 provides a comprehensive listing of references, and appendices are included for case studies, team contacts, and acronyms. Case studies include the Aerojet site in Rancho Cordova, California; the American Pacific Corporation site near Henderson, Nevada; and the Naval Weapons Industrial Reserve Plant in McGregor, Texas. These case studies document the remediation of perchlorate in soil and groundwater using a variety of technologies.

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1. INTRODUCTION AND SCOPE

Perchlorate is both a naturally occurring and manmade anion consisting of one chlorine atom bonded to four oxygen atoms (ClO_4^-). Highly soluble and mobile in water, perchlorate is generally very stable in the dissolved state. Most of the attention focused on perchlorate occurrence has concerned groundwater and surface water. However, perchlorate can also be found in soil and vegetation and has entered the human and environmental food chains. The potential for 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 thus result in decreased thyroid hormone production.

In general, past management practices did not prevent the release of perchlorate to the environment because it was not recognized or regarded as a contaminant of concern. Widespread perchlorate contamination and natural occurrence in the United States was observed after the spring of 1997 when an analytical method was developed with a quantitation level of 4 parts per billion (ppb). Advances in analytical chemistry have allowed for the detection of perchlorate at gradually lower levels ever since and have proven perchlorate to be more widespread in the environment than previously thought. Two recent studies found perchlorate at detectable concentrations in every person tested. A multistate study at Texas Tech University found perchlorate in the breast milk of 20 women (Kirk et al. 2005). Another study conducted by the Centers for Disease Control and Prevention included a random subsample of 2820 study participants (males and females) aged 6 and older, and perchlorate was found in every person tested (Blount et al. 2006).

Public awareness and concern regarding perchlorate have increased as a result of several factors:

- Perchlorate is an emerging contaminant with associated health uncertainties and subsequent fear of the unknown.
- Initial environmental detections of perchlorate releases were interesting because of their association with solid rocket propellant manufacturing and disposal areas.
- Drinking water supplies of a large number of Americans have detected perchlorate.
- More recent studies have reported perchlorate occurrence in the human food chain.
- Perchlorate has the potential to impact sensitive subsets of the general population (e.g., pregnant women, fetal development, and young children).
- The growing database of occurrence shows that perchlorate is detected in all media (groundwater, surface water, soil, vegetation and animal tissue) and found around the world.

In the United States, the American Water Works Association funded a study of the occurrence of perchlorate in drinking water (Brandhuber and Clark 2005, 2006). Relying on numerous data sources, including state and federal programs, the study found that perchlorate occurs nationally in drinking water, with regional hot spots. The levels found were generally low levels, typically below 12 μg/L. The majority of detections in the study (Figure 1-1) were not associated with identified releases of perchlorate. The study also found that the number of detections continue to increase as the perchlorate detection levels decrease.

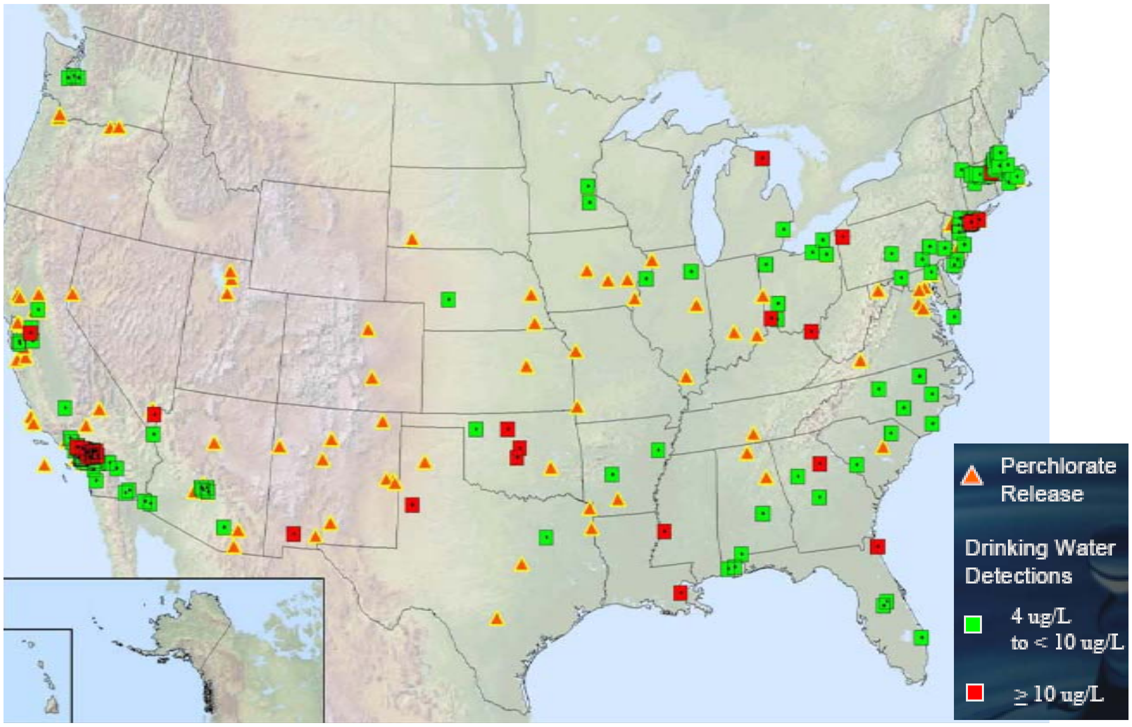


Figure 1-1. Perchlorate releases and drinking water detections.

1.1 ITRC Perchlorate Team

The Interstate Technology & Regulatory Council (ITRC) Perchlorate Team was formed in 2004 to address technical issues associated with perchlorate. The Perchlorate Team consists of representatives from environmental agencies, state and federal agencies, private consultants, vendor companies, academia, and public stakeholders. See Appendix B for contact information.

This is the Perchlorate Team's second document. The first, *Perchlorate: Overview of Issues, Status, and Remedial Options* (ITRC 2005), provides regulators and other stakeholders a basic overview of a broad spectrum of information regarding perchlorate sources, sampling and analysis techniques, risk issues, risk management strategies, and regulatory status. A brief summary of remediation technologies is included. Please see that overview for background material not included in this remedial technologies document.

ITRC develops and delivers training courses via the Internet to reach a geographically dispersed audience of the environmental community. These courses are based on ITRC guidance documents and create a unique forum for the exchange of technical and regulatory information. The Perchlorate Team conducts an Internet training course related to the first overview document. A training course based on the current document will be offered commencing in 2008. A current course listing and class schedule are maintained at www.itrcweb.org.

1.2 Purpose

The purpose of this document is to review technologies applicable to the remediation of perchlorate in water and soil. In addition, the social, political, and regulatory barriers to the deployment of these technologies are examined. The goal of the document 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.

This document is intended to serve as a technical and regulatory reference for state and federal regulators, consultants, project managers, and other stakeholders during selection of a cleanup technology for perchlorate. Where possible, important regulatory issues to consider during site characterization, design, construction, and monitoring are identified and discussed. Case studies are included to highlight various applications and potential complicating issues that may arise when implementing particular technologies.

Table 1-1 lists the remedial technologies discussed in this document.

Table 1-1. Perchlorate remediation technologies

Physical	Biological
Ion exchange	Monitored natural attenuation
Granular activated carbon	In situ bioremediation
Membrane/filtration technologies	Ex situ bioremediation
Emerging technologies	Phytotechnology
	Constructed wetlands

1.3 Organization

This document is divided into 11 chapters. Chapters 1–4 provide information that should be considered prior to selecting a remedial technology. Chapters 5–9 describe various technologies applicable to the treatment of water and soil and include potential stakeholder concerns associated with those technologies. The information is weighted towards technologies applicable to water treatment, since perchlorate is highly soluble and mobile and the majority of perchlorate sites include water as an impacted medium. Chapter 10 discusses potential stakeholder concerns, and Chapter 11 provides an extensive listing of references. Appendix A contains case studies, Appendix B provides team member contact information, and Appendix C defines the numerous acronyms used throughout the document.

1.4 Additional Resources

Governmental agencies, private organizations, and academia have expended significant resources to develop scientifically defensible information regarding the occurrence of perchlorate in the environment, in drinking water and food supplies, and in humans. Research has also been done on the risk of perchlorate to humans and ecological receptors and to develop remedial technologies. Key among the research groups are the U.S. Environmental Protection Agency (EPA), the Strategic Environmental Research and Development Program (SERDP), and the Environmental Security Technology Certification Program (ESTCP) of the Department of

Defense (DOD), the U.S. Food and Drug Administration (FDA), the U.S. Geological Survey (USGS), academic institutions, and various state environmental agencies. It is important to understand that this document provides only a snapshot in time of the currently available information. The available information on perchlorate is expanding rapidly. Chapter 11 lists references used in the preparation of this document. Readers are encouraged to continually review the latest research to remain up to date on perchlorate.

1.5 Future Endeavors

Past waste management practices did not prevent the release of perchlorate to the environment because it was not recognized as a contaminant of concern. In the hope of preventing future releases, Massachusetts and California have developed best management practices for perchlorate-containing materials. Additionally, ongoing studies by USGS have revealed that naturally occurring perchlorate is more widespread than previously believed. Differentiating between naturally occurring and anthropogenic perchlorate is the subject of much current research and is also driving the development of analytical techniques designed to reliably detect perchlorate at lower concentrations. These developments might guide any future efforts by ITRC concerning perchlorate.

2. SITE EVALUATION CONSIDERATIONS

2.1 Introduction

The success or failure of a treatment technology depends on understanding the nature of the problem. For example, the Town of Tewksbury, Massachusetts found perchlorate in the public water supply system (MassDEP 2005). The source of the perchlorate was identified as a manufacturing plant in the adjacent town of Billerica that discharged wastewater containing neutralized perchloric acid to the municipal sewage system and ultimately to the Merrimack River, where Tewksbury obtains its water supply. The Town of Tewksbury avoided installing a costly drinking water treatment system by working with the Town of Billerica, the Massachusetts Department of Environmental Protection (MassDEP), and the manufacturing plant in a collaborative effort to control the discharge of perchlorate at the source. Thus, the public and the environment were protected using source control treatment as the appropriate technology. This example is discussed more extensively the box on p. 5.

The purpose of any site evaluation, like this example from Massachusetts, is to characterize the sources of the contaminant as well as its fate and transport in the environment. Rather than start with a blank slate, site investigators start with a conceptual site model (CSM), which is gradually refined through sampling and other investigative techniques. Reliance on the CSM leads to the selection of appropriate treatment technologies to address the contaminant.

2.2 Setting Goals and Objectives

Investigations of sites with known or suspected perchlorate contamination are similar to those for other contaminants. Establishing the desired outcome at a site will maximize the efficiency and success of the investigation. For example, the desired outcome may be to protect an underlying aquifer from perchlorate contamination. Other outcomes may be to establish how (or whether) property development can occur at a site with perchlorate soil contamination or to develop a strategy to protect the public from perchlorate found in drinking water sources.

Perchlorate Remediation Example—Source Discharge Control

In August 2004, low levels (1–3 μg/L) of the perchlorate ion were first detected in the Town of Tewksbury, Massachusetts public water supply system, which draws its water from the Merrimack River, the second largest river in the state. This finding precipitated an effort by MassDEP to locate the source of perchlorate discharge to the river involving a systematic and iterative sampling program tracking the contaminant upstream of the Tewksbury water intake. The sampling program focused on three potential sources of perchlorate discharge: industries that directly discharge to the Merrimack River and the Concord River (a tributary), the processes at the wastewater treatment plants that discharge to the rivers, and industries that discharge to the municipal sewerage systems.

Eventually, the source was traced to the discharge from the Town of Billerica Wastewater Treatment Plant, located on the Concord River, 5 miles upstream from the Tewksbury intake in the Merrimack River. Testing at the wastewater treatment plant included the influent, prior to chlorination, and the effluent. Monitoring of the effluent from the Billerica wastewater plant from September to November 2004 showed levels of perchlorate in the range of 12–800 μg/L. Influent levels during this period ranged from nondetections to 640 μg/L. The plant is a secondary treatment system servicing a community of 50,000 with an average daily flow of 3.1 million gallons/day (mgd), including 0.40 mgd of industrial wastewaters. At this average flow rate, approximately 3–5 kg/day of perchlorate was being discharged from the plant. This finding was consistent with the 2–4 μg/L concentrations of perchlorate that were being detected in the Concord River downstream of the discharge, where river flow rates varied in the range of 250–600 cubic feet per second (CFS). The highest level detected was 10.3 μg/L of perchlorate, recorded in September 2004, when the Concord River flow rate was at its lowest (142 CFS). While the Concord River is approximately one-tenth the size of the Merrimack, the water from the Concord River hugs the southern bank of the Merrimack River channel for several miles downstream of the rivers' confluence. The Tewksbury water intake is located near the southern bank.

The use of a modified EPA Method 314.0 ion chromatography (IC) was shown to reliably detect and quantify 1 cg/L (ppb) or greater concentrations of perchlorate in water samples collected from the Merrimack and Concord Rivers (i.e., less than 500 μS/cm specific conductance). However, this method could not provide definitive identification and quantification of the perchlorate ion in wastewater due to potential matrix interferences, so MassDEP used ion chromatography/tandem mass spectrometry to conduct testing/verification testing of wastewater matrices.

Investigations undertaken by the Town of Billerica and MassDEP identified approximately 40 suspect industries discharging to the Billerica sewerage system and prioritized them based on reported chemical use. Eventually, these investigations identified the apparent sole source of perchlorate discharge to the municipal sewerage system: a processor of surgical and medical materials, which was using approximately 200 gallons/month of perchloric acid. Although only a small portion of this acid was discharged (as rinse water) to the sewer system, it equated to an average of 5 kg/day of perchlorate. Perchloric acid use at this facility was conducted in "batch" operation processes, which explained the variability (and spikes) in perchlorate data into and exiting the Billerica wastewater plant. It is interesting to note that this industrial wastewater discharge was not in violation of the facility's permit, as perchloric acid and perchlorate were not (at that time) regulated contaminants in the wastestream.

Currently, this company is treating its wastewater prior to discharge into the Billerica sewerage system, using an ion exchange technology that reduces influent perchlorate concentrations of 2000 mg/L to less than 0.050 mg/L in the effluent.

Initial investigation planning involves setting specific objectives, which will become the measures for determining the success of the investigation. For a perchlorate site, specific objectives may include the following:

- determining the source (industrial production, fertilizer application, inadvertent by-product, disposal, natural geologic deposit, or other)
- understanding how the perchlorate is distributed and its fate in the environment
- evaluating how perchlorate enters a drinking-water system
- identifying potential co-contaminants
- establishing natural or ambient concentrations of perchlorate
- determining receptors and complete exposure pathways

Once specific project objectives have been established, the project team should evaluate expected uncertainties and reach consensus regarding the acceptable level of uncertainty. The team must discuss how these uncertainties affect the realization of the desired project outcome. For example, at a specific site it is found that perchlorate concentrations in soil are highly variable and represent a significant level of uncertainty. However, it may be possible to model perchlorate mass loading to the underlying aquifer with sufficient accuracy for project decision making to occur. This modeling is calibrated using groundwater concentration data from monitoring wells. In this case, the high level of variability in soil would not be a constraint to achieving the desired project outcome (control of the groundwater concentration level), and a special data collection strategy to resolve this would not be necessary. However, a properly designed groundwater monitoring network would be essential.

An understanding of the governing regulatory program (Comprehensive Environmental Response, Compensation and Liability Act [CERCLA], Resource Conservation and Recovery Act [RCRA], state-led program, etc.) will establish the framework for the investigation and subsequent activities. Each of these regulatory programs requires the investigation team to perform specific planning activities (although the terms used for these activities differ), which include establishing clear project goals, determining the land use, researching applicable regulatory criteria, making effective use of all existing data, careful thought into ensuring sample representativeness, and preparation of detailed work plans. The investigation team must confront inherent challenges, such as geologic and contaminant heterogeneity. Effective site investigation planning will involve the preparation of a preliminary CSM, which summarizes all that is known or can be surmised regarding the contamination origin, fate, transport, and receptors.

2.3 Stakeholder Participation and Community Involvement

The success of a site investigation and remedial technology in cleaning up a site is measured not only by the effectiveness of a particular technology, but by the acceptance of the stakeholders and community affected by the project. The key to a better decision process is to identify potentially interested stakeholders early and invite them to participate on the project team.

Local residents may have specific information about the site history or operational practices that is helpful in guiding the investigation. Community stakeholders may have specific concerns about a particular medium or how that medium provides a benefit to the community and why it should be protected. For example, local anglers may have concerns about eating fish caught in a surface water body impacted by perchlorate. There may be a large local population that relies on fishing for subsistence. This information must be included in the exposure pathways analysis.

Additionally, community stakeholders may have specific concerns about the remedial technologies considered for a site. If a treatment system is to be located near a business or residence, noise and aesthetic concerns need to be taken into consideration. There may be concerns about injection of microorganisms for an in situ biological treatment system or about shipment of residual for off-site treatment or disposal.

2.4 Conceptual Site Model

EPA defines a CSM as, "a planning tool that organizes information that already is known about a site and identifies the additional information necessary to support decisions that will achieve the goals of the project" (www.epa.gov/oswer/riskassessment/glossary.htm#c). The CSM can have different meanings to different disciplines. For example, risk assessment professionals may use the term to refer to an evaluation of complete receptor exposure pathways, and a geologist may think of a CSM in terms of a hydrologic model for the site. To avoid confusion, it is useful for each project team to discuss terminology.

The importance of gathering all existing information about a site and organizing it within a preliminary CSM cannot be overemphasized. The project team uses the CSM to gain a common understanding about the site, to identify data gaps, and eventually for decision making. Some of the benefits associated with creating the CSM include improved team communications, better data interpretation, and ultimately more efficient and effective environmental restoration.

The CSM is not a static work product but is continuously updated as the field work is conducted and data gaps are filled. The CSM integrates (in words, figures, models, etc.) what is known about the site history, perchlorate distribution, geology/hydrogeology, hydrology, geochemistry, potential receptors, and perchlorate fate/transport. A CSM can be presented in many different formats (see Figures 2-1 and 2-2). Initially, multiple variations of the CSM may be possible, and one of the investigation objectives is to determine which is most relevant to the site.

2.4.1 Conceptual Site Model Inputs

At the most basic level, the CSM represents knowledge of site contamination issues. Information from many sources is used to assemble the CSM, as shown below in Table 2-1. Inputs for a typical CSM are discussed in the following subsections.

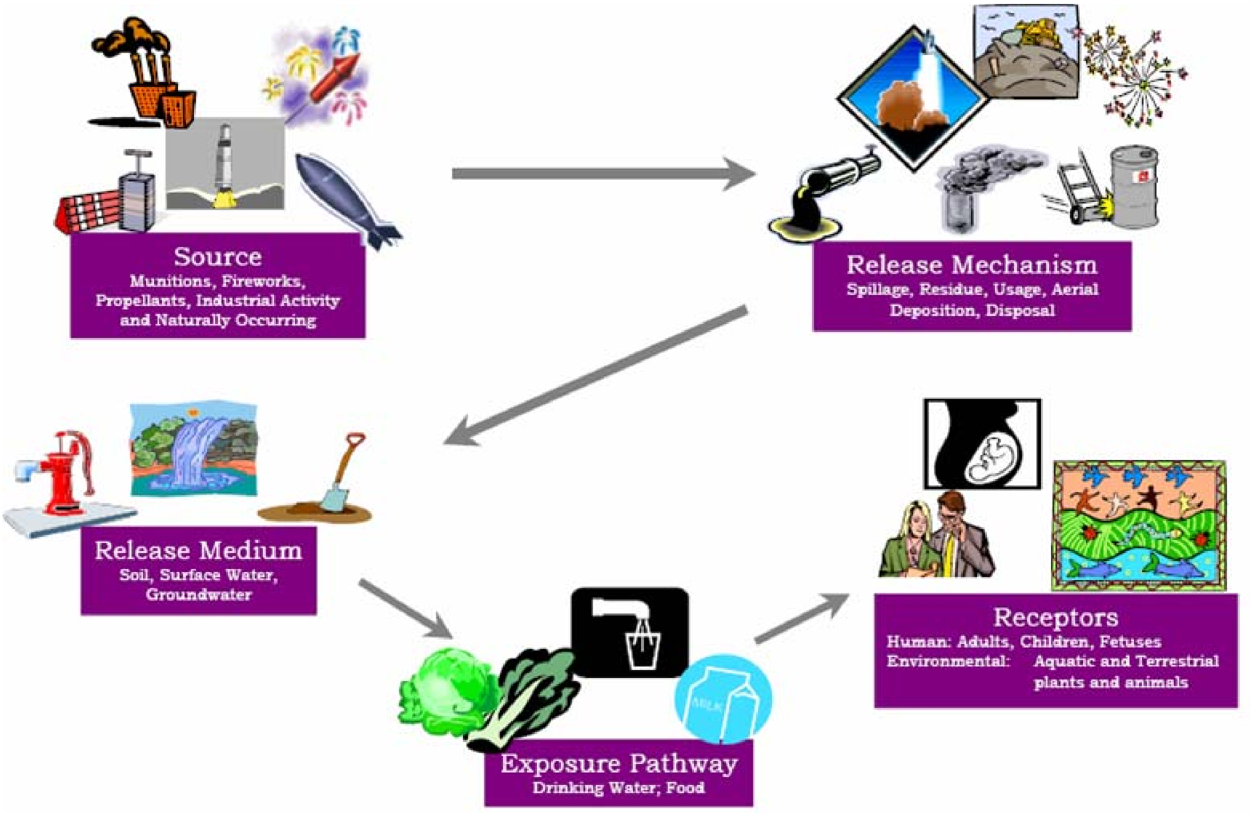


Figure 2-1. Sources of perchlorate for consideration in the CSM.

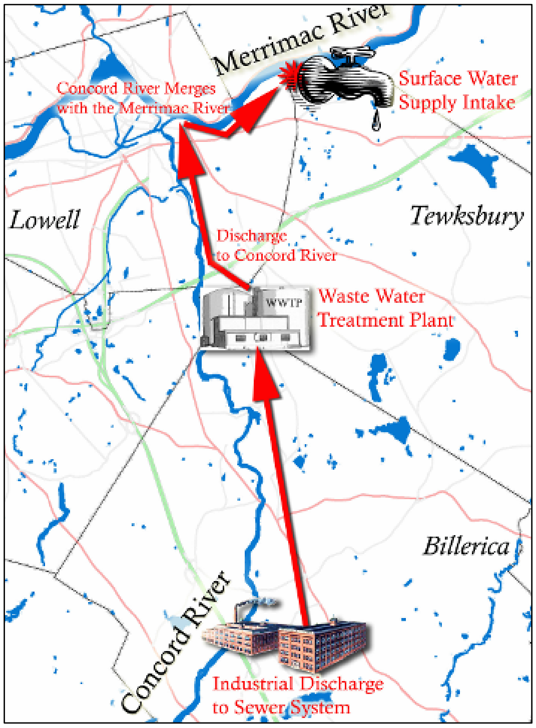


Figure 2-2. Simple CSM.

Table 2-1. CSM data sources

Investigation objectives	CSM component	Potential data sources
• Determining the source (industrial production, application, inadvertent by-product, disposal, natural geologic deposit, or other) • Identifying potential co-contaminants	• Source • Release mechanism	• Historical records • Community stakeholders • Aerial photos • Site contaminant data • Professional judgment
• Understanding how the perchlorate is distributed and its fate in the environment • Establishing natural or ambient concentrations of perchlorate, if applicable	• Affected media • Fate and transport	• Geologic data • Hydrogeologic information • Topography • Meteorology
• Evaluating how perchlorate enters a drinking water system or an ecosystem • Determining receptors and complete exposure pathways	• Exposure route/pathway • Potential receptors	• Toxicity and exposure data • Community stakeholders • Biological surveys • Site development or infrastructure information

2.4.2 Historical Site Information

Potential sites with perchlorate contamination may be identified in three ways. First, facilities known to have produced, used, or disposed of perchlorate-based products are likely to have released perchlorate into the environment. Second, site assessments conducted in support of property transfer or reuse may uncover past releases of perchlorate. These sites are similar to the first category except that oversight agencies may be unaware of potential perchlorate releases until the site assessment determines that they may be present. Finally, discovery of perchlorate in drinking-water supplies may point to upstream sources. These cases are especially challenging, as widespread environmental sampling (using lower detection limits than available just a few years ago) continues to demonstrate the presence of perchlorate in the environment in areas with no known point sources (Jackson et al. 2004, Jenkins and Sudakin 2006). Extensive testing of waterways, aqueducts, or groundwater may be necessary to trace the perchlorate back to the source. Forensic techniques, such as chlorine or oxygen isotope analysis, may be required to distinguish among potential sources, which may include point sources, nonpoint sources (such as agriculture), or even natural deposits.

Typical sources of site history information include (but are not limited to) facility records, aerial photographs, and previous site-sampling information. Using the site history can aid the investigation in the following ways:

- guide the placement of groundwater monitoring wells
- evaluate the potential area or areas to be remediated
- provide information on which contaminants may be present
- provide information to estimate the volume of a perchlorate-containing chemical release
- provide information regarding the likelihood that the release was continuous or intermittent over time as well as the overall time frame of the release

Perchlorate: Overview of Issues, Status, and Remedial Options (ITRC 2005) provides a comprehensive list of potential source activities that may have generated perchlorate.

How perchlorate was used may provide additional information such as the type of potential co-contaminants. The presence of co-contaminants at perchlorate sites depends on facility-specific operations and historical practices. For example, the majority of major weapon systems with solid propulsion, explosive devices, or pyrotechnic devices contain perchlorate compounds. At these sites, typical co-contaminants are volatile organic compounds (VOCs), halogenated solvents, and explosive compounds such as trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-trizine (RDX), and high-melting-point explosive (HMX) (ITRC 2002). The presence of these compounds could make perchlorate treatment systems more difficult to design. Table 2-2 shows co-contaminants that have typically been found at perchlorate sites.

Table 2-2. A partial list of characterized perchlorate-contaminated sites with identified co-contaminants

Site	Contaminated media	Other identified contaminants
Aerojet Facility, Rancho Cordova, California	Groundwater	Trichloroethylene (TCE), N-nitrosodimethylamine (NDMA), nitrate, sulfate
Aerojet Facility, San Gabriel, California[a]	Groundwater	Nitrate, TCE
Big Dalton Well Site, Los Angeles, California[a]	Groundwater	Nitrate, sulfate
La Puente, California[a]	Groundwater	NDMA, 1,4-dioxane, sulfate, VOCs
Confidential site	Groundwater	Nitrate, chlorate[b]
DOD site, West Virginia	Groundwater	Nitrate, sulfate
Edwards Air Force Base, California	Groundwater	Nitrate, sulfate
Henderson, Nevada	Groundwater	Sulfate, sodium, calcium, magnesium, nitrate, boron, hexavalent chromium, chlorate
Lawrence Livermore National Laboratory, Site 300, Livermore, California	Groundwater	VOCs, nitrate, explosive compounds
Pueblo Chemical Depot, Colorado	Soil, groundwater	HMX, RDX, nitrate

[a] These are three different plumes from the same site, San Gabriel Valley Area 2 Superfund Site, also known as the Baldwin Park Operable Unit.

[b] Chlorate may be present as a co-contaminant as well as a potential degradation product. Isotopic analyses of these surrogate chemicals associated with perchlorate may similarly provide a means of source identification and cost apportionment.

Source: Hjeresen et al. 2003.

2.4.3 Geological and Hydrogeological Information

Geology and hydrogeology should be considered due to their potential impact on perchlorate distribution, dispersion, flow path orientation, concentration, depth, and distance traveled. For example, if evaporite deposits are present, the potential for naturally occurring perchlorate to exist must be considered in addition to any anthropogenic sources.

Perchlorate is highly soluble and therefore is likely to be found in the groundwater underlying the location of the original release. The first place to investigate on a site where perchlorate was used is near the expected source area(s). The quantity of perchlorate released, the number of releases, and the time period over which the releases occurred provide some guidance for sample locations. Large single, continuous, or intermittent releases of perchlorate are conditions that indicate a need for soil testing, as well as testing of groundwater/surface water at any point sources, especially in dry or desert environments. Surface soil samples may not contain perchlorate but deeper samples might, so surface and subsurface samples should be taken if soil testing is recommended.

In a dry or desert environment with a deep groundwater table, there can be a precipitation front of perchlorate below the surface but above the groundwater. Perched aquifers, discontinuities in confining layers, seasonal water-level changes, and potential density currents are other complicating factors that point out the importance of understanding the groundwater flow regime. Existing groundwater monitoring wells can be used, along with temporary push-point wells to permit investigators to quickly evaluate the nature and extent of a source. Perchlorate acts like nitrate when dissolved in water and tends to move with the groundwater flow unless stagnant conditions exist. Dissolved-phase perchlorate is not appreciably retarded under most hydrogeologic conditions, and therefore long plumes may develop.

2.4.3.1 Topography

The relationship between topography and perchlorate occurrence can be subtle or direct. Since perchlorate is highly soluble in water, it is easily flushed into drainages and to surrounding surface water bodies or directly into groundwater. Manmade topographic infrastructure such as buried pipelines, surface channels, and even paving or other structures may preferentially redirect groundwater flows, adding to the remediation challenge.

2.4.3.2 Meteorology

The more precipitation, the less likely perchlorate will accumulate due to its high solubility. With anthropogenic sources, precipitation can act to disperse or flush the source and transport dissolved perchlorate to surface water or groundwater. In an arid environment, the dispersal may be limited.

2.4.3.3 Background Sampling

Perchlorate occurs both naturally and as a manufactured compound. The best-known instance of natural perchlorate occurs in mineralogical association with nitrate of soda caliche deposits in Chile. Chilean nitrate ore has been imported into the United States since at least the late 1800s for use as fertilizer; for saltpeter used in gunpowder; and as feedstock to making nitric acid, explosives, fireworks, and additional end products. The natural occurrence of perchlorate and the historically widespread use of Chilean nitrate ore that contained perchlorate can complicate the assessment of a site. The project team should address these issues during the sampling plan design where background (concentrations that represent natural conditions) or ambient (a combination of natural levels and/or nonspecific off-site sources) concentrations of perchlorate may be present.

2.4.4 Fate and Transport Issues

Perchlorate may be released into the environment in the form of a number of different salts, including ammonium perchlorate, potassium perchlorate, sodium perchlorate, and others. All are highly soluble in water, though the solubility of the various salts varies. Perchlorate may also be released into the environment in the form of a liquid, as in the Merrimack River example discussed earlier. This liquid form of perchlorate increases the potential, as well as the speed, of a spill reaching groundwater or surface water.

Perchlorate does not appreciably bind to soil particles, and so the movement of perchlorate in soil is largely a function of the amount of water present and soil permeabilities. Evaporative sequences may alter or inhibit the vertical migration of perchlorate. Perchlorate salts released to the soil in solid form readily dissolve in whatever moisture is available. If sufficient infiltration occurs, perchlorate will be readily leached from the soil. Plants take up soil moisture containing perchlorate in solution through the roots, and several ecological studies have demonstrated the tendency of some plants to concentrate perchlorate in their tissues (Urbansky et al. 2000, Ellington et al. 2001). Perchlorate may be held in solution in the vadose zone by capillary forces. Perchlorate may also be held in the vadose zone by binding agents that were mixed during rocket motor production. A release of perchlorate and associated agents may bind with soil particles and serve as a source for continued leaching to groundwater. In arid regions, crystallized perchlorate salts may accumulate at various soil horizons due to the cycle of evaporation and infiltration.

At the dilute concentrations typically found in groundwater, perchlorate behaves conservatively, with the center of mass of the plume moving at the same average velocity as the water. Dispersion can cause the contaminant front to move faster than the average groundwater velocity. Perchlorate is kinetically very stable under environmental conditions and does not react or degrade in solution under typical conditions. Perchlorate does not biodegrade in groundwater unless sufficient levels of biodegradable organic carbon are present, oxygen and nitrate are depleted, and perchlorate-degrading anaerobic bacteria are present. The combination of high solubility, low sorption potential, and the lack of degradation tends to create plumes that are large and persistent.

If perchlorate is released as a high-concentration brine solution, its movement in the groundwater may be controlled by density effects (Flowers and Hunt 2000). The density contrast between the brine and groundwater may cause the brine to move vertically with minimal influence of groundwater movement and little or no dilution. Brine pools may form on top of confining layers, and significant perchlorate mass may move into low-permeability confining layers by diffusion. The brine pools and perchlorate mass absorbed in confining layers may serve as a long-term source that releases to the groundwater by diffusion. This type of release may occur where perchlorate has been manufactured, at rocket motor washout facilities, or other locations where perchlorate has been slurried or handled in concentrated brines.

2.4.5 Exposure Pathway and Receptors

Once the potential for perchlorate occurrence at a site has been established, an important consideration is to evaluate how a person or ecological receptor (animal or plant) might come into contact with it. This will require an evaluation of current and potential future uses at the site.

The project team should evaluate whether perchlorate has impacted a public water source such as groundwater or surface water. Besides the obvious exposure from drinking and bathing, is the impacted groundwater or surface water source used for growing food crops or animal feed that will subsequently be ingested by people? What is the potential future land use? Could the site be redeveloped to residential or other sensitive exposure pathway uses?

A biological survey should be conducted to evaluate whether contaminated media may impact any ecological receptors. Does contaminated runoff provide water to plants? Do these plants uptake perchlorate sufficiently to affect the plant's life cycle? Will animals that ingest these plants be exposed to perchlorate at concentrations that could cause an adverse affect? If perchlorate is present in surface water, are aquatic organisms affected? Does the surface water body serve as a water source for animals that could be adversely affected?

In some cases, the analysis of potential pathways and receptors may point to additional site characterization needed to address these concerns. In other cases, the project team may find that there is no direct exposure pathway. For example, perchlorate may contaminate groundwater that is not being used as a water source because the aquifer is naturally contaminated with high dissolved solids or high concentrations of naturally occurring arsenic.

2.5 Sample Collection Strategy Considerations

Preparing the preliminary CSM as a part of an investigation planning process (for example, the data quality objectives process) will result in an understanding of the type and density of data needed to resolve uncertainties. In addition, specific data requirements associated with remedial systems under consideration should be gathered during the investigation. When considering analytical methods, the project team should evaluate how the work will be performed (i.e., a static versus a dynamic work plan), potential analytical interferences, co-contaminants, specific requirements of certain regulatory agency programs or DOD policies, and cost. Additionally, some site assessments may require the project team to consider applying more complex techniques that provide a better understanding of the source of the perchlorate, how it is moving in the environment, and whether or not natural attenuation might be possible. Table 2-3 is a matrix that may aid the user in considering the data needed for the design and operation of perchlorate remediation technologies.

2.5.1 Physical and Geochemical Parameters

Collection of standard physical and geochemical parameter data is appropriate for suspected perchlorate-release areas. For example, in arid regions, crystallized perchlorate salts may accumulate at various horizons in the soil due to evaporation of infiltrating rainfall that leached perchlorate from shallower depths. Detailed field logging to document soil types and lithology may identify the potential for such accumulation. Identification of perchlorate-containing minerals is also important in evaluating the potential for naturally occurring perchlorate.

Table 2-3. Data needs matrix for perchlorate CSM development

	Source and historical information					**Contaminant distribution**				**Hydrology**		**Geology and hydrogeology**							**Geo-chem**	**Co-contam-inants**
	Activities employing perchlorate or perchlorate-containing products	**Perchlorate specie(s)**	**Time frame of release(s)**	**Number of releases**	**GW monitoring wells available**	**Amount per release**	**Surface area contamination: large/small**	**Discharge to GW?**	**Discharge to SW?**	**Climate: arid/moist? e.g., <20" per year?**	**Precipitation frequency?**	**Hydraulic transmission characteristic of formations**	**Confined/unconfined**	**Regional GW gradient direction**	**Local GW gradient direction**	**Areal continuity of formations**	**Karst or high-flow situations?**	**Fractured bedrock presence**	**Geochemical characteristics**	**Co-contaminants present?**
Water Remediation																				
Ion Exchange																				
Concentrated Brine Treatment																				
Catalytic Chemical Reduction																				
Ferric Chloride Reduction																				
Biological Reduction																				
Biological Processes																				
Ex Situ Bioremediation																				
Continuous-Flow Stirred-Tank																				
Reactors																				
Fluidized Bed Reactors Packed-Bed Reactors																				
Other Bioreactor Designs																				
In Situ Bioremediation																				
Fixed Biobarriers																				
Mobile Amendments ***Soil Remediation***																				
In Situ																				
Ex Situ Thermal Processes																				
Emerging Processes																				
Vapor-Phase Electron Donor																				
Injection Constructed Wetlands																				
Nanoscale Bimetallic Particles																				
Titanium Chemical Reduction																				
Zero-Valent Iron Reduction																				
Under UV Light																				
Electrochemical Reduction																				
Capacitive Deionization Reverse Osmosis/Electrodialysis																				
Monitored Natural Attenuation																				
Nanofiltration/Ultrafiltration																				
Catalytic Gas Membrane																				

Laboratory analyses for parameters necessary to evaluate potential remedial techniques are important. Co-contaminants such as explosives can make treatment systems difficult to design. Biodegradation of perchlorate in groundwater will not occur unless sufficient amounts of biodegradable organic carbon are present, oxygen and nitrate are depleted, and perchlorate-degrading anaerobic bacteria are present.

Potential Interferences in Analyzing for Perchlorate

There are a number of potential interferents in the analysis of perchlorate, and the quality control (QC) program must take them into account. Some examples of interferents that have been identified as causing false positives in IC include the following:

- Sulfate ion (SO_4^{2-}) elutes before ClO_4^- on most IC columns and tends to tail into the retention time of ClO_4^- due to the broad elution. If there is poor chromatographic resolution, hydrogen sulfate formed from the ^{34}S isotope of sulfur ($H^{34}SO_4^-$, *m/z* 99) can interfere with the qualitative identification of perchlorate. This also applies to IC/mass spectrometry (MS) or liquid chromatography/MS methods if the single ion monitoring mode of detection is used and the *m/z* 99 ion is used for quantitation.
- Polar anions, such as pyrophosphate ($P_2O_7^{4-}$), tripolyphosphate ($P_3O_{10}^{5-}$), and thio compounds, including aromatic sulfonates, such as 4-chlorobenzenesulfonic acid (4-Cl BSA).

One specific concern for perchlorate sampling is the use of commercial laboratory detergents, such as Alconox, Alcotabs, Liqui-Nox, and Neutrad, for equipment decontamination. Laboratory analysis of some detergents has reportedly identified detectable levels of perchlorate. Therefore, if reusable equipment is used for sampling, decontamination must be documented as effective through the use of QC samples to ensure contributions from laboratory and field equipment are not causing high bias in analytical results.

Assessment of degradation potential is based primarily on a review of site-specific data that include the determination of ambient levels of electron donors, electron acceptors, metabolic by-products, geochemical indicators, dispersion trends, and hydrogeology. Other less common means of assessing degradation potential, such as field tests, laboratory microcosm studies, and microbiological analyses, are described later in this document.

2.5.2 Laboratory Analytical Methods

Analytical methodologies for perchlorate are briefly discussed below. Key factors for choosing the appropriate analytical method include the following:

- policy issues—acceptance of method by regulatory agencies
- state/federal laboratory certification (if required by the state or the program)
- sensitivity—the capability of a method or instrument to discriminate between measurement responses representing different levels (e.g., concentrations) of a variable of interest (DOD 2007)
- selectivity—the capability of a test method or instrument to respond to a target substance or constituent in the presence of nontarget substances (DOD 2007)

Analytical chemists use several techniques to detect perchlorate in the environment. Until 2005, the primary analytical method for perchlorate compliance was EPA Method 314.0. However, this method cannot provide a definitive identification and quantification of the perchlorate ion. Use of EPA Method 314.0 was mandatory for the analysis of perchlorate in drinking water under the Unregulated Contaminant Monitoring Rule (UCMR) that expired in December 2003. A number of states may continue to require the use of Method 314.0 for compliance monitoring and also to satisfy requirements for perchlorate testing at facilities operating under Clean Water Act National Pollutant Discharge Elimination System (NPDES) permits. The second Contaminant Candidate List under the UCMR, which was finalized in February 2005, allows for the use of Methods 314.0, 314.1, 331.0, or 332.0 (see Table 2-4). It is important to note that perchlorate sampling and analytical techniques require special considerations due to potential interferences, laboratory contamination, and potential false positives. DOD has mandated the use of SW-846 Methods 6850 liquid spectrometry/mass spectrometry (LC/MS) or 6860 liquid chromatography/tandem mass spectrometry (LC/MS/MS) for wastewater, groundwater, and other aqueous samples and for soil samples associated with environmental restoration/cleanup or range assessment projects. DOD also mandates the use of EPA Methods 331.0 (LC/MS and LC/MS/MS), 332.0 ion chromatography/mass spectrometry and ion chromatography/tandem mass spectrometry (IC/MS and IC/MS/MS) for drinking water samples. If 314.0 is used, all results above the method reporting limit must be confirmed using an MS method (DOD 2007).

Table 2-4. Perchlorate analytical laboratory methods comparison (*Source:* DOD 2007)

Method (technique)	Applicability	Limitations	Target reporting limits
EPA 331.0 (LC/MS) (LC/MS/MS)	• DOD-owned drinking water systems • Applicable to drinking water samples, including those with high total dissolved solids (TDS)	• Pretreatment recommended for samples with high concentrations of sulfate • Validated for drinking water samples only	Drinking water— 0.1 µg/L (LC/MS) 0.02 µg/L (LC/MS/MS)
EPA 332.0 (IC/MS) (IC/MS/MS)	• DOD-owned drinking water systems • Applicable to drinking water samples, including those with high TDS	• Pretreatment recommended for samples with high concentrations of sulfate • Validated for drinking water samples only	Drinking water— 0.1 µg/L (IC/MS) 0.02 µg/L (IC/MS/MS)
SW-846 Method 6850 (LC/MS) (LC/MS/MS)	• Environmental restoration • Operational ranges • Wastewater • Aqueous samples including those with high TDS • Soil samples		Drinking water and groundwater—0.2 µg/L Soil—2 µg/kg Wastewater—<1 µg/L
SW-846 Method 6860 (IC/MS) (IC/MS/MS)	• Environmental restoration • Operational ranges • Wastewater • Aqueous samples to include those with high TDS • Soil samples		Drinking water and groundwater—0.2 µg/L Soil—2 µg/kg Wastewater—<1 µg/L

Method (technique)	Applicability	Limitations	Target reporting limits
U. S. Federal Food and Drug Administration Method (IC/MS/MS)	- Low-moisture foods, bottled water, and milk		Low-moisture foods—3.0 µg/kg Bottled water—0.5 µg/L Milk—3.0 µg/L
Other Available Methods			
EPA 314.0 (IC)	- Mandatory for drinking water samples reported under UCMR 1 - Aqueous samples with low dissolved solids (conductivity <1 mS/cm TDS) and chloride, sulfate, and carbonate concentrations <100 mg/L each	- Subject to false positives due the lack of specificity of the conductivity detector - Validated for drinking water samples only - Inappropriate for use in samples with high TDS	Drinking water—4 µg/L
EPA 314.1 (IC)	- Drinking water samples	- Reduces but does not eliminate potential for false positives - Validated for drinking water samples only - Long analytical run time - Limited commercial availability - Requires confirmation of perchlorate results above reporting limit	Drinking water—0.13 µg/L
Draft SW9058 (IC)	- Aqueous samples with low dissolved solids (conductivity <1 mS/cm TDS) and chloride, sulfate, and carbonate concentrations <100 mg/L each	- Subject to false positives due to the lack of specificity of the conductivity detector - Inadequate QC criteria - Method is expected to undergo significant revision prior to publication	Low-TDS groundwater—4 µg/L

EPA Method 314.0 was used for a nationwide occurrence study to determine perchlorate in source water throughout the country. This emerging contaminant was identified for nationwide occurrence investigation as part of the UCMR. This method depends on the conductivity of perchlorate which elutes from a chromatographic column. Since the detection mechanism is conductivity, this method, if run above the “maximum conductivity threshold,” can be prone to false positives and false negatives. Method 314.0 has been used extensively as a low-cost method of screening water samples to help develop the CSM for a number of cases presented in this document. Other methods issued as guidance by the EPA Office of Solid Waste use a determinative MS to identify and quantify perchlorate by mass. These methods are less susceptible to interferences than the conductivity method described above.

Two perchlorate field-screening methods have been employed with varying degrees of success (see Table 2-5). These techniques include the use of ion-selective electrodes and/or colorimetry. The use of field-screening methods may be appropriate to maximize the sample density and achieve fast turnaround times. For example, a mobile field laboratory could be established using IC or an appropriate field method. Perchlorate specificity and low detection limits could be achieved by analyzing a percentage of the sample splits at a fixed laboratory using the more determinative and more expensive IC/MS/MS or LC/MS/MS method. Refer to the ITRC perchlorate overview document (ITRC 2005) for a more detailed discussion of analytical methods.

Table 2-5. Perchlorate field-screening methods comparison

Method (technique)	Applicability	Analytical limitations	Aqueous reporting limits
Ion-selective electrode	• Can potentially detect perchlorate in the low-ppb range • Potential for in situ sampling for groundwater-monitoring wells • Commercially available models suitable for both field and laboratory applications	• Commercial availability of low-ppb electrodes unknown • Presence of ions can interfere with the perchlorate electrode	Low ppb (as tested); 200 μg/L (commercially available)
Colorimetry	• Used for surface water, well water, bioreactor effluent, and soil extracts • Method published: U.S. Army Corps of Engineers (USACE) ERDC/CRREL TR-04-8 by Phillip G. Thorne	• Humic and fulvic acids from soil surface or root zone may cause false positives, requiring cleanup procedures • Presence of chlorophyll or machine oils will cause false positives	1.0 μg/L

2.5.2.1 Stable Isotope Analysis for Identifying Perchlorate Sources

The most common analytical method to quantify perchlorate concentrations in water, EPA Method 314.0 (IC), is incapable of distinguishing natural perchlorate from synthetic perchlorate. However, a more specialized isotopic method has now been developed that appears to meet this objective. This technique quantifies percentages of the stable isotopes of chlorine (^{37}Cl/^{35}Cl) and oxygen (^{18}O/^{16}O and ^{17}O/^{16}O) in perchlorate using isotope-ratio mass spectrometry (IRMS) (Ader et al. 2001, Sturchio et al. 2003, Bao and Gu 2004, Böhlke et al. 2005). In general, these isotopic values are reported as part-per-thousand differences between the isotopic ratio in the sample and a standard for each element (denoted as "per mil" or "δ" values (Sharp 2007). For many compounds, stable isotope ratios of key elements differ based on their origin and/or mechanism of formation. Research conducted through the DOD ESTCP program indicates that this is the case for perchlorate. In particular, current data indicate that the chlorine isotope ratio (^{37}C/^{35}Cl reported as δ^{37}Cl) in the naturally occurring perchlorate derived from Chile is considerably lower than that of manmade perchlorate, and the oxygen isotope (^{18}O/^{16}O reported as δ^{18}O) ratio for the caliche-derived material is appreciably higher than for the synthetic materials (Figure 2-3) (Böhlke et al. 2005, Sturchio et al. 2006, 2007). This is true for both the caliche mineral and for fertilizers produced and imported from this mineral. In addition, the Chilean-derived perchlorate has an unusually high ratio of $^{17}O/^{16}O$ (reported as $\Delta^{17}O$, which is a difference from expected values based on relative mass) (Bao and Gu 2004, Böhlke et al. 2005, Sturchio et al. 2006). This value is much higher than would be expected in synthetic perchlorate (Figure 2-4). This ^{17}O excess, which is presumably derived from the formation of perchlorate from ^{17}O-enriched ozone in the upper atmosphere, has not been detected in any synthetic samples of perchlorate. Thus, three stable isotope ratios ($^{37}Cl/^{35}Cl$, $^{18}O/^{16}O$, $^{17}O/^{16}O$) have been shown to differ significantly between natural Chilean perchlorate and manmade perchlorate.

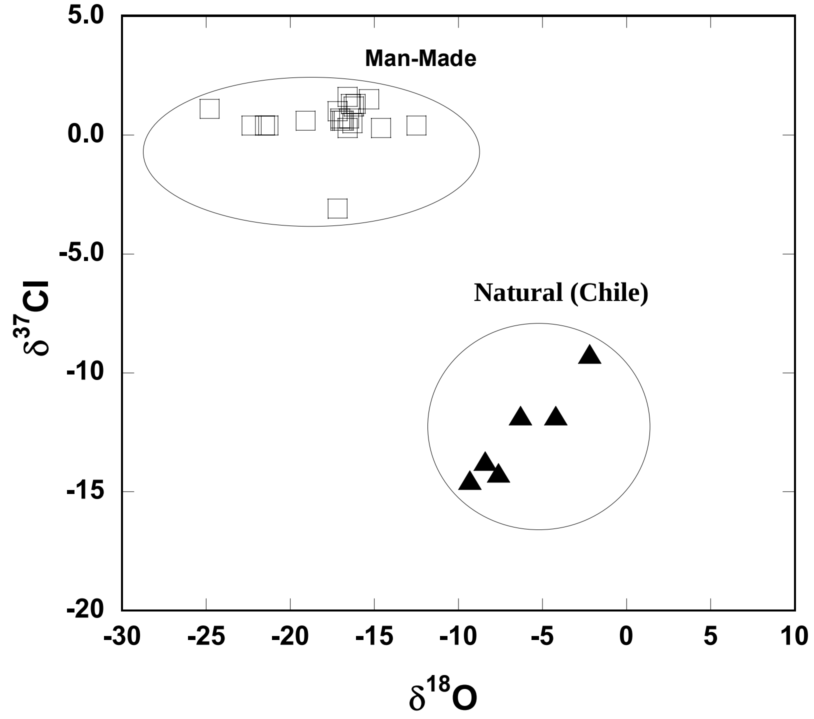


Figure 2-3. Comparison of isotopic values for manmade and natural perchlorate.

Groundwater Sampling. Approximately 10 mg of perchlorate is required to be collected in the field to ensure that enough material is present after purification to obtain necessary isotopic values. For plumes with low perchlorate concentrations, collecting this quantity of perchlorate can be a significant challenge. For example, if the perchlorate concentration in a well is 5 ppb, then 2000 L (~530 gal) of water is required to obtain the necessary 10 mg of perchlorate. Obviously, shipping this much water is impractical. Rather, small columns with perchlorate-specific ion exchange (IX) resin have been developed for field use (Böhlke et al. 2005). Water is passed through these columns, and the perchlorate is trapped by the IX resin. Although several hours may be required for sample collection (flow rates of 1–3 L/min are typical for these columns), the columns are capable of trapping 10 mg of perchlorate on a small volume of resin. The perchlorate is then extracted from the resin and purified prior to IRMS. Techniques for both extraction and purification have been developed (Bao and Gu 2004, Böhlke et al. 2005, Sturchio et al. 2006).

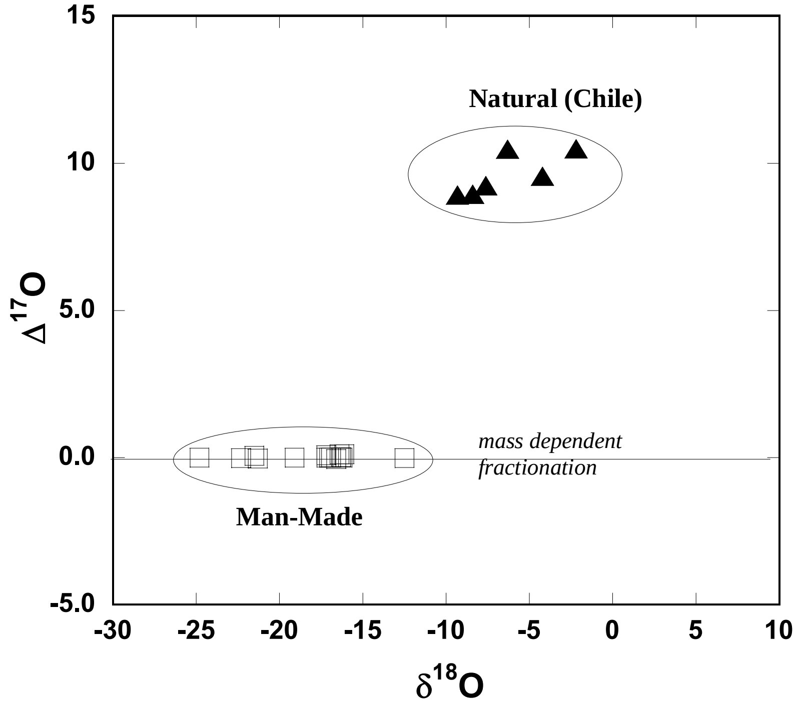


Figure 2-4. Elevated value of ^{17}O occurs in natural Chilean perchlorate.

Groundwater Data. Evaluations of chlorine and oxygen isotopic signatures or perchlorate in groundwater have been conducted at several locations around the United States. Isotopic signatures similar to those quantified for manmade perchlorate sources have been observed at several of these sites. Isotopic values representative of natural (Chilean) perchlorate, including the distinctive ^{17}O enrichment, have also been observed at various locations (Böhlke et al. 2005, Sturchio et al. 2006). At one of the sites tested, perchlorate derived from DOD contractor activities was found in close proximity to that from the past application of Chilean nitrate fertilizers (based on isotope ratio data). The stable isotope data clearly support groundwater plume mapping conducted previously at this location. The natural perchlorate was detected in groundwater upgradient and sidegradient of a well-established plume. There was no easily identified pathway from the known source area to several of the wells with perchlorate occurrence, and the isotope data revealed that these wells contained natural perchlorate. However, in the absence of stable isotope data, it would be difficult, if not impossible, to prove that any of the perchlorate at this location was natural in origin, irrespective of the hydrogeological data and plume maps.

Interestingly, an isotopic signature unlike that from either natural or synthetic perchlorate has been observed in several wells in West Texas (Böhlke et al. 2005, Sturchio et al. 2006). A widespread occurrence of perchlorate in groundwater, which encompasses more than 50,000 square miles and includes several different groundwater aquifers, has been described in West Texas (Jackson et al. 2005, 2006; Rajagopalan et al. 2006). Various theories have been proposed for this occurrence, but based on the wide distribution and quantities of perchlorate detected, this material is most likely of natural origin in the United States (indigenous mineral or soil source). The isotopic data suggest that either this perchlorate was formed by a different mechanism than that of the Chilean evaporites or that the perchlorate has been modified by biological, physical, or geochemical processes after deposition, thus altering the original isotopic signature of the perchlorate. Isotopic studies are ongoing through ESTCP Project ER-0509 to explain the origin of the West Texas perchlorate.

Evaluation of Method 314.0: From *The Occurrence and Sources of Perchlorate in Massachusetts* (MassDEP 2005)

The primary method used to date to test public water supplies for perchlorate in Massachusetts has been EPA Method 314.0, "Determination of Perchlorate in Drinking Water Using Ion Chromatography," Rev. 1.0, November 1999. In using this method, however, MassDEP has specified that laboratories achieve a reporting limit of 1 µg/L. This is accomplished by the use of lower concentration spiking solutions and standards, and a series of initial and ongoing quality control requirements and limits. (www.mass.gov/dep/brp/dws/files/perchlor.pdf)

MassDEP has conducted two rounds of "single blind" Proficiency Test (PT) studies to determine if laboratories are able to comply with method modifications and achieve a 1 µg/L reporting limit. In total, 17 laboratories participated in one or both of these testing efforts, including 7 labs that had demonstrated an initial capability to conduct this procedure ("MassDEP-approved labs"). Each study involved a blank sample, and a sample spiked at 1.04 µg/L (first study) and 1.25 µg/L (second study) of perchlorate, at conductivity levels on the high end of Massachusetts' drinking water supplies (approx. 500 µS/cm @ 25°C). (www.mass.gov/dep/ors/files/perchpt.pdf)

In the first study, 13 of 15 laboratories—including all 7 MassDEP-approved labs—successfully analyzed the spiked samples, reporting a perchlorate concentration within ±2 standard deviations of the study mean, with a mean recovery of 83% (i.e., biased slightly low). One of the 17 laboratories reported a "false positive" detection of perchlorate in the blank sample, but at a concentration below the 1 µg/L reporting limit. The results were similar in the second study, with 13 of 16 laboratories—including all 7 MassDEP-approved labs—reporting acceptable results. In the second study, the mean recovery of the (1.25 µg/L) spike was 83.9%, with a standard deviation of 0.116 µg/L.

A subsequent "double blind" study was also conducted by the American Water Works Association of the 7 MassDEP-approved laboratories, this time using samples with higher concentrations of dissolved salts (i.e., 1200 µS/cm) more typical of other areas of the country. Despite this challenge, 6 of the 7 MassDEP-approved laboratories performed acceptably; the exception being a laboratory located in Arizona that did little work within Massachusetts and that reported <0.3 µg/L perchlorate in all samples not prepared in reagent water.

Overall, these data and results enabled the agency to conclude that the use of the MassDEP-modified Method 314.0 is sufficient to achieve a 1 µg/L reporting limit on drinking water matrices common in Massachusetts, with a low probability of a false-positive detection above the reporting limit.

Field experiences have further supported the validity of this finding. Specifically, in reviewing over 600 analyses of drinking water samples, MassDEP is not aware of a single case of a "false positive" detection above the 1 µg/L reporting limit, provided all specified steps and methodological modifications are followed. Split samples conducted on approximately 30 drinking water samples have demonstrated good correlation between the MassDEP-modified EPA Method 314.0 and an LC/MS/MS procedure (draft EPA Method 331.0). In a few cases, matrix interference in a drinking water sample (e.g., raw water sample from the Merrimack River) precluded quantitation by EPA 314.0; however, quality control (QC) requirements in the modified method (i.e., retesting/spiking samples with detects above 0.8 µg/L) clearly revealed the condition. Although MassDEP-modified EPA Method 314.0 has performed well for its intended application in Massachusetts (i.e., analysis of drinking water with relatively low dissolved salts), it cannot provide definitive identification and quantification of the perchlorate ion and cannot be relied upon to quantitate levels of perchlorate less than 1 µg/L. It is for this reason that MassDEP has used an LC/MS/MS technique to verify positive results from a Method 314.0 analysis, as well as conduct testing/verification testing of wastewater, hypochlorite, and other non–drinking water matrices.

Summary of Stable Isotope Data. The isotopic values of δ^{37}Cl, δ^{18}O, and Δ^{17}O vary significantly and consistently between synthetic perchlorates and natural perchlorate derived from Chilean deposits. Moreover, perchlorate collected from various contaminated groundwater sources has been observed to display isotopic signatures similar to synthetic sources at some locations and to natural Chilean material, presumably derived from imported fertilizers, at others. These data suggest that stable isotope analysis of Cl and O can be applied to distinguish natural perchlorate of Chilean origin from synthetic perchlorate in both solids and in groundwater environments. Perchlorate with isotopic characteristics unlike either synthetic or natural Chilean material has been observed in groundwater in West Texas. This material is suspected to be naturally occurring, but perhaps produced or modified through a mechanism unlike that of the Chilean evaporite deposits. Additional studies are necessary to determine the origin of this perchlorate.

2.5.2.2 Contaminant Transport Modeling

It may be possible to predict the location of a perchlorate source through computer modeling if accurate information on the site hydrogeology and historical perchlorate concentration data can be obtained. At many sites, the first indication of the presence of perchlorate is detection in groundwater. As discussed above, perchlorate is mobile in soil because it readily dissolves into water (precipitation wetting fronts, etc.), which may complicate finding the original release location.

Perchlorate can enter the environment in combination with other chemicals, such as solvents, compounds also found in the original product (explosives, fertilizer, etc.), and manufacturing impurities. The project team can explore the relationships between two or more detected chemicals to better understand the nature of the original release and how the perchlorate is moving in the environment using a variety of mathematical techniques from simple ratio comparisons to more complicated statistical procedures like multiple parameter regression analysis.

2.5.2.3 Natural Attenuation

Project objectives may include determining whether natural attenuation of perchlorate (see Chapter 6) is occurring. Typical methods to explore this question—such as checking for anaerobic conditions, the presence of dissolved carbon, and the reduction of electron acceptors—can be supplemented by more direct measurements for evidence of biological reduction. Techniques include the following:

- checking for perchlorate-reducing bacteria (polymerase chain reaction [PCR], molecular and immunological probes)
- evaluations of biologically mediated chloride fractionation (biogeochemical analysis, a form of stable-isotopic analysis)
- creating in situ microcosms to evaluate degradation in a controlled experiment

3. REMEDY SELECTION CONSIDERATION

3.1 Background

As the site assessment concludes, the project team makes judgments regarding site remediation. When treatment is determined to be necessary, a feasibility study or similar evaluation is typically conducted to select the optimum treatment system. Decisions of fundamental importance include establishing the goals of the remediation and determining whether the contamination will be treated in situ or ex situ. This chapter provides general information relevant to perchlorate treatment considerations. While these considerations are presented individually, in practice it is often necessary to combine remedial strategies in series or parallel to arrive at the best solution. Figure 3-1 is a general flowchart for remedy selection obtained from the Navy's *Environmental Restoration Program Manual* (DON 2006).

3.2 Application of CSM for Remedy Selection

Development of a CSM and understanding the natural processes that are present at a site guide the selection of remedial techniques and the remediation system design process. Analysis of concentration trends can be used to determine whether an ongoing source of perchlorate exists at a site. As an example, for enhanced bioremediation of perchlorate, the CSM must include a description and an evaluation of site-specific geologic features that will affect the method(s) of substrate emplacement. Given that underground injection is a common method of substrate addition, careful attention should be placed on the presence and location of preferential flow paths versus the location of the contaminant mass. Injected fluids will follow the more permeable zones along the paths of least resistance. If contaminants are localized in these more permeable zones, then conventional injection approaches are likely to achieve an acceptable substrate distribution.

3.3 Site and Regulatory Program Considerations

It is necessary to determine under what regulatory framework the remedial action will be conducted. For example, the project may fall under the authority of EPA or the jurisdiction of a state regulatory agency. Selected aspects of federal and state remedial planning processes are presented below. For information regarding promulgated standards for perchlorate, see *Perchlorate: Overview of Issues, Status, and Remedial Options* (ITRC 2005) and the Internet training course associated with this document.

3.3.1 Federal Requirements

Using the National Oil and Hazardous Substances Contingency Plan (NCP) as the basis, EPA established a national goal and a series of expectations that are reflected in the Superfund regulations pertaining to remedy selection. These regulations established a multistage feasibility study process that includes setting remedial action objectives, identification of potential remedial technologies, development of alternatives, preliminary screening of possible alternatives, more detailed evaluation of alternatives, and finally selection of a preferred alternative. EPA developed nine criteria for evaluating remedial alternatives to ensure consideration of all relevant factors:

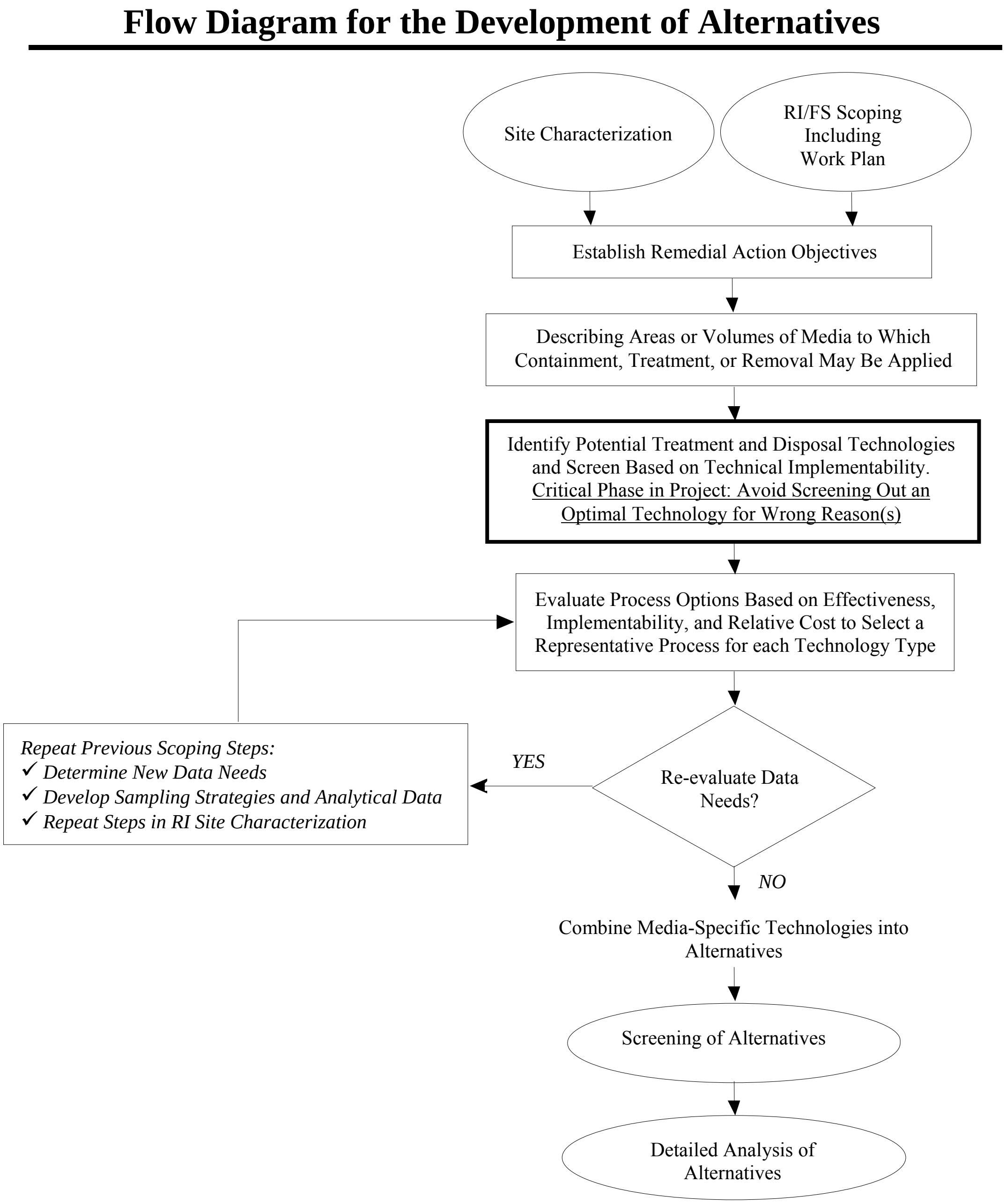


Figure 3-1. Remedy selection flowchart. (Courtesy of the Department of the Navy)

1. protection of human health and the environment
2. compliance with applicable or relevant and appropriate regulations (ARARs)
3. long-term effectiveness and permanence
4. toxicity, mobility, or volume reduction through treatment
5. short-term effectiveness
6. implementability
7. cost
8. state agency acceptance
9. community acceptance

These criteria were derived from the NCP as well as additional technical and policy considerations that were proven to be important in selecting amongst remedial alternatives. The nine-criteria analysis is conducted in two steps. First, an individual evaluation of each alternative with respect to each criterion is completed. Second, a comparison is made between the options to determine the relative performance of the alternatives and to identify the relative advantages and disadvantages.

The results of the feasibility study are first presented to the public in a proposed plan, which summarizes preliminary conclusions regarding the preferred alternative. Following receipt and evaluation of public comments, a final decision is made and documented in the record of decision (ROD) (EPA 1997b). Table 3-1 provides useful remedy selection references and Web sites.

Table 3-1. Useful remedy selection references and Web sites

References		
Source	**Title**	**Number/date**
EPA	*Rules of Thumb for Superfund Remedy Selection*	EPA 540-R-97-013, August 1997
EPA	*Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA*	EPA/540/G-89/004, October 1988
EPA	*The Feasibility Study, Development and Screening of Remedial Action Alternatives*	OSWER 9355.3-01FS3, November 1989
EPA	*Getting Ready: Scoping the RI/FS*	OSWER 9355.3-01FS1, November 1989
EPA	*A Guide to Developing and Documenting Cost Estimates During the Feasibility Study*	EPA 540/R-D0/002, July 2000
EPA	*Guide to Preparing Superfund Proposed Plans, Records of Decision, and Other Remedy Selection Decision*	EPA 540-R-98-031, July 1999
DON	Department of the Navy *Environmental Restoration Program Manual*	August 2006
NAVFAC	Naval Facilities Engineering Command (NAVFAC) *Guidance for Optimizing Remedy Evaluation, Selection, and Design*	UG-2060-ENV, April 2004

Web sites	
Title	**URL**
Federal Remediation Technologies Roundtable	www.frtr.gov
EPA Presumptive Remedy Web site	www.epa.gov/superfund/resources/presump/pol.htm
EPA Hazardous Waste Cleanup Information	http://clu-in.org
EPA Monitored Natural Attenuation Web site	www.epa.gov/swerust1/oswermna/mna_epas.htm
EPA Technology Innovation Program	www.epa.gov/tio
NAVFAC Environmental Restoration and Base Realignment and Closure Web site	https://portal.navfac.navy.mil/go/erb
Remediation Technologies Development Forum	www.rtdf.org
Air Force Center for Environmental Excellence	www.afcee.brooks.af.mil
Environmental Security Technology Certification Program	www.estcp.org
Strategic Environmental Research and Development Program	www.serdp.org
Army Environmental Command	www.aec.army.mil/usaec

3.3.2 State Requirements

Because overlapping state and/or federal requirements may apply to contaminated sites, it is often necessary to determine which state regulatory program has authority over the investigation and cleanup. Throughout the remainder of this chapter, California regulatory programs will be cited as examples. For example, under the Department of Toxic Substances Control (DTSC) Hazardous Waste Permitting Program in California, if contamination remains on a site following the closure of a permitted hazardous waste management unit, corrective action activities are most frequently handled during the permitting and closure/post-closure period. However, under the DTSC site mitigation program, remedial actions may already be proceeding or scheduled to occur at the same facility under the Federal Superfund Program or the State of California Site Mitigation Program.

Additionally, there is an overlap in the responsibility of DTSC and the California State Water Resource Control Board (SWRCB) and Regional Water Quality Control Boards (RWQCB). The DTSC is the primary state agency responsible for the abatement of all hazardous substance release sites. However, as protectors of water quality, the California SWRCB and RWQCBs have jurisdiction over sites that include or potentially include surface and groundwater contamination. In many cases, both the DTSC and the SWRCB/RWQCB must be involved and their respective ARARs be satisfied.

The California DTSC Site Mitigation Program is a useful example because it parallels the federal CERCLA process and is consistent with the NCP. Site cleanup objectives are developed early in the process to guide the site investigation and development of remedial alternatives. The nine NCP criteria are used to compare the advantages and disadvantages of the remedial alternatives under consideration.

In California, remedial action plans must also meet the requirements of Health and Safety Code (HSC) §25356.1, which requires a statement of reasons setting forth the basis for the selected remedial action, an evaluation of the consistency of the remedial action with the federal regulations, and the following six specific factors.

1. Health and Safety Risks—Section 25356.1(d)(1)
2. Beneficial Uses of Site Resources—Section 25356.1(d)(2)
3. Effect of the Remedial Actions on Groundwater Resources—Section 25356.1(d)(3)
4. Site-Specific Characteristics—Section 25356.1(d)(4)
5. Cost-Effectiveness of Alternative Remedial Action Measures—Section 25356.1(d)(5)
6. Potential Environmental Impacts of Remedial Actions—Section 25356.1(d)(6)

These requirements do not apply to sites on the National Priority List (NPL) provided that the DTSC or RWQCB concurs with the remedy selected by EPA's ROD.

If a California regulatory agency is the lead regulatory agency for a project, the California Environmental Quality Act (CEQA) and implementing guidelines apply. CEQA requires public agencies to conduct an analysis of potential environmental impacts related to any project subject to its discretionary approval. The objective of the CEQA analysis is to determine whether a proposed remedial action may cause a significant adverse impact on the environment and, if so, to propose feasible mitigation measures. Such findings must be fully disclosed to the public. The public review of the CEQA documents and of a proposed remedy should be done concurrently.

Requirements in other states may or may not be similar to California's requirements; therefore, a project team should always coordinate with the appropriate state regulatory agencies. Failure to do so could result in unwanted delays.

3.4 Initial Project Considerations

There are a number of questions that must be answered very early in the remedy selection process. Establishing the remedial objective is the most important. All subsequent decisions will be influenced by this fundamental question. It is also important to establish the numerical cleanup concentrations, if necessary, and the desired time frame for the remedy to be complete. Decisions regarding in situ versus ex situ treatment will also benefit from early consideration by the project team. These considerations are discussed in the sections that follow.

3.4.1 Remedial Objectives

Before initiating the remedy selection process, certain key goals must be identified. For example, will the remedy address perchlorate-contaminated drinking water, or is the goal to treat the source area? Numerical goals established for perchlorate cleanups may be applied to drinking water. Numerical concentration discharge limits may be applied to perchlorate treatment-process waste streams. The project team should identify these numerical values early to ensure that the remedial alternatives under consideration can achieve the goals. More aggressive treatment technologies may be necessary if low perchlorate concentrations must be achieved in a relatively short time period. For source areas and groundwater plumes, it may not be possible to uniformly achieve the desired numerical goals within reasonable time frames. Under these conditions, it may be necessary to establish specific points of compliance where the numerical goals can be achieved or develop other remedial objectives that can be achieved.

3.4.2 Remedial Time Frame

The issue of time also influences selection of a remedy. When treating perchlorate-contaminated drinking water, the remedy is generally expected to achieve the remedial objectives immediately. More time is generally available when treating a perchlorate source area or groundwater plume. The treatment time frames can be highly variable, often depending on the proximity of receptors or groundwater resources to be protected. Inherent physical limitations of removing or destroying perchlorate in soil and/or groundwater may prevent the achievement of remedial goals within the desired time frames (such as with natural attenuation). The duration of treatment will have a significant impact on the ultimate cost of a remedy.

3.4.3 In Situ vs. Ex Situ Treatment

Perchlorate source treatment in soil and groundwater can be conducted either in situ or ex situ. Both approaches have advantages and disadvantages that must be considered on a case-by-case basis when selecting the approach. For example, ex situ treatment of soil is generally not applied for contamination over 20 feet below the ground surface because of the difficulty and expense of excavation. Another example is the application of in situ monitored natural attenuation (MNA) of perchlorate, which is not well understood at this time.

3.5 Site Characterization and Technology Considerations

The overall objectives of the feasibility study are to develop and evaluate potential remedies that permanently and significantly reduce the threat to public health, welfare, and the environment; select a cost-effective remedial action alternative that mitigates the threat(s); and achieve consensus among the parties on the selected response action. The process of identifying, evaluating, and selecting an appropriate remedy begins with a review of remedial technologies and methods that are known to be effective for the contaminant, that are appropriate to the site, and that can reduce the threat posed by the contaminant. The process entails gathering and organizing information on the contaminant distribution, geology/hydrogeology, and related site characteristics. The general categories of remedial actions are listed below and progress from actions generally requiring lower logistics and/or costs to those actions requiring greater logistics and/or costs (DON 2006):

- no further action
- land use controls
- containment and other engineering controls
- in situ treatment/mass removal
- ex situ treatment/mass removal

Effective technologies are available for treating perchlorate. Development of remedial objectives, CSMs, and preliminary screening are the first steps in evaluating the potential for selecting a remediation technology for perchlorate.

Development of a CSM may involve some or all of the following characterization steps:

- Location and Nature of the Perchlorate Release. The physical and chemical characteristics of perchlorate affect the fate and transport of the contaminant and must be taken into account when developing the CSM.
- Hydrogeology. Depth to groundwater and groundwater seepage velocity should be taken into account when designing in situ or groundwater extraction treatment approaches. Aquifer heterogeneity and preferential flow paths will complicate the effective application.
- Plume Dynamics. The practitioner should use historical monitoring data to assess whether the plume is stable, expanding, or receding. This may involve statistical testing.
- Location of Sensitive Receptors. The distance to a potential receptor, property boundary, or exposure pathway may be an important regulatory consideration. Groundwater modeling is a useful tool to help with the evaluation.
- Evaluation of Risk. An exposure pathway analysis may be required to determine the level of risk posed by the contaminant release. Active treatment methods may not be needed at sites undergoing natural attenuation if there is no risk of exposure and the time frame for remediation is acceptable. To date, MNA of perchlorate has not yet been proven although it is assumed to be plausible.

Additional site characterization, laboratory microcosm studies, or small-scale field tests may be required as predesign steps before a full-scale system can be designed and a cost calculated for comparison to other remedial technologies. If a determination is made to proceed with remediation, additional site-specific factors will continue to influence the design of the remedial system and the interpretation of performance results. These are discussed in the following sections.

3.5.1 Location of the Perchlorate

The site evaluation process should delineate the horizontal and vertical extent of the perchlorate occurrence in both the soil and groundwater. For drinking-water sources, the project team needs to understand which water sources contain perchlorate and require treatment (e.g., drinking water wells, surface water). Treatment of a drinking-water source where the water is supplied directly to the public will require acceptance by the appropriate regulatory authorities. Currently, ex situ perchlorate treatment of drinking water with ion exchange or biological reduction has conditional acceptance by the California Department of Health Services. Each site must receive site-specific approval for use of these technologies on an individual wellhead or source. The use of in situ biological treatment on a drinking-water source aquifer must consider the potential for mobilizing metals or other harmful groundwater constituents that could then migrate to a production well. Potential for biofouling or plugging of the aquifer should be evaluated. Drinking-water purveyors in the area slated for treatment should be well informed of any potential changes to their source-water chemistry or issues that might impact their production rates.

Sites with relatively deep plumes (i.e., >100 feet) are most likely to be treated with an ex situ treatment technology, particularly if the aquifer in question is used for drinking water. However, in situ treatment using various groundwater pumping or recirculation approaches is also being tested with success in deeper aquifers (Hatzinger et al. 2005). Several in situ approaches are presently being evaluated by the DOD ESTCP program (www.ESTCP.org). The depth of the contamination will also influence the effectiveness of potential remedies and the time frame for operation.

Soil treatment is generally restricted to shallow sites where excavation or in situ treatment can be applied (Cox et al. 2006). Techniques of attempting to flush the soil with percolating water and then capture it once it reaches the groundwater are currently being tested at Edwards Air Force Base (AFB) (Battey, Shepard, and Curtis 2006). Other methods that employ vapor-phase delivery of reagents are under development and may allow treatment of deep vadose zone sites (Evans 2006a, Evans and Trute 2006).

Remedial approaches for shallow groundwater sites will be influenced by the distribution and concentration profile of the perchlorate and the site geology, which is discussed in the following sections. Certain remedial approaches require very precise understanding of the subsurface extent of perchlorate. Other remedial methods can be successfully applied even when the perchlorate extent is not as precisely defined.

3.5.2 Concentration and Extent of Perchlorate

Technology selection is dependent on the starting perchlorate concentration and/or the mass of perchlorate present in the groundwater. The optimum technology for treating a public drinking-water supply that contains 1–10 µg/L may be different from the treatment approach for a groundwater plume that contains 5,000–10,000 µg/L. The scale, magnitude, or extent of the problem can also influence the treatment approach taken. A small, defined groundwater plume that is clearly delineated may be treated in its entirety using one of several in situ approaches, whereas a mile-wide and mile-long plume threatening a drinking-water reservoir may require a technology that intercepts the plume and provides hydraulic control to prevent further plume spread.

One example to help illustrate these considerations is the plume at the National Aeronautics and Space Administration (NASA) Jet Propulsion Laboratory (JPL). An ex situ biological remedial approach to degrade the perchlorate combined with reinjection of the treated water was chosen to remediate the deep hot spot area underneath the facility. At the outer edge of the plume, where the perchlorate concentrations were much lower, wellhead treatment with a selective IX resin deployed at the drinking-water purveyor's facility was chosen (Slaten, Fellows, and Fields 2004). A different approach was implemented at the former McGregor Naval Weapons Industrial Reserve Plant (NWIRP), where the areal extent of contamination required the use of a containment approach (shallow biobarrier) to protect drinking-water sources from being impacted by the different production-area plumes (Black 2003).

Figure 3-2, developed specifically for the treatment of the groundwater at the NASA JPL site, helps illustrate that different perchlorate concentrations may need different remedial approaches.

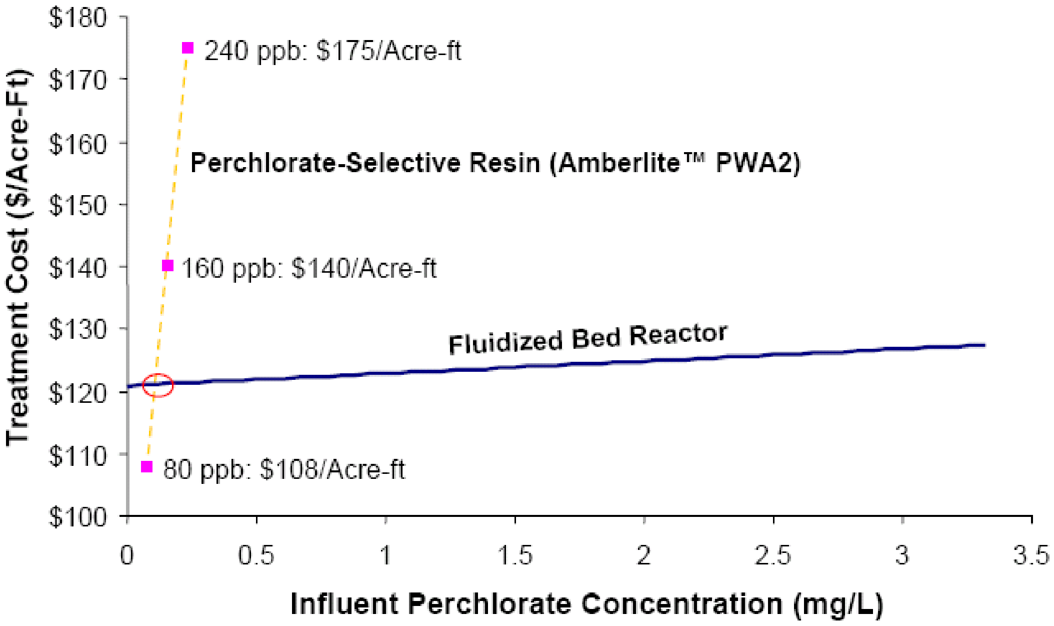


Figure 3-2. Estimated treatment costs comparison for NASA JPL.
(*Source:* Guarini et al. 2006)

3.5.3 Geology and Hydrogeology

Not all treatment technologies will work in all geologic conditions. For example, source treatment in fractured bedrock may not be possible, leading the project team to consider containment strategies instead. Certain geologic conditions may prevent consideration of ex situ treatment technologies. Fractured bedrock results in complex perchlorate distribution and limits application of remedial technologies like pump and treat for plume control.

The uncertainty in characterizing subsurface hydrogeology complicates all in situ treatment technologies and must be considered during the site-selection and design process. Inadequate characterization of the site hydrogeology can lead to remedial system failure. However, in many cases, the system can be designed to mitigate difficult hydrogeologic conditions. Difficult hydrogeologic conditions that may preclude cost-effective delivery of amendments include excessive groundwater flow velocity, low permeability, high levels of aquifer heterogeneity, or excessive depth to groundwater (i.e., high drilling costs). In geologic settings with the extremes of very high and very low groundwater flow velocities, it may be impractical to maintain reducing conditions. In high-flow settings, this might be due to the magnitude of groundwater and native electron acceptor flux. In low-flow settings, the limited effective radius of influence (ROI) from any one injection point may make subsurface injections too costly due to longer treatment times.

3.5.4 Secondary Water Quality Issues

The term “secondary water quality” refers to water quality issues or concerns, apart from the primary contaminants being treated, which typically result from the substrate addition. The potential for adverse impacts as a result of the in situ treatment approach should be considered during the site screening process. While some site conditions may exacerbate these adverse impacts, in most cases they can be mitigated by design alternatives. This requires an understanding of the biogeochemical and hydrogeologic conditions of the aquifer system to be treated and of the potential impacts that may occur.

Application of in situ enhanced anaerobic bioremediation can cause profound changes in the distribution of contaminants and the geochemistry of the treated aquifer. Degradation of secondary water quality can occur as a result of mobilization of formerly insoluble forms of metals that occur naturally in the aquifer matrix (especially iron, manganese, and sometimes arsenic). Other secondary water quality parameters that may be impacted include chemical oxygen demand (COD), biochemical oxygen demand (BOD), pH, TDS, and sulfides that affect taste and odor. These parameters should be monitored if regulated at the site.

Changes occur primarily within the anaerobic treatment zone and may be of concern if drinking water aquifers are present and primary/secondary drinking water standards are enforced. Table 3-2 lists some of the common parameters monitored during enhanced bioremediation and associated federal water quality standards. This list is not inclusive, as many states enforce additional water quality standards. These changes can affect the ability to meet remedial goals and should be considered when designing a treatment approach.

Table 3-2. Key water quality parameters for enhanced anaerobic bioremediation sites

Compound or element	Molecular formula	EPA MCL (mg/L)[a]	EPA secondary standard[b]
General water quality parameters			
Nitrate (as nitrogen)	NO_3^-	10	--
Nitrite (as nitrogen)	NO_2^-	1.0	--
pH	--	--	>6.5, <8.5
Chloride[c]	Cl^-	--	250 mg/L
Total dissolved solids[c]	--	--	500 mg/L
Metals			
Arsenic[c]	As	0.01	--
Selenium	Se	0.05	--
Iron[c]	Fe	--	0.3 mg/L
Manganese[c]	Mn	--	0.05 mg/L

[a] EPA MCL = EPA maximum contaminant level; mg/L = milligrams per liter.

[b] National secondary drinking water regulations are nonenforceable guidelines. However, states may choose to adopt them as enforceable standards.

[c] These are compounds or elements that in some cases may increase in concentrations as the result of anaerobic bioremediation co-contaminants (e.g., vinyl chloride) are generally temporal and limited to the immediate treatment area. Nonetheless, the potential exists for migration of adversely impacted groundwater, and these issues are typically addressed through additional monitoring.

In general, the reduced groundwater environment induced by substrate addition may increase the mobility of some naturally occurring (but regulated) metals in the reactive zone (e.g., iron, manganese, and arsenic). This is not always a problem; in some cases migration of metals such as arsenic may be retarded by adsorption to the aquifer matrix. Additionally, the mobilized inorganics may be precipitated/immobilized downgradient of the reactive zone when the conditions return to a more oxidizing state. COD, BOD, TDS, and sulfides that affect taste and odor are necessarily elevated in the anaerobic reactive zone due to biodegradation of the substrate. Generation of reduced sulfur compounds (e.g., thiols or mercaptans) or alcohols (e.g., 2-butanol or isopropanol) may occur under extreme fermentation conditions.

3.5.5 Presence and Concentrations of Co-Contaminants

Co-contaminants are other contaminants present with the perchlorate. Typical co-contaminants include VOCs; halogenated solvents; and explosive compounds such as TNT, RDX, and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (ITRC 2002). Ex situ treatment trains that address multiple co-contaminants have been designed. An example is the treatment train developed at the U.S. Department of Energy (DOE) Los Alamos National Laboratory (LANL) High-Explosive Wastewater Treatment Facility to address perchlorate and high explosives (Rickman 2003).

The microorganisms that can biodegrade perchlorate can be differ from those capable of degrading the co-contaminants, and the conditions for optimal removal of perchlorate may not be the conditions for optimal biodegradation of the co-contaminant. However, in some situations, the presence of co-contaminants may actually promote favorable conditions for perchlorate degradation. Co-contaminants can also impact the selection of abiotic treatment approaches.

Different contaminants may have different affinities for IX resins or sorption sites on activated carbon, causing interference with the perchlorate adsorption treatment process. Wherever possible, these possible interactions should be evaluated in laboratory microcosms, bench tests, or field pilot tests before committing to a full-scale implementation.

Nitrate concentration can be very important in determining which remedial approach to choose. Often, nitrate levels are in the parts per million (ppm) range and perchlorate levels are in the ppb range (Logan 2001; Hatzinger et al. 2002; Henderson, Lutes, and Sugiyama 2006). Some IX resins remove both perchlorate and nitrate, while others are highly selective for perchlorate. Anaerobic biological systems degrade both perchlorate and nitrate. Frequently, the electron donor concentration required for the site is determined by the amount of oxygen and nitrate at the site, not perchlorate.

There is a known occurrence of naturally occurring uranium buildup in some perchlorate-specific IX resin beds after prolonged use, thus limiting the use of this technology where this may occur (Edwards AFB Site 133, Gu and Brown 2006). Existing evidence also tends to suggest that high sulfate levels are problematic for biological reduction of perchlorate.

3.5.6 Microbiology

Biological degradation of chlorate (ClO_3^-) was first observed in the 1920s and is the basis of an assay for BOD in wastewater (Bryan 1966, Logan 1998). Perchlorate-reducing bacteria are widespread in the environment (Coates et al. 1999, Logan 2001) and are phylogenetically diverse, including members in the alpha, beta, gamma, and epsilon subclasses of the *Proteobacteria* phylum (Coates and Achenbach 2004). A variety of perchlorate-reducing bacteria have now been isolated, many of which are members of the genera *Dechloromonas* and *Azospira* (formerly called *Dechlorosoma*) (Achenbach et al. 2001; Xu et al. 2003; Coates et al. 1999; Waller, Cox, and Edwards 2004). Perchlorate-reducing bacteria can be strict anaerobes, microaerophiles, or facultative anaerobes (Rikken, Kroon, and van Ginkel 1996; Chaudhuri et al. 2002), giving them the ability to grow either in the presence or absence of air, provided proper nutrients are available in the environment. The metabolic versatility of these organisms increases their sustainability in both contaminated and pristine environments.

Using this metabolic versatility, these organisms are capable of degrading perchlorate, chlorate, and in most cases, nitrate. Perchlorate-reducing bacteria are nonfermenting microorganisms that use either chlorate or perchlorate as a terminal electron acceptor and a variety of different organic substrates (e.g., acetate, propionate, lactate, etc.) as electron donors, i.e., energy sources (Herman and Frankenberger 1999, Coates et al. 1999, Hatzinger 2005). Laboratory microcosm studies have shown that perchlorate-reducing bacteria are indigenous to many soils, sediments, surface waters, and groundwater. Moreover, these organisms can often be stimulated to degrade perchlorate to below detection by adding a microbial growth substrate (Wu et al. 2001; Hatzinger et al. 2002; Waller, Cox, and Edwards 2004; Tan, Anderson, and Jackson 2004). The bacteria oxidize the organic substrate to carbon dioxide (or sometimes an intermediate) and subsequently reduce perchlorate to the innocuous products chloride and oxygen. As shown in Figure 3-3, the reduction of perchlorate proceeds initially to chlorate (ClO_3^-) and then chlorite (ClO_2^-) (van Ginkel et al. 1996, Kengen et al. 1999). The enzyme perchlorate reductase is known to carry out the initial step, and a second enzyme, chlorite dismutase, subsequently reduces the chlorite to chloride (Cl^-) and oxygen (O_2) (Coates et al. 1999). An immunoprobe for the chlorite dismutase gene has been developed to detect perchlorate-reducing bacteria in environmental samples (O'Connor and Coates 2002).

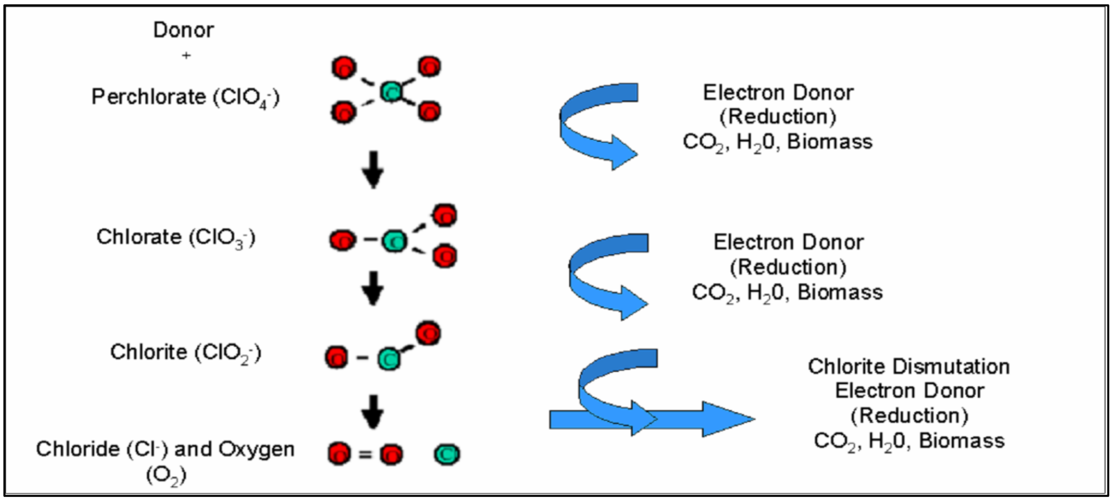


Figure 3-3. Biodegradation pathway for perchlorate.

For in situ biodegradation to occur, favorable geochemical conditions must be present. Given that perchlorate-reducing bacteria are considered ubiquitous within the environment, bioaugmentation with an enriched consortium has yet to be shown as necessary. At the most promising sites for perchlorate reduction, geochemical conditions are appropriate for their growth and evidence of anaerobic biological reduction is already observed. Figure 3-4 illustrates the sequence of utilization of various electron acceptors found in a perchlorate environment, graphically demonstrating why depletion of oxygen and nitrate concentrations must be accomplished before perchlorate can be degraded. It also illustrates why achieving oxygen reduction potential (ORP) levels necessary for sulfate reduction and methanogenesis are not necessary or preferred for stimulating anaerobic perchlorate reduction. Thus, potentially favorable geochemistry includes a pH between 6.5 and 7.5, ORP between 0 and –100 mV, low oxygen concentrations, and low nitrate levels (ITRC 2002).

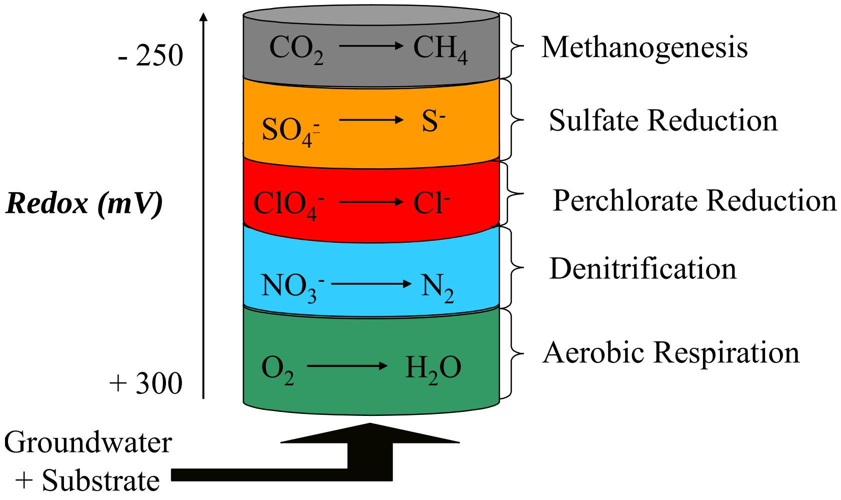


Figure 3-4. Utilization of electron acceptors.

Although shown to be ubiquitous, appropriate perchlorate-reducing microorganisms may be present, but less active at some sites. These sites may take longer to respond to biostimulation. Chapter 6 provides additional discussion of the biological reduction of perchlorate.

3.5.7 Treatment Strategy

The decision regarding whether to remediate perchlorate in situ or ex situ can be influenced by a number of factors, including whether the plume is stable, expanding, or receding. For example, an expanding plume near a potential receptor may not be the ideal site for enhanced in situ bioremediation and may be controlled with an ex situ treatment process (Slaten, Fellows, and Fields 2004). Alternatively, enhanced bioremediation may not be needed at sites undergoing natural attenuation if there is no risk of exposure and the time frame for remediation is acceptable. Other factors include the ability to address multiple contaminants. Often, treatability studies or pilot testing of both in situ and ex situ systems will be necessary.

3.5.8 Technology Availability

Project teams are generally limited to considering remedial technologies that are proven and commercially available. Under select circumstances, the application of an emerging technology may be considered; however, this will be infrequent unless the technology holds great promise for a particular site.

3.6 Conclusions

The feasibility study normally is prepared in draft-final and final versions, thus allowing the regulatory agencies and stakeholders the opportunity to review and comment on the selected alternative. A decision document is often prepared simultaneously, once more giving the stakeholders the opportunity to provide input before the final decision is made. More detailed information on some of the technical topics discussed above is presented in the chapters that follow.

4. REGULATORY CONSIDERATIONS

Regulatory requirements regarding remedial system installation and operation at sites with perchlorate in groundwater or soil could involve various local, state, and federal government departments. These entities might require compliance to various rules or permits that directly or indirectly involve the operation of planned remedial systems. Regulatory compliance and/or permit issuance can become time-consuming and delay inception of remedial efforts. Examples of such direct or indirect permit requirements for operation of an ex situ and in situ perchlorate remedial system are presented in Figure 4-1 for Kerr McGee (currently Tronox) and American Pacific Corporation (AMPAC) in Henderson, Nevada.

This chapter provides a brief review and some examples of regulatory requirements that might impact perchlorate remedial efforts. A review of the examples in Figure 4-1 of two full-scale ex situ and in situ remediation systems should give the reader a good understanding of the potential permit and other local and state compliance requirements. As each state and local government varies in the type and extent of regulatory requirements and time constraints, information regarding compliance with local, state, federal, or tribal regulations to install and operate a perchlorate treatment system should be researched and obtained at the outset of a project to prevent unforeseen delays.

Kerr McGee FBR System Permit Requirements	**American Pacific in Situ Bioremediation Permit Requirements**
• Water appropriations permit from Nevada Division of Water Resources to pump large volumes of groundwater • NPDES Permit from Nevada Division of Environmental Protection (NDEP) to discharge treated water at <0.018 mg/L • Rolling stock permit for underground pipes plus an archeologist study for the trenches • Air permit from Clark County Air Quality Management District for bioplant for volatiles to bring in ethanol and store it, and a vermiculite permit for anything that can produce particulate matter (PM) 10 in dust • Bureau of Alcohol, Tobacco, Firearms, and Explosives tax reporting permit for ethanol • Sludge produced is landfilled at a permitted commercial landfill • The one-time-use IX system, no longer in operation, produced spent resin, which required disposal by incineration where the incinerator company had the necessary permits	• Underground Injection Control (UIC) Permit issued by NDEP Bureau of Water Pollution Control (see Figure 4-2 time line) • Water Appropriations Permit from Nevada Division of Water Resources • Encroachment or equivalent permits from Clark County and local city governments • Miscellaneous building and construction permits • Miscellaneous power, water, and sewer usage permits for the in situ bioremediation plant

Figure 4-1. Example of in situ and ex situ treatment permits.

4.1 Waste/Wastewater Management and Disposal

Disposal of waste and wastewater generated from a perchlorate treatment system might be subject to federal, state, local, and tribal regulations such as RCRA and air and water quality regulatory levels. As indicated in Figure 4-1, treatment and disposal of spent resins produced from IX systems might require local and state regulatory oversight and permits. Wastewater generated from a pump-and-treat system requires state discharge or NPDES discharge permits from states and federal regulatory agencies. As an example, at NWIRP McGregor in Texas, NPDES effluent limitations and monitoring requirements authorize the discharge of treated groundwater on an intermittent and flow variable basis as follows: perchlorate at 0.006 mg/L on daily average or 0.013 mg/L for daily maximum or at 0.018 mg/L for a single grab with a pH between 6.0 and 9.0. This daily stat average report and monitoring frequency are required for one time per day. Additionally, appropriation of large volumes of water to operate treatment systems might require some type of regulatory approval or permit.

4.2 Underground Injection Control

Injection of amendments into the groundwater to stimulate in situ bioremediation of perchlorate is becoming an increasingly favored technology option. Injection of any substance into a well or boring is regulated under UIC as part of the Safe Drinking Water Act. Injection of any fluid into a well is prohibited under this law unless prior approval is granted by a regulatory citation reference. The UIC program defines five classes of wells, of which Class V injection wells apply toward in situ remedial efforts. Some states have the primary responsibility (primacy) for enforcement of the UIC program. Depending on the state, EPA has granted either complete primacy, partial primacy, or no primacy over the UIC program. Those states which fall under the EPA primacy may not require a permit as the UIC program is regulated by rule; however, notification might be required. States with UIC primacy over Class V wells may or may not require permits to inject amendments into the groundwater of the state to prevent potential contamination of drinking water. Issuance of a UIC permit can be time-consuming. The process should be researched and initiated at the outset of a remediation project. Figure 4-2 shows the current status of UIC state primacy. Updated information on the status of state primacy can be found at www.epa.gov/safewater/uic/primacy.html. Figure 4-3 documents an example UIC permit process for AMPAC in Henderson, Nevada. Nevada has primacy over its UIC program and requires a permit to inject.

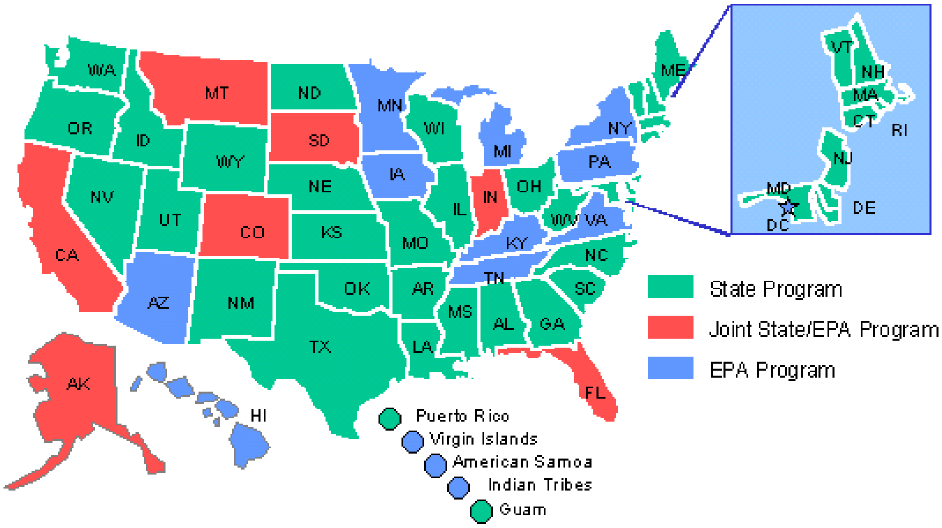


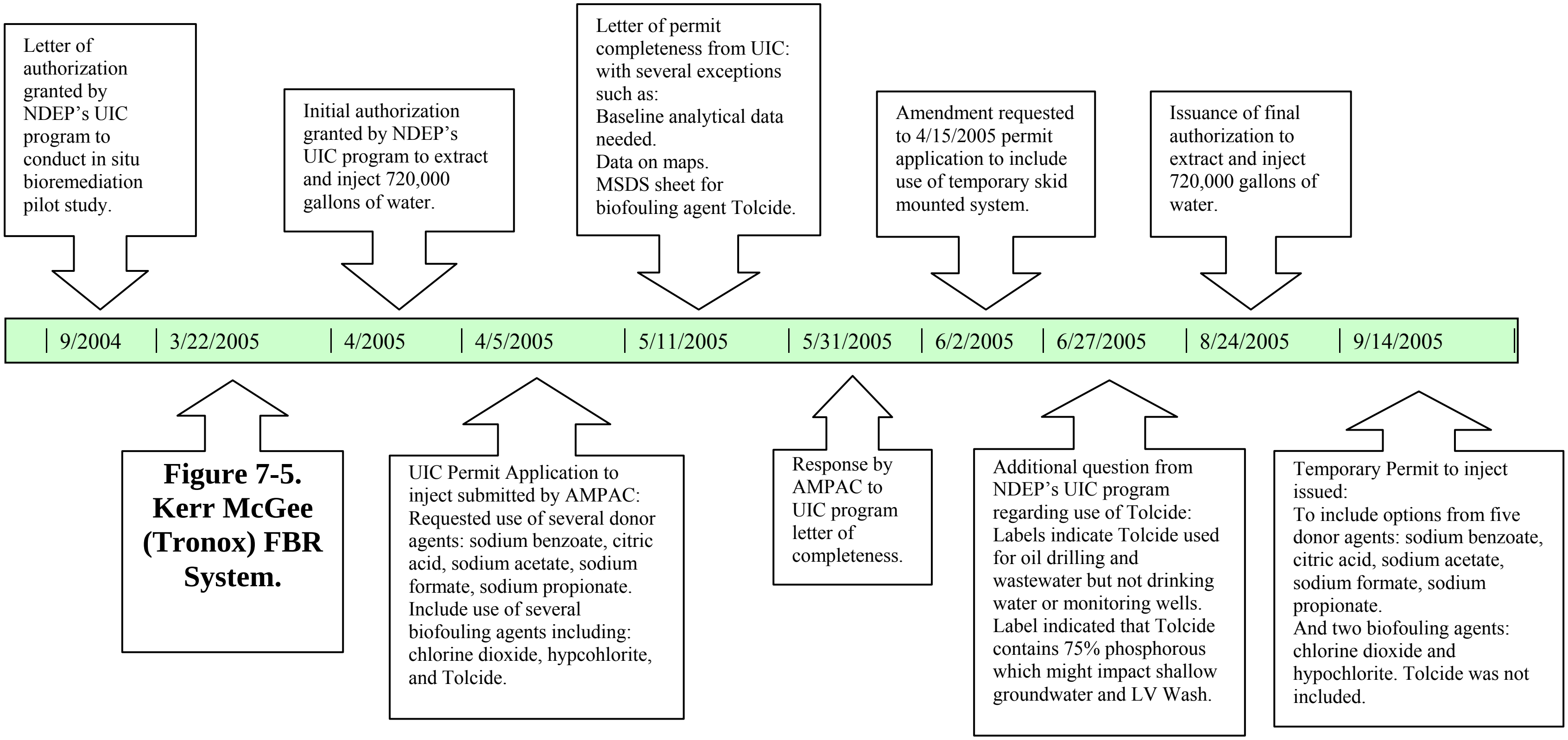
Figure 4-2. EPA UIC primacy.

4.3 Air Quality

Air-quality permitting requirements depend on the remediation technique employed and the applicable state and local regulations. For example, if the technique calls for the operation of a biological reduction plant as described in Figure 4-1, testing may be required for emissions of volatile organics from the storage tanks and/or for any dust-producing materials with particulate matter (PM) 10 that may be used. Some states require permits for PMs of 2.5–5 in dust. Each state has air-quality requirements that need to be investigated as they apply to the remediation techniques implemented.

4.4 OSHA and Health and Safety

General health and safety and Occupational Safety and Health Administration (OSHA) requirements for both physical and chemical hazards of any treatment system must be incorporated into the specific health and safety plan. Chemical additives for various treatment technologies involving either chemical oxidation or biological reduction might involve specific health and safety requirements during preparation and deployment. Bioremediation of perchlorate is a common and effective treatment technology that requires the use of chemicals and sometimes biological additives. Material Safety Data Sheets (MSDS), if available, for in situ and ex situ bioremediation chemical amendments or biofouling agents should be reviewed and the exposure concerns addressed. This information should be written into the health and safety plan, and copies of the appropriate MSDS sheets should be attached.



Letter of authorization granted by NDEP's UIC program to conduct in situ bioremediation pilot study.

Initial authorization granted by NDEP's UIC program to extract and inject 720,000 gallons of water.

Letter of permit completeness from UIC: with several exceptions such as:
Baseline analytical data needed.
Data on maps.
MSDS sheet for biofouling agent Tolcide.

Amendment requested to 4/15/2005 permit application to include use of temporary skid mounted system.

Issuance of final authorization to extract and inject 720,000 gallons of water.

Figure 7-5. Kerr McGee (Tronox) FBR System.

UIC Permit Application to inject submitted by AMPAC:
Requested use of several donor agents: sodium benzoate, citric acid, sodium acetate, sodium formate, sodium propionate.
Include use of several biofouling agents including: chlorine dioxide, hypcohlorite, and Tolcide.

Response by AMPAC to UIC program letter of completeness.

Additional question from NDEP's UIC program regarding use of Tolcide:
Labels indicate Tolcide used for oil drilling and wastewater but not drinking water or monitoring wells.
Label indicated that Tolcide contains 75% phosphorous which might impact shallow groundwater and LV Wash.

Temporary Permit to inject issued:
To include options from five donor agents: sodium benzoate, citric acid, sodium acetate, sodium formate, sodium propionate.
And two biofouling agents: chlorine dioxide and hypochlorite. Tolcide was not included.

Figure 4-3. American Pacific UIC permit time line. (*Source:* NDEP AMPAC UIC Permitting File)

5. PHYSICAL PROCESSES FOR WATER

Physical treatment processes remove perchlorate from impacted media without altering its chemical composition. Considerable progress has been made in developing innovative physical processes for removing perchlorate from drinking water, groundwater, and surface water. Some technologies are proven and commercially available while others are still in the research and development phase.

In general, physical processes require impacted water to be managed using an ex situ pump-and-treat (P&T) system. Groundwater is extracted (pumped) and then treated in an aboveground system that generates perchlorate-laden waste streams (liquid and/or solid). Since physical processes do not alter the chemistry of the perchlorate ion, the waste streams need to be managed and disposed of or treated properly to avoid reintroduction of the perchlorate into the environment.

The evaluation and selection of a treatment method for a particular P&T system focuses on technical feasibility and costs (capital and operational) considerations of the technology/method for achieving remediation goals. Key parameters that influence treatment design and efficacy include data quality objectives, hydrogeologic conditions, plume size, influent concentrations, and discharge requirements.

Treatment strategies should be designed and implemented in a manner that will accommodate changing conditions over the life cycle of a P&T project. At many sites, modifying treatment capacity or methods to respond to changing influent chemistry or flow rate over time can improve system performance and reduce cost. As with pumping, treatment optimization requires ongoing monitoring (EPA 1997a).

The following are physical processes for treatment of perchlorate-impacted water:

- ion exchange
- granular activated carbon (GAC)
- reverse osmosis
- nanofiltration/ultrafiltration
- electrodialysis
- capacitive deionization
- other innovative and emerging technologies

Each of these is discussed in the following sections. Depending on site conditions, physical processes can be used in conjunction with other processes for a more efficient remediation system.

5.1 Ion Exchange

Ion exchange is the most proven and widely accepted physical process technology to meet existing perchlorate treatment goals. IX is a process by which ions of a given species are displaced from an insoluble exchange material by ions of a different species in solution. The net result is that the targeted ions are removed from water through sorption onto resins. IX has been successfully used since the 1940s for drinking water treatment (softening and deionization) and other industrial processes. Many different types of cation and anion exchange products prepared as resins are commercially available. This technology was one of the first ex situ technologies considered for remediation of perchlorate-contaminated waters. While other ex situ and in situ technologies have been developed and are undergoing evaluation, IX is a proven and accepted technology.

During IX, perchlorate, which is a negatively charged ion (anion), is exchanged with another anion, typically chloride (Cl^-). Ion exchange medium (IX resin) contains positively charged functional (ionizable) groups having affinity for anions (e.g., perchlorate). The resins can be made from synthetic materials, inorganic materials, or natural polymeric materials that contain the functional groups onto which exchangeable ions are attached. When perchlorate-impacted water flows through the resin, perchlorate anions attach to the resin and release the bound chloride ions.

The effectiveness of IX depends on several variables, including the presence and concentrations of competing ions. Many of the other anions commonly present with perchlorate in groundwater compete with the perchlorate ion in the exchange process. These other anions include sulfate (SO_4^{2-}), nitrate (NO_3^-), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and bromide (Br^-). Trace ions, such as chlorate, bromate, and arsenate, can also compete with perchlorate for exchange sites (ITRC 2005).

Although conventional IX resins are capable of removing perchlorate, the effectiveness is hampered due to competing anions. Also, organics, TDS, calcium, or iron in the influent can clog resin beds and reduce system effectiveness. Therefore, selective resins are preferred for treatment of perchlorate in water.

In recent years, perchlorate removal using IX has advanced significantly with the development of selective ion exchange, a process that targets perchlorate using specially designed resins. Selective resins for anion exchange are primarily strong-base resins; however, recent studies have been conducted showing promise for using weak-base resins.

Resins are categorized based on the ion that is exchanged with the type of ion in solution, such as chloride-form resins. Another way of categorizing resins is by the type of ion in solution that the resin preferentially exchanges (i.e., sulfate-selective or nitrate-selective resins). Because nitrate has IX properties similar to those of perchlorate, some nitrate selective resins have the surface resins preferentially exchange nitrate and perchlorate over sulfate. As the resin bed reaches saturation, these selective resins prevent sulfate from displacing the adsorbed nitrate or perchlorate anions. The resins can be disposed of after saturation, or, because IX is a reversible chemical reaction, regeneration and reuse may be an option.

Two types of IX treatment systems are available for perchlorate removal:

- regenerable (fixed-bed or moving-bed design) treatment systems, where perchlorate is stripped from the resin prior to resin reuse

- single-use (fixed-bed design) treatment systems, where nonregenerable resin loaded with perchlorate is properly disposed (e.g., through incineration)

Figure 5-1 is a flow chart of the IX process for perchlorate using a regenerable system (Option 1) and a single-use system (Option 2).

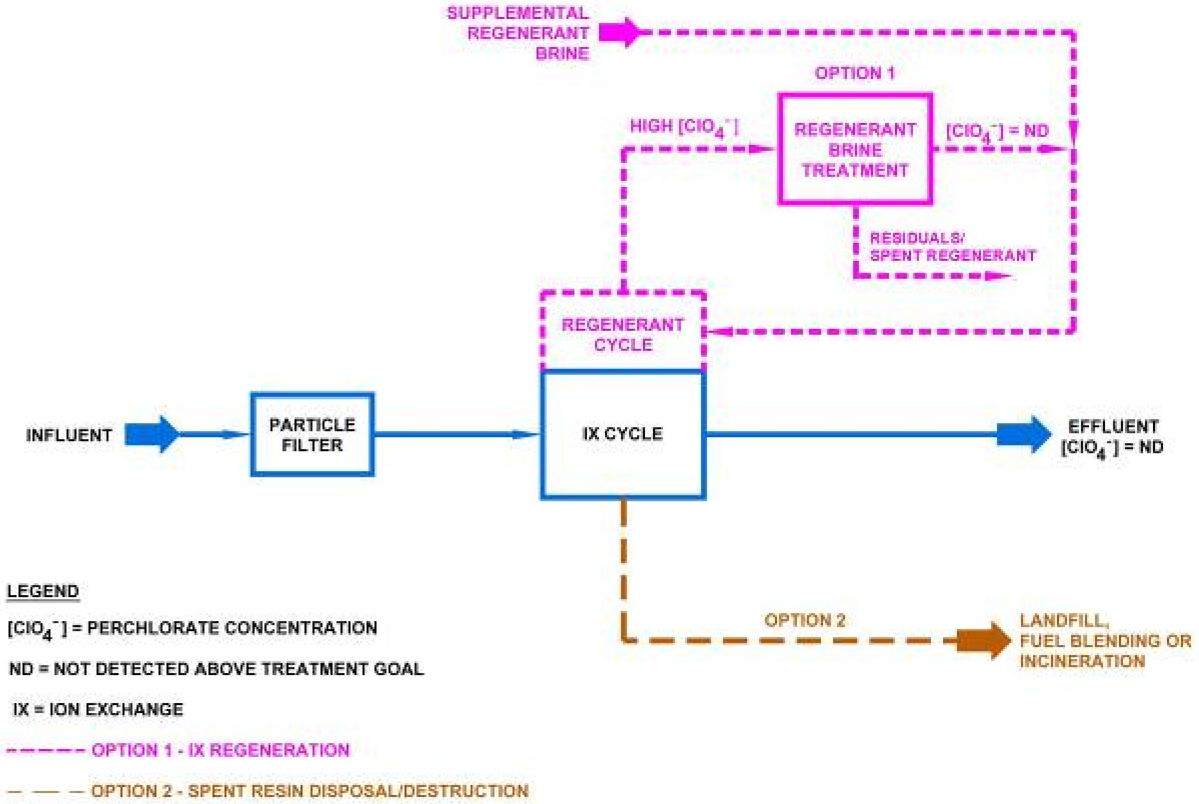


Figure 5-1. Ion exchange flow chart.

5.1.1 Single-Use Treatment Systems

Single-use, fixed-bed system designs have been the primary systems used at full scale for treating perchlorate-impacted waters. During operation, contaminated water is pumped through one or more vessels/columns that hold the resin where IX takes place. A vessel/column is usually 2–6 feet in diameter and 1–6 feet tall and can contain millions of small resin beads that form the resin bed.

Perchlorate is attracted to the resin by an opposing charge mechanism. As it attaches to the resin, it displaces a chloride ion. Over time, the resin becomes saturated with perchlorate and competing ions, reaching its adsorption capacity and thus allowing breakthrough. Monitoring perchlorate concentrations in the column discharge is required to know when this occurs. The resin bed is then taken out of service and the resin disposed of (e.g., incinerated), and fresh resin is brought online to ensure ongoing removal efficiency. Multiple columns are often run in series (lead-lag or lead-lag-polish configurations) to ensure that water exiting the process is adequately treated and breakthrough does not occur.

The rate of perchlorate removal depends on a number of factors, such as the perchlorate concentration in the water, the presence and concentration of competing ions, flow rate, size of the resin beads, and the diffusion characteristics of ions within the porous structure of the beads.

New single-vessel systems that do not require the expense of a lead-lag system and that more effectively use the resin bed are in full-scale operation at two sites in California. One such system's vessel is based on a reverse-flow, packed-bed design. The resin is removed from the system at the midpoint, and fresh resin is added behind the wavefront (ESTCP 2006b).

5.1.1.1 Single-Use Resins

Newer resin designs take advantage of an even greater selectivity for perchlorate, making it possible to operate an IX unit for a protracted period of time. Although costly, use and disposal of single-use resins avoid the difficulties and liabilities associated with the perchlorate-laden waste streams that are produced during resin-regeneration processes.

Several advanced IX resins have been developed and demonstrated to have improved perchlorate selectivity and adsorption capacity. Such advanced resins have helped to dramatically decrease the overall treatment costs associated with this technology, and more resins are in development today. A resin's selectivity or affinity for perchlorate is influenced by properties of the bead, the ions being exchanged, and the solution in which the ions are present.

Use of strong-base anion exchange resins to remove perchlorate from water relies on the higher affinity or preference of the resins for the perchlorate ion compared to other anions present in the water (Boodoo 2003). All strong-base anion resins in the chloride form can remove perchlorate to varying extents, and currently these are the primary resins used for perchlorate treatment. Selective strong-base resins for perchlorate treatment are available through various companies, including the following:

- Calgon Carbon (CalRes 2000 series)
- ResinTech (SIR-110-HP)
- Rohm & Haas (Amberlite PWA-2 and Duolite A-102-D)
- Purolite (A-520E and A-530E)
- US Filter/Siemens (A-284 and K-9708)
- Dow Chemical (DOWEX PSR 2 and DOWEX PSR 3)
- Lanxess-Sybron (Ionac SR-6 and SR-7)

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 and produced by Purolite (A-530E), this resin is particularly effective in removing trace quantities of perchlorate in groundwater while also managing large volumes (see Figure 5-2). The bifunctional name stems from the resin's having two functional groups that work together rather than one group, which is typical in all other resins. A field experiment demonstrated that the bifunctional resin was able to treat >100,000 bed volumes (BVs) of groundwater before a 10% breakthrough of perchlorate occurred (running at ~2 BV/minute with an initial perchlorate concentration of ~50 mg/L). The bifunctional resins are particularly effective in removing trace quantities of perchlorate in groundwater to below the detection limit (~1 mg/L). Using pertechnetate (TcO_4^-) as an analog (with similar chemical properties as perchlorate), these bifunctional resins were able to remove $TcO4^-$ from contaminated groundwater at below 0.001 µg/L levels. No pretreatment is needed to remove either dissolved organic matter or other competing anions (such as Cl^-, SO_4^{2-}, HCO_3^-, or NO_3^-), which may be present at 3–5 orders of magnitude higher than that of perchlorate in the groundwater or surface water. The treatment process does not involve addition or removal of unwanted organic or inorganic compounds or nutrients in the water because of the high selectivity of the bifunctional resins (Gu and Coates 2006).

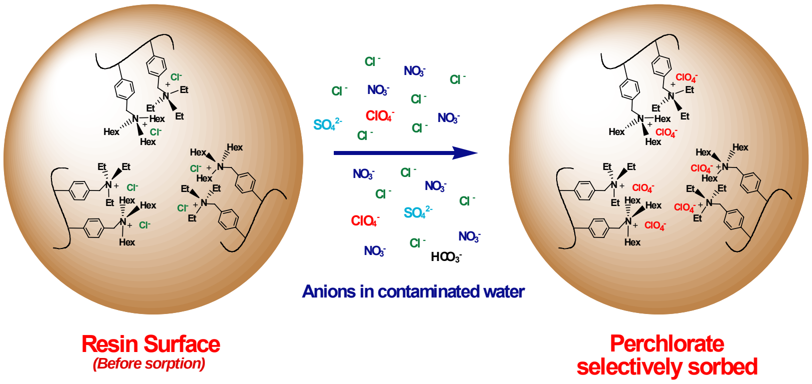


Figure 5-2. Bifunctional resin for selective sorption of perchlorate.

Data from operational systems and research studies have revealed advantages and disadvantages of single-use resins, as shown in Table 5-1.

Table 5-1. Single-use resins strengths and limitations

Strengths	Limitations
• Newer resin designs take advantage of an even greater selectivity for perchlorate, making it possible to operate the IX unit for a protracted period of time • Exhausted resin can be removed and sent to a landfill for disposal • Incineration of spent resin, with certificates to verify destruction, ensures mitigation of the perchlorate • Full-scale systems with single-use resins are in operation providing data and costs for decision making	• Conventional anion exchange resin has a relatively low perchlorate selectivity, limiting its overall perchlorate-removal capacity, and requires frequent regeneration • Landfill disposal of spent IX resin is not destructive and does not release liability • The number of incineration facilities certified for disposal is limited • Single-use resins can cause fouling, plugging, channeling, bacterial contamination, agglomeration, and compaction problems

5.1.1.2 Management of Single-Use System Residuals

As IX 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 vast majority of full-scale IX applications for perchlorate treatment employ single-use treatment systems, requiring resin disposal. Options for disposal of the resin are discussed below.

Landfill. Perchlorate-laden resin can be disposed of in a permitted landfill but must be analyzed to determine hazardous or nonhazardous waste classification. Although landfill disposal could be considered, it is not widely used and does not eliminate the generator's ongoing liability.

Incineration. Most spent-resin management options center around thermal destruction, via either fuel blending or hazardous-waste incineration. The incineration of spent IX resin, with certificates to verify destruction, ensures mitigation of the perchlorate problem. One spent-resin management option that is widely used for resins is based on styrene-divinylbenzene copolymers and involves thermal destruction by blending the resin with boiler fuel (ITRC 2005).

Regenerate Spent Single-Use Resins. Calgon Carbon Corporation is working under a license with ORNL to develop a technology to regenerate single-use spent resins using a ferric chloride solution acidified with hydrochloric acid, creating a tetrachloroferrate ion ($FeCl_4^-$). The tetrachloroferrate ion displaces the perchlorate from the IX resin. Desorption of the tetrachloroferrate ion from the resin takes place with water or a dilute acidic solution, so the resin becomes available again for perchlorate removal. The perchlorate-rich regenerant solution is subsequently reduced using ferrous chloride under elevated temperatures ($<200^oC$) and/or pressures (~20 atm). Although this regeneration technology could be used either on or off site, it is likely that off-site regeneration will be appropriate for most low-resin-usage applications (Gu and Coates 2006).

5.1.2 Regenerable Treatment Systems

Regenerable systems also have been used at full scale for treating perchlorate-impacted water. In these columns, as the IX capacity of resins is progressively exhausted, the water produced deteriorates in quality. When the effluent water quality becomes unacceptable, a column is taken off-line so that the resin can be regenerated using a regenerant solution to displace the adsorbed perchlorate ions. Due in part to perchlorate's strong affinity for the conventional resins, very large quantities of concentrated sodium chloride brine are required to displace the perchlorate during regeneration. Several hundred pounds of sodium chloride regenerant per cubic foot of resin at salt concentrations from 6% to saturation are typically used (Jensen, Guter, and Solomon 2005). Therefore, selective resins are being used for better system effectiveness through less regeneration cycles than are required when using conventional (nonselective) exchange resins. There are two types of regenerable system designs: fixed bed and moving bed.

Fixed-Bed System Design. In a regenerable fixed-bed system design, anion resin is packed into one or more fixed resin beds and used to remove perchlorate from water that is pumped through the treatment vessels. Unlike a nonregenerable system, where the saturated resin is periodically removed for disposal and replaced with virgin resin, the perchlorate-saturated resin in a regenerable system is reloaded either on or off site. Resin regeneration involves backwashing, regeneration with a solution containing a high concentration of exchange ions, and a final rinsing to remove any traces of the regenerant solution from the resin. The final rinsing is conducted to extend the life of the exchange resin and to ensure proper flow characteristics before the next adsorption cycle. The regenerated resin is then returned to the fixed-bed system and reused. As in the single-use, fixed-bed system, perchlorate breakthrough is monitored in the vessel/column effluent. Using multiple fixed-beds allows continuous operation; water can be treated in performing beds while resins in exhausted/loaded beds are regenerated (Boodoo 2003). Management of regenerant wastes containing perchlorate is discussed in a following section.

Moving-Bed System Design. Although not as widely used today, a moving-bed system has been used to treat perchlorate. This design includes a continuous system that includes 20–30 IX beds mounted on a slowly rotating carousel. The rotation of the carousel moves the beds slowly through the required sequence of operations that normally includes adsorption, regeneration, rinse, and displacement. These operations are ongoing simultaneously as the carousel rotates. The different fluids are distributed through a 2-in-1 valve with 20–30 ports, allowing for either concurrent or countercurrent flow in all operation cycles. Countercurrent regeneration and countercurrent rinse water flow, along with low resin volume, combine to reduce the amount of chemicals and solvent required to regenerate and clean the resin (Chiang and Megonnell 2005).

5.1.2.1 Regenerable Resins

Weak-base perchlorate-selective resins also have been tested successfully and are providing performance data for evaluation and implementation. Weak-base anion resins are pH-dependent and regenerable. At low pH, functional groups on these resins have a positive charge (i.e., $R\text{-}NH_3^+$). However, at high pH, the resin functional groups lose a proton and are converted to the uncharged (i.e., $R\text{-}NH_2$) "free-base" form, enabling complete regeneration using small volumes of regenerant solution (ESTCP 2006c). The weak-base resin that has been tested at two sites is Purolite D-4170, a commercially produced macroporous polystyrene divinylbenzene weak-base anion resin.

The weak-base anion exchange process consists of three unit operations: pretreatment, ion exchange, and post-treatment. Pretreatment consists of pH adjustment to lower the pH of the untreated feed water so that the weak-base anion resin is maintained in the ionized form. The pH is adjusted while under pressure, so that carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) alkalinity is converted to carbonic acid. Since carbonic acid is in equilibrium with dissolved carbon dioxide (CO_2) gas, system pressure maintains CO_2 in solution and allows pretreatment and IX to be accomplished using a single pumping operation. Post-treatment consists of a stripping operation (air or liquid-membrane stripping) and pH control (caustic and/or calcite contactor) to return treated water to acceptable levels of pH and alkalinity.

Regeneration is accomplished by adding enough caustic to 2–3 BVs of potable water to neutralize the functional groups on the resin. This solution is circulated through the resin bed. When the regeneration is complete, the solution is drained from the column and held for subsequent treatment. A rinse is conducted to remove residual perchlorate from the resin before protonation (becoming acidic). The concentrated perchlorate in the spent regenerating solution is treated by biodegradation or zero-discharge, scavenger treatment using a strong-base, single-pass (or -use) resin (Applied Research Associates, Inc. 2006).

Selective weak-base anion resins for perchlorate treatment are available mainly through Purolite, but other companies have conducted tests regarding removal of perchlorate in water, including Lanxess-Sybron (Ionac AFP-329).

A new resin-regeneration technology was developed for regenerating the bifunctional (single-use) and other selective anion-exchange resins (e.g., Biquat, marketed as Purolite A-530E) using the ferric chloride-HCl displacement technique. Laboratory experiments indicated that a nearly 100% recovery of IX sites was achieved by washing with as little as 2 BVs of the ferric chloride regenerant solution in a column flow-through system. There was no significant deterioration of the resin's performance with respect to perchlorate removal after repeated loading and regeneration cycles (Gu and Coates 2006).

Data from operational systems and research studies have revealed advantages and disadvantages of regenerable resins, as shown in Table 5-2.

Table 5-2. Regenerable resins strengths and limitations

Strengths	Limitations
• Regenerated resin can be returned to a system and reused • Regenerable resins can provide a longer run time between regeneration • Weak-base anion resins produce low effluent volume (<0.02% of treated water, 50 times more efficient than regenerating with brine), and treated water can be discharged to sewer	• Conventional IX resins suffer from poor regenerability, and a waste stream is produced during the regeneration process that requires further treatment • Selective resins typically require a more complex solution for regeneration • Weak-base anion resin technology requires pretreatment and post-treatment operations along with a higher capital investment

5.1.2.2 Management of Regenerable System Residuals

The regeneration process results in a waste regenerant solution (concentrated perchlorate brine with high TDS) and a waste rinse water. The IX technology removes sulfate, nitrate, perchlorate, and arsenic; all of them require the use of a sodium chloride regenerant to restore chloride in the system. Thus, they all produce the brine wastewater by-product. Some newer resin designs, however, take advantage of a greater selectivity for perchlorate, making it possible to operate the IX unit for a protracted period of time, while removing only the problematic perchlorate and not all of the other ions in the influent stream (ITRC 2005).

Although regeneration of IX resins is widely practiced in general, management of the regenerant brine containing high levels of perchlorate in the presence of high concentrations of chlorides and other anions poses significant challenges. The brine can be managed by regeneration using chemical processes, biological processes, or disposal.

Perchlorate-rich regenerant solution can be reduced using ferrous chloride under elevated temperatures (<200°C) and/or pressures (~20 atm). This regeneration method tested by ORNL/Calgon Carbon was discussed in the spent single-use resin Section 5.1.1.2 (Gu and Coates 2006).

Another innovative technology has been developed at ORNL for a complete destruction of perchlorate in ferric chloride regenerant solutions. While perchlorate is destroyed, the treatment process does not alter the properties of the regenerant solution so that it can be used repeatedly and no waste regenerant is produced. In this treatment process only a reduced volume of regenerant is required, and the disposal of hazardous wastes containing perchlorate is eliminated (Gu and Coates 2006).

Resin can be regenerated by contact with a perchlorate and sulfate and/or nitrate dissolving salt brine (5–20 wt% NaCl). This process desorbs the perchlorate, nitrate, and sulfate off the resin. The concentration of perchlorate in the brine from groundwater containing approximately 20 µg/L perchlorate can be reduced to about 10 mg/L. The brine, which is considered to have a nitrate and sulfate absorption suppressing level of salt, however, can be treated with a perchlorate-specific resin, such as the Purolite A-520E resin, which preferentially adsorbs the perchlorate but also picks up some nitrate and/or sulfate, which is thereafter displaced by additional perchlorate. When the perchlorate is transferred to the A-520E resin, the concentration of perchlorate in the waste brine can be below detection levels, and the treated brine is acceptable for disposal. The concentration of perchlorate on the A-520E resin can be approximately 300 mg/L (Jensen, Guter, and Solomon 2005).

Catalytic chemical reduction of perchlorate using ammonia as the reductant on the concentrated brine of the IX system has been pilot-tested. The process was conducted under high pressure and temperature. The test results demonstrated effective destruction of perchlorate to levels below the detection limit of 125 µg/L.

Biological treatment of spent brine was pilot-tested using groundwater from the San Gabriel Basin perchlorate site. Rinse water, brine, and acetic acid were mixed with bacteria. The batch was continually mixed and monitored for nitrate and perchlorate removal. Nitrate removal was achieved; however, perchlorate removal needed additional time.

Biological reduction has also been tested by Applied Research Associates, Inc. using a membrane-bioreactor system for the treatment of perchlorate in the brine produced by regenerable IX systems. Through this process, the treated brine can be reused for the regeneration of perchlorate-laden resin. This system has been successful at treating perchlorate-laden brine with TDS levels as high as 7% in the laboratory and underwent field-testing in late 2004. See Chapters 6 and 7 for a discussion on how biological reduction works on reducing perchlorate.

Brines have also been managed by disposal through brine lines and brine wells. Cities in California and other western states have used brine disposal lines which discharge at ocean outfalls. These lines were originally constructed to carry waste brines from the oil and gas industry but are now used for concentrates from desalters and ion exchange systems (HDR Engineering Inc. 2001). These lines provide disposal of highly saline discharges. Additional brine lines have been proposed in California, but whether the discharge of perchlorate and other anions such as nitrate will be allowed into these lines and existing lines in the future and at what levels is something that should be reviewed by the project team.

Brine from industrial processes has also been disposed through brine wells. However, disposal of perchlorate-laden brine through brine wells is not accepted by most states. Underground injection of brine for disposal requires a state permit. Spent brine return flow wells are described in Title 40 Code of Federal Regulations (CFR) Part 146.5(e) as "wells used to inject spent brine into the same formation from which it was withdrawn after extraction." Many states do not allow the injection of hazardous waste. Brines may be regenerated to produce a nonhazardous waste, but underground injection may still need permitting.

5.1.3 Applicability

Ion exchange was one of the first technologies considered as a remediation alternative for removal of perchlorate. Full-scale systems have been placed in operation at government, military, and private facilities. Pilot-scale systems and bench studies are continually being conducted to refine the IX process. Table 5-3 shows examples of constructed IX systems for the treatment of perchlorate.

Table 5-3. Effectiveness of ion exchange methods

Projects	**Throughput and treatment effectiveness**	**Media**
Single-use (nonregenerable) IX treatment systems, fixed-bed design, full scale		
Aerojet, Sacramento, CA—Full-scale, operational single-use system (see case study). The systems use a proprietary, nonregenerable, perchlorate-selective resin that is NSF 61 certified for potable use. Data source: California Region 5 Water Control Board.	2000 gallons per minute (gpm) Influent: 50 µg/L Effluent: <4 µg/L	Drinking water
Aerojet, Sacramento, CA—Full-scale. Groundwater Extraction and Treatment (GET) B, GET D, GET H, GET J, and GET K facilities. These systems have used anion exchange resins. Data source: California Region 5 Water Control Board.	800–1000 gpm Influent: 10–200 µg/L Effluent: <4 µg/L	Groundwater
Phoenix Goodyear Airport North, City of Goodyear, AZ—Full-scale IX system since 2005. Carbon system design with resin. System includes carbon treatment and air-strippers for co-contaminant TCE. Groundwater ~100 feet below ground.	440 gpm Influent: 20 µg/L Effluent: <2 µg/L	Groundwater
Camp Edwards portion of the Massachusetts Military Reservation (MMR), Cape Cod, MA—A two-line IX/GAC system with Calgon Carbon products was operational in 2007. Each line has two vessels of selective resin coupled with three vessels of carbon. Holding tanks on site to manage extraction/reinjection groundwater. Data sources: USACE and MassDEP.	1000 gpm Influent: 14 µg/L Effluent: <0.35 µg/L	Groundwater
City of Redlands, CA—Full-scale, operational IX system 2004, using selective resin. Rees city well on Pennsylvania Avenue being treated. Rialto-Colton Groundwater basin. Data source: CDPH 2005.	1100 gpm Effluent: <4 µg/L	Drinking water
City of Colton, CA—Full-scale, operational IX system 2003, using selective resin. City wells #15, 17, and 24. Rialto-Colton Groundwater basin. Data source: CDPH 2005.	2000 gpm Influent: 10 µg/L Effluent: <4 µg/L	Drinking water

Projects	Throughput and treatment effectiveness	Media
City of Rialto, CA—Full-scale, operational IX system 2003, using selective resins. City wells Chino 1 and 2 being treated separately. Rialto-Colton Groundwater basin. Data source: CDPH 2005.	1800–2000 gpm	Drinking water
Tippecanoe Treatment Facility, City of Riverside, CA—Full-scale, operational start-up in December 2002. Rialto-Colton Groundwater basin. Data source: CalEPA 2004.	5000 gpm Effluent: 6.4 µg/L average in 2001 4.6 µg/L average in 2002	Drinking water
Fontana Union Water Co., Fontana, CA—IX resin, operational January 2004.	5000 gpm Influent: 15 µg/L Effluent: <4 µg/L	Drinking water
Lincoln Avenue, Altadena, CA—Operational IX system 2004.	2000 gpm Influent: 20 µg/L Effluent: <6 µg/L	Drinking water
California Domestic Water Company, Whittier, CA—Full-scale IX system, operational start-up July 2002. First commercial installation of a single-use system. Co-contaminants NDMA and nitrates.	5000 gpm Influent: 14 µg/L Effluent: <4 µg/L	Drinking water
Former Kerr-McGee facility (Tronox), Henderson, NV—Full-scale, single-use IX system treated captured surface water in a seep area, no longer in operation. Water in seep area was pumped and treated 2001–2004 until a biological fluidized-bed reactor (FBR) came on line. Data source: ITRC 2005.	300–600 gpm Influent averages ~30 mg/L Effluent: <0.5–2 mg/L, averaging 1.3 mg/L	Surface water Groundwater
Former Kerr-McGee facility (Tronox), Henderson, NV—Full-scale, single-use IX system installed to replace the regenerable system and to allow continuous treatment of extracted groundwater from the Athens Road wells until a FBR was placed on line in 2004.	850 gpm Influent: 200–300 mg/L Effluent varies <0.5–2 mg/L, averaging 1.3 mg/L	Groundwater
Naval Weapons Industrial Reserve Plant, McGregor, TX—Full-scale, no longer in operation. Modular system was brought in to treat a blended influent from the collection/biobarrier trenches averaging 1–2 mg/L perchlorate. System was replaced by a biological FBR.	Influent: 2000 µg/L Effluent: <4 µg/L	Surface water Groundwater
W. San Martin Colony and County water wells, W. San Martin, CA—Full-scale operational system using a commercially available nitrate selective anion exchange resin whose IX properties are similar to nitrates.	800 gpm Influent: 17 µg/L Effluent: <4 µg/L	Drinking water
Single-use (nonregenerable) IX treatment systems, fixed-bed design, pilot scale		
Stringfellow Site, Riverside Co., CA—Full-scale system consists of two 10-ft^3 beds in series. The highly selective IX resin is expected to last several months before changeout is required.	24 gpm Influent: 25 µg/L Effluent: <4 µg/L 30,000 BV exchanges Change lead bed at three-month intervals	Groundwater

Projects	Throughput and treatment effectiveness	Media
Castaic Lake Water Agency, Santa Clarita, CA—Pilot-scale completed. Study on three single-use selective IX resins. Influent feed water concentration was spiked to approximately 50 ppb perchlorate. All the resins removed perchlorate, with breakthrough occurring 25,000–76,000 BVs. Data source: Carollo Engineers, Inc.	2400 gpm Influent: 50 µg/L Effluent: <1 µg/L	Drinking water
Site 9, Vandenberg AFB, CA—Pilot-scale completed. Two 560-gal tanks, each containing ~42 ft^3 of a selective strong-base anion resin. Columns are arranged in series (lead-lag configuration) and installed inside a double-contained treatment pad. Data source: U.S. Air Force Center for Environmental Excellence (AFCEE).	Influent: 204 µg/L Effluent: <4 µg/L Cost: $81K/year for operation and maintenance	Groundwater
Regenerable IX systems, fixed-bed design, full scale/pilot scale		
Site 285, Edwards AFB, CA—Full-scale system, including a chemical regeneration process and destruction module, became operational in the spring of 2003 and had removed 32 pounds of perchlorate from approximately 9 million gallons of water processed through 2004. Four vessels containing a bifunctional resin were used in the system. Data source: Gu and Brown 2007.	30 gpm Influent: 300 µg/L Effluent: <4 µg/L	Groundwater
Buildings 815, 830 DISS, and 854 PRX, Lawrence Livermore National Laboratory (LLNL), Livermore, CA—Full-scale, operational; start-up 2000. Regenerant flow rate 0.25–0.5 gpm/ft^3. Commercially available regenerable nitrate-selective anion exchange resin is effective for perchlorate. Anion exchange is part of a treatment train, preceded with biological treatment to remove nitrate and followed with GAC to remove TCE.	Influent: 10 µg/L Effluent: <4 µg/L	Groundwater
Fontana Water Company, Fontana, CA—Pilot-scale demonstration of drinking-water application completed. IX resin was successfully regenerated. The resin used a commercially produced macroporous polystyrene divinylbenzene weak-base anion resin, which has a projected service life of seven years. Data source: ARA.	Influent: 6 µg/L Effluent: < 0.19 µg/L Treatment rate: 3–4 gpm/ft^3 Treatment capacity: 9700 BVs	Drinking water
Redstone Arsenal, Huntsville, AL—Pilot-scale completed 2006. Resin process effectively removed perchlorate from groundwater without being impacted by TCE present (up to 3100 µg/L). Multiple regenerations were conducted to demonstrate repeatable performance. The spent regenerating solution, <0.05% of the treated water, was successfully treated by biodegradation and by a "zero-discharge" scavenging approach. The resin used was a commercially produced macroporous polystyrene divinylbenzene weak-base anion resin. Data source: ARA.	Influent: 2200 µg/L Effluent: <4 µg/L Treatment rate: 1.5–3 gpm/ft^3 Treatment capacity: 6500 BVs	Groundwater

Projects	Throughput and treatment effectiveness	Media
Regenerable IX systems, moving-bed design, full scale/pilot scale		
La Puente Valley County Water District, CA—Continuous anion exchange and regeneration system. Full-scale operation designed to treat up to 600 µg/L perchlorate began operating 2000. Uses a strong-base anion, acrylic, Type 1 gel resin. Co-contaminants are NDMA and 1,4-dioxane. Data source: CalEPA 2004.	2500 gpm Influent: 200 µg/L Effluent: 4 µg/L	Drinking water
Former Kerr-McGee facility (Tronox), Henderson, NV—Full-scale, no longer in operation. Perchlorate destruction module started in 2002 and operated for about six months to treat extracted groundwater. Actual flow rates varied 200–560 gpm. Maintenance problems were caused by high TDS, hardness, and sulfate. Operation was discontinued due to corrosion in heat exchangers. Data sources CalEPA 2004, ITRC 2005.	450 gpm Influent: 80–100 mg/L Effluent: <2 mg/L	Groundwater
Big Dalton Well, Baldwin Park, CA—Pilot-scale, continuous anion exchange and regeneration system completed. Brine produced was 0.75% of the inflow. Data source: CalEPA 2004.	5 gpm Influent: 18–76 µg/L Effluent: <4 µg/L	Drinking water

5.1.4 Strengths and Limitations

Ion exchange is applicable when perchlorate concentrations are high or low and can be operated on groundwater with high TDS and dissolved solids. Table 5-4 lists the strengths and limitations of ion exchange.

Table 5-4. Ion exchange system strengths and limitations

Strengths	Limitations
• Ion exchange is a proven technology with supporting data that has been placed in full-scale operation • Single-use systems offer the advantage of simplicity—modular in design and typically delivered and installed quickly • Single-use systems do not generate a perchlorate-laden waste stream (brine) that is created during resin regeneration • Regenerable systems offer the advantage of small footprints, high regeneration efficiencies, and automated operation	• Organics, TDS, calcium, or iron in the influent can clog resin beds, reducing system effectiveness • Single-use systems require the replacement of exhausted resins, which must be removed from the facility and sent for disposal • Single-use resins can cause fouling, plugging, channeling, bacterial contamination, agglomeration, and compaction problems • Regenerable systems produce brine that requires disposal • System effectiveness can be reduced by leachables from new resins or by resins that are old

5.1.5 Treatment Train

IX is often preceded by treatments such as filtration and oil-water separation to remove organics, suspended solids, and other contaminants that can foul the resins and reduce effectiveness (EPA 2005b). IX can be used to treat perchlorate as a stand-alone system or in combination with other perchlorate-remediation processes. GAC has been used in conjunction with IX systems as a pretreatment primarily to remove co-contaminants (e.g., TCE and other VOCs). IX can also serve as a polishing step for biological treatment processes or electrodialysis reversal systems. GAC and electrodialysis are discussed further in Sections 5.2 and 5.5, respectively.

5.1.6 Costs

Capital costs for system design, installation, and operation and maintenance (O&M) depend on site conditions and cleanup goals. Due to the high water solubility of perchlorate, costs to treat large volumes of groundwater can be high.

In general, IX is more cost-effective when perchlorate concentrations are low (<50 µg/L). Common anions in groundwater, including nitrate, sulfate, and bicarbonate, compete with perchlorate for binding sites on IX resins. As the concentrations of these anions increase, the cost of IX for perchlorate removal also tends to increase. Low perchlorate selectivity of resins leads to relatively high treatment costs associated with early versions of IX systems that were deployed for perchlorate removal.

Perchlorate treatment efficiency is measured as the number of BVs treated before breakthrough and/or regeneration. BV refers to the volume of the IX vessel that is occupied by exchange resin. Water treatment is also measured on an acre-foot basis. An acre-foot is a unit of measurement commonly used in the drinking water industry to describe large quantities of water, such as the amount of water treated in a drinking water system. An acre-foot is the volume of water that would cover one acre of land (43,560 square feet) to a depth of one foot, equivalent to 326,851 gal of water.

Single-Use Treatment Systems. The majority of operational IX systems use single-use (nonregenerable) resins. Operation of single-use treatment systems is simple, and the capital investment required is low compared to that of regenerable treatment systems. Conversely, operating costs associated with the periodic replacement and disposal of resin can be relatively high. In general, the operating costs associated with nonregenerable IX systems range $100–150/acre-foot (U.S. Filter 2004).

Selectivity of an IX resin is extremely important for reducing the long-term operating cost of perchlorate treatment. When using disposable (single-use) IX resin, it is important to maximize the adsorptive capacity of the resin to minimize operational costs. Water that contains high TDS can significantly hinder IX effectiveness and can become cost-prohibitive to treat (ITRC 2005).

Disposable resins can provide effective removal of perchlorate at relatively high flow rates. Resins with very high affinities for perchlorate are the best candidates for achieving low perchlorate leakage and long useful life. 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 (Boodoo 2003).

Regenerable Treatment Systems. Regenerable IX is significantly cheaper when the perchlorate can be disposed via brine lines (if permitted by the state). In the absence of such disposal, there is currently no cost-effective treatment technology for the brine. Data from systems that use regeneration indicate high costs, and no biological or other chemical approaches have been applied at commercial scale. 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.

However, studies have demonstrated that the operational costs for weak-base regenerable anion resin systems are lower than those for other regenerable or single-use resins. The operational costs for weak-base anion resin are estimated at $70–85/acre-foot (2008 $US). The operational-cost components include acid and caustic consumption in pretreatment, post-treatment, and regeneration operations; weak-base anion-resin replacement; scavenger-resin replacement (drinking water only); biodegradation (remediation only); electricity; and labor (ESTCP 2006c).

5.2 Granular Activated Carbon

A highly adsorbent material with very large surface-to-volume ratios, GAC is commonly used to remove contamination from water. As water passes through the carbon, contaminants stick to the surface of the particles. Carbon is used in over half of the water treatment facilities in the United States, and its use dates back to the 1950s. Carbon is also used in home drinking-water filter systems to remove odors, taste, and excess chlorine.

GAC is manufactured from high-carbon-content materials such as coal, wood, or coconut shells. To create more surface area onto which contaminants can adsorb, the carbon material is activated by heating. 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.

Although standard GAC has not been found to efficiently remove perchlorate, the adsorptive capacity may be increased through coating the surface with a thin layer of a surface-active substance. This coating produces a modified or tailored GAC (T-GAC). The tailoring agent, or surfactant, creates a positively charged matrix on the GAC's carbon surface that attracts the negatively charged perchlorate ion. As in IX, other competing ions such as nitrate and thiosulfate may also be attracted to the tailored surface. Once treated with the tailoring agent, the enhancement (monomers, polymers, etc.) function as an IX process, rather than just adsorption, where the perchlorate is adsorbed and chloride is released.

Over the course of operation, the T-GAC's adsorptive sites will be taken up by perchlorate and competing ions, exhausting the carbon and rendering it spent. Similar to IX, breakthrough of the contaminant occurs when the effluent contaminant concentration exceeds the treatment objective. The effluent must be monitored for contaminant breakthrough so that GAC can be managed (replaced or regenerated) as the carbon becomes exhausted and can no longer adsorb contaminants. Figure 5-3 is a generalized schematic of the GAC treatment process.

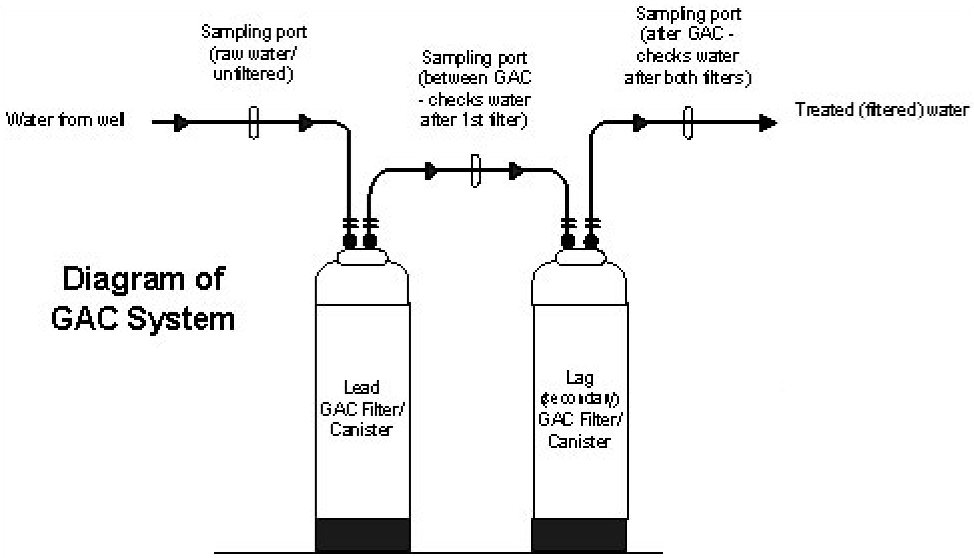


Figure 5-3. GAC Treatment process.

Numerous efforts are under way to tailor GAC and improve the adsorptive properties. Research at Penn State University in collaboration with EPA, by the American Water Works Association Research Foundation (AWWARF), and by private companies is being conducted to examine enhancements (e.g., monomers, polymers, organic iron complexes or quaternary amines) that can be added to improve the perchlorate adsorption capacity of GAC (Parette and Cannon 2006; Chen, Rangel-Mendez, and Cannon 2005). These enhancements can both significantly increase the perchlorate adsorption and allow for regeneration of the T-GAC once spent. Specifically, a surfactant-tailored GAC technology has been developed. This tailoring extends the GAC's bed life for adsorbing perchlorate up to 35 times longer than conventional, nontailored GAC (ESTCP 2006d). AWWARF showed that when GAC was tailored with cetyltrimethyl ammonium chloride (CTAC), the carbon adsorbed 30–35 times more perchlorate than the virgin GAC. At one operating system, this extended perchlorate breakthrough from 1,200 BV for virgin GAC to 34,000 BV for CTAC-tailored GAC (Parette and Cannon 2006, Gu and Coates 2006).

The tailoring agent may need testing to ensure that the formation of NDMA does not occur. NDMA is on the EPA Unregulated Contaminant Monitoring list as an emerging contaminant of potential concern. However, in controlled, demonstration-scale trials by Penn State University, NDMA has been monitored for but never found.

Treatment Train. GAC systems can include multiple beds in series to manage regeneration; beds first in the series will require regeneration first, and fresh beds can be added at the end of the series. Multiple beds can also allow continuous operation because some beds can be regenerated as others continue to treat water. GAC has effectively been used in conjunction with other processes such as IX.

Management of Residuals. Carbon adsorption using GAC is not a destructive process, and exhausted carbon requires regeneration or disposal. Thermal reactivation, the most commonly used regeneration method for activated carbon, provides a means to restore the capacity of the carbon at a cost less than would be incurred by replacing the exhausted GAC. Thermal reactivation is normally done off site in a rotary kiln, fluidized bed, or multiple hearth furnace. Laboratory tests conducted by Penn State University showed that thermal regeneration of T-GAC breaks down the perchlorate ion during the process and 90% of adsorptive capacity can be restored. Research is ongoing for means of chemically regenerating the T-GAC with an anionic reducing compound so that the T-GAC could sustain an acceptable overall adsorption capacity between thermal reactivation cycles. When a T-GAC's perchlorate adsorption capacity becomes exhausted, reducing solutions can restore much of its adsorption capacity by washing out the adsorbed perchlorate. Perchlorate-laden T-GAC has been regenerated with sodium borohydride achieving over 50% recovery of the T-GAC's capacity for removing perchlorate, thus extending the service life of the T-GAC (Cannon and Chen 2005).

Spent GAC may require treatment prior to ordinary or hazardous waste disposal (Graham, Cannon, and Parette 2004). Disposal of exhausted carbon can be managed by the supplying vendor. However, a manifest from the vendor should be attained to certify proper disposal. Landfill disposal could cause perchlorate to desorb from the carbon contaminating off-site areas and does not eliminate the generator's ongoing liability. Incineration of exhausted GAC, with certificates of destruction, destroys the perchlorate ion and reduces the GAC to a small amount of ash with no secondary toxic contaminants to manage.

5.2.1 Applicability

Full-scale and pilot-scale systems are in operation using GAC and T-GAC. Table 5-5 lists the effectiveness of T-GAC as known from actual cases.

Table 5-5. Effectiveness of tailored granular activated carbon

Projects	Treatment effectiveness	Media
Crafton-Redlands Plume, City of Redlands, CA—Full-scale, operational GAC system installed to treat VOC contamination for drinking-water supply, later found effective to treat low concentrations of perchlorate.	Influent: 60–138 μg/L GAC bed regenerated every 6 weeks for perchlorate treatment	Drinking water
Camp Edwards portion of the MMR, Cape Cod, MA—A two-line GAC/IX system operational in 2007. Data source: USACE and MassDEP.	1000 gpm Influent: 14 μg/L Effluent: <0.35 μg/L	Groundwater
Edwards AFB, CA—Full-scale, liquid-phase GAC system constructed to remove VOCs.	Influent: 92 μg/L 2003 data: ineffective for perchlorate	Drinking water
City of Monterey Park, CA—Full-scale, coconut GAC to treat low levels of perchlorate.		Drinking water
Crafton-Redlands Plume, City of Redlands, CA—Pilot-scale, commercially available GAC can be tailored to extend the service life for perchlorate removal from 1 month to 2.5 years.	Influent: 60–140 μg/L Effluent: <6 μg/L	Drinking water

5.2.2 Strengths and Limitations

GAC that has not been tailored for perchlorate removal has only limited effectiveness. Table 5-6 lists the strengths and the limitations of GAC.

Table 5-6. Tailored granular activated carbon strengths and limitations

Strengths	Limitations
• Tailored or modified GAC has been an effective technology as part of a treatment train • Can be regenerated for reuse • Proven technology	• Nontailored, liquid-phase GAC is not efficient for treating perchlorate since perchlorate is highly water soluble • Produces a waste stream requiring management • Applicable only when perchlorate concentrations are low (~100 µg/L) • Nitrate and sulfate will "plug" even tailored GAC and result in faster breakthrough times for perchlorate • GAC adsorption for perchlorate might require pretreatment for removal of suspended solids, silica, or mica from streams to be treated • If not removed, suspended solids in a liquid stream may accumulate in the adsorption column, cause a pressure drop, and then have to be removed by backwashing • Water-soluble co-contaminants with a high polarity can reduce the ability of GAC to remove perchlorate from water • An increase in flow rate through the adsorption column can decrease adsorption of contaminants (Graham, Cannon, and Parette 2004)

5.2.3 Costs

The cost to remove organics is approximately $1 per pound of GAC. T-GAC for perchlorate removal is more expensive. Capital costs including containers, labor, replacement, transport, and O&M are some factors that should be considered in system design. Costs are highly sensitive to the amount of competing ions present and can vary greatly. For a T-GAC demonstration (using alkyl quaternary ammonium), the anticipated costs for tailored carbon treatment, including media, operations, and restoration costs, were expected to be approximately $60–120 (2008 $US) per acre-foot of water treated for groundwater that contained an influent of 40–70 µg/L perchlorate.

5.3 Reverse Osmosis

Reverse osmosis (RO), also known as hyperfiltration, is a membrane filtration technology wherein water is demineralized using a semipermeable membrane operating at high pressure. RO is a physical separation method that has long been used to remove ions from drinking-water supplies, and the technology is commonly used to treat groundwater with high TDS levels. To separate perchlorate from water using the RO process, water containing perchlorate is driven under pressure through a semipermeable membrane that does not allow contaminants with a molecular size greater than the membrane cut-off size to pass (Figure 5-4). Purified water passes through the RO membrane into a fresh-water section, leaving a perchlorate-laden brine solution (see schematic below). Liquid in the fresh-water section (permeate) can be used; the brine solution (rejectate) requires further treatment or appropriate disposal. Membranes are classified by the particle size that

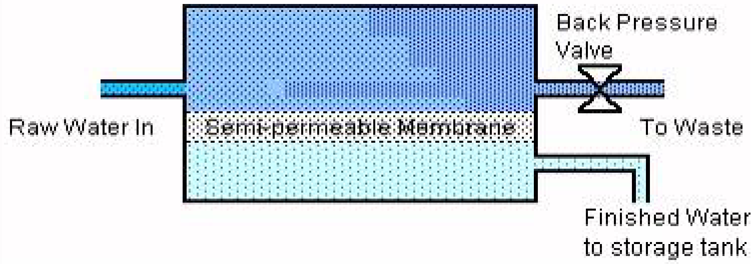


Figure 5-4. Schematic of the reverse osmosis process.

the membrane removes. Typical membrane pore sizes are in the range of 0.0001 micron in diameter and smaller. The filter pore size removes nearly all ions in source water to produce high-purity water.

Treatment Train. RO can be used as a pretreatment step or as a polishing technique to further reduce perchlorate concentrations from water treated by other technologies including bioreactors, GAC, IX, and other filtration membranes. RO can operate as a stand-alone technology to remove perchlorate at low-concentrations and produce drinking-quality water. RO has been certified by NSF International and the American National Standards Institute (NSF/ANSI) for removal of perchlorate for that purpose. A protocol to evaluate drinking-water treatment devices for perchlorate-removal effectiveness has been added to NSF/ANSI Standard 58: Reverse Osmosis Drinking Water Treatment Systems.

Management of Residuals. RO is not a destructive process, so the reject or brine solution containing perchlorate and other contaminants must be further treated prior to disposal. Management of residuals is subject to state specific regulations. The residuals can be treated by the following means:

- ex situ biological treatment (see Chapter 7)
- discharge to surface water
- land application
- injection wells
- evaporation ponds
- evaporators
- wastewater collection systems
- wastewater treatment plant effluent

5.3.1 Applicability

Full- or pilot-scale systems have not been placed in operation at the time of this publication. Table 5-7 lists bench-scale studies.

Table 5-7. Reverse osmosis bench-scale studies

Projects	Treatment effectiveness	Media
NASA, JPL Pasadena, CA—A laboratory treatability study was performed to assess the effectiveness of RO to remove perchlorate from groundwater. A thin-film composite and a cellulose-acetate membrane were tested. In both tests, 80% of influent stream was recovered as permeate and 20% as rejectate. High energy requirements due to operating pressures required.	Influent: 800 µg/L Thin-film permeate 12–6 µg/L, thin-film rejectate 3600 µg/L Acetate permeate 680 µg/L, acetate rejectate 1600 µg/L	Groundwater
AWWARF, Boulder, CO—Reverse osmosis and nanofiltration.	Influent: 18–1000 µg/L Effluent: Unknown	Drinking water
Clarkson University—Reverse osmosis, completed 2004.	Influent: 125–2,000 µg/L Effluent: 5–80 µg/L	Groundwater
NSF International—Perchlorate reduction, 2004. Bench-scale studies of water filters. www.nsf.org/certified/dwtu	Influent: 130 µg/L Effluent: <4 µg/L	Drinking water

5.3.2 Strengths and Limitations

RO has been used for many years to remove impurities from water and is now being tested for its ability to remove perchlorate. Table 5-8 shows strengths and limitations of the technology.

Table 5-8. Reverse osmosis strengths and limitations

Strengths	Limitations
• Proven and certified technology • Can treat high-TDS water and concentrated brines • Filtration available for public water supplies • Effective as part of a treatment train, can be used as a stand-alone filtration system for private water supplies with low concentrations • Automated systems	• Membrane resilience and fouling • Produces a waste stream requiring management • Membrane filters have small pore sizes and require a higher operating pressure than other membrane treatment technologies • The lack of ionic selectivity in the semipermeable membrane can alter the pH of the effluent stream and make it corrosive • Post-treatment may require sodium chloride or sodium bicarbonate to make water palatable (Urbansky et al. 2000)

5.3.3 Costs

Labor costs are usually low due to the automated nature of most systems. However, due to high capital and O&M costs, membrane filtration technology may not be cost-effective. RO costs depend on power needs, the water chemistry (pretreatment, post treatment, and pH adjustment), and labor. As an example, power requirements are on the order of 10 hp to treat 30 gpm and up to 15 hp for 60 gpm, which remains constant while the system is running. A 10-hp, 3-phase motor costs approximately 15 cents/hour to operate. The chemical costs for treatment involve antiscalants and membrane-cleaning chemical needs. Calibration of pH probes requires weekly attention. Cleaning a system requires a chemical recirculation procedure. There are additional costs for disposal and/or treatment of the brine produced by the system. Vendors can supply point-of-use RO systems to reduce perchlorate that can be equipped in-line at a tap-water source. Such systems have been priced at approximately $600 (2008 $US).

5.4 Nanofiltration/Ultrafiltration

Nanofiltration and ultrafiltration are two other membrane treatment technologies similar to RO, except these technologies use membranes with larger pore sizes operating at lower pressures. The synthetic, porous material of membranes acts like a shield, preventing particles of a defined size or larger from passing as pressure forces water through the membranes.

Nanofiltration uses membranes to preferentially separate different fluids or ions. Nanofiltration is not as fine a filtration process as RO and does not require as much energy. Also known as "membrane softening," this process consists of a membrane with a pore size in the range of approximately 0.0001–0.005 microns; hence, the membrane filters particles with diameters ranging 1–50 angstroms. Since the perchlorate molecule size has a hydrodynamic radius of 3.5 angstroms (0.00035 microns), nanofiltration is not expected to work well in separating perchlorate from water.

Ultrafiltration is a selective fractionation process that uses membranes with pore sizes larger than nanofiltration. This process was developed to fractionate and concentrate solutions with colloidal and high-molecular-weight material using pressures up to 145 psi. The membrane removes most nonionic material and passes most ionic material, depending on the size of the molecule. Filtered water from this process contains low-molecular-weight organic solutes and salts. The ultrafiltration process removes particles in the 0.0025–0.1 micron range, much larger than the size of the perchlorate ion. In Figure 5-5, which illustrates the membrane process characteristics, the dark shading indicates removal, and the light shading indicates partial removal.

	Microfiltration (1–0.1 microns)	Ultrafiltration (0.1–0.005 microns)	Nanofiltration (0.005–0.0001 microns)	Reverse osmosis (hyperfiltration) (<0.0001 microns)
Metals	→	→	→	▒
PERCHLORATE 0.00035 micron	→	→	▒	■
Viruses	→	→	■	■
Bacteria	→	■	■	■
Suspended solids	■	■	■	■

Figure 5-5. Membrane process characteristics.

Treatment Train. Nanofiltration and ultrafiltration have been used with other membrane technologies in a series of filtering steps for water treatment. Either or both could serve as a pretreatment step to separate suspended particles that may cause fouling and thus maintain the integrity of or protect RO membranes and reduce the downtime required for membrane cleaning.

As ultrafiltration targets compounds that are larger than those removed by nanofiltration, ultrafiltration also fails to effectively remove perchlorate from water. However, surfactant-modified ultrafiltration has been tested to modify a negatively charged membrane to enhance perchlorate rejection. Studies showed that perchlorate was rejected by electrostatic and/or steric exclusion. The steric exclusion was due to decreasing membrane pore size caused by the adsorption of the cationic surfactant (Yoon et al. 2003).

Management of Residuals. Nanofiltration and ultrafiltration are not destructive processes; the filtered solution containing perchlorate and other contaminants must be further treated prior to disposal. Management of residuals is subject to state-specific regulations. The residuals can be treated by the following means:

- ex situ biological treatment (bench scale, see Chapter 7)
- discharge to surface water
- land application
- injection wells

- evaporation ponds
- evaporators
- wastewater collection systems
- wastewater treatment plant effluent

5.4.1 Applicability

Typical nanofiltration and ultrafiltration applications include water softening, desalination of dyestuffs, acid and caustic recovery, and color removal. Full- or pilot-scale perchlorate-treatment systems have not been placed in operation at the time of this publication.

A bench-scale study funded by AWWARF in 2004 provided performance data to assess the effectiveness of nanofiltration and ultrafiltration processes to remove perchlorate from water. In general, results indicated that perchlorate can be significantly excluded from like-charged membranes with pores that are large relative to the size of the perchlorate ion. However, this rejection capability decreases in the presence of a sufficient amount of other ions that can screen the apparent electrostatic force field. Consequently, the study proved the ineffectiveness of perchlorate removal using nanofiltration and ultrafiltration, based on the fact that the membrane pore sizes are larger than the hydrodynamic radius of the perchlorate ions.

5.4.2 Strengths and Limitations

Nanofiltration and ultrafiltration have been used for many years to remove impurities in water. However, use of these processes to remove perchlorate is limited. Table 5-9 notes the strengths and limitations of these processes.

Table 5-9. Nanofiltration/ultrafiltration strengths and limitations

Strengths	Limitations
• Can pretreat high-TDS water, may be effective as part of a treatment train • Use less energy with lower operating pressures than reverse osmosis	• Ultrafiltration membrane pore size too large for removal of perchlorate ions • Nanofiltration membrane pore size has limited effectiveness on removing perchlorate ions • Perchlorate removed forms a waste stream that requires management • Fouling of membranes

5.4.3 Costs

The cost for nanofiltration skid systems capable of treating 1,500–25,000 gal/day range approximately $14,000–51,000. Storage tanks in the 100–5,000-gal range may cost $325–5,000 (2008 $US).

5.5 Electrodialysis

Electrodialysis is a type of membrane treatment technology that uses an electrical current to effect separation. The electrodialysis process entails water passing through flow channels of alternating semipermeable and permeable IX membranes while a direct current (DC) voltage potential field is applied across the membranes. As the influent feed flows through the channels between the membranes, the DC voltage potential induces the cations to migrate through the cation-transfer membrane towards the negatively charged anode. Simultaneously, the anions (perchlorate) migrate through the anion-transfer membrane toward the positively charged cathode. Figure 5-6 shows the process.

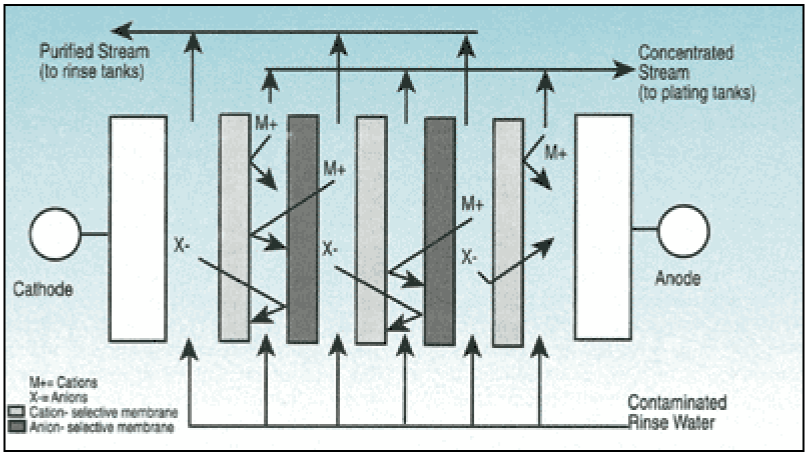


Figure 5-6. Electrodialysis concept.

Electrodialysis was commercially introduced in the early 1960s, about 10 years before RO. In the early 1970s, an American company commercially introduced the electrodialysis reversal process, which operates on the same general principle as standard electrodialysis with the exception that both the product and the brine channels are identical in construction. Several times each hour, the polarity of the electrodes is reversed, and the flows are simultaneously switched so that the brine channel becomes the product water channel, and the product-water channel becomes the brine channel. The result is that the ions are attracted in the opposite direction across the membrane stack. Immediately following the reversal of polarity and flow, enough of the product water is dumped until the stack and lines are flushed out and the desired water quality is restored. The current reversal process is useful in breaking up and flushing out scales, slimes, and other deposits in the cells before they can build up and create a problem. Flushing allows unit operation with fewer pretreatment chemicals and minimizes membrane fouling.

Treatment Train. Electrodialysis has been tested as a stand-alone technology and in combination with other perchlorate-treatment technologies. For example, electrodialysis can be used for pretreatment with IX. Customized electrodialysis membranes constructed from IX resin material allow perchlorate removal via both approaches.

Management of Residuals. Electrodialysis is not a destructive process and produces a contaminated brine waste stream that requires treatment and/or proper disposal. The concentrate resulting from this method may require large quantities of water for further treatment prior to disposal (Urbansky and Schock 1999).

5.5.1 Applicability

Full-scale systems have not been placed in operation; however, two pilot-scale systems have been tested. Table 5-10 shows the effectiveness of this treatment technique.

Table 5-10. Effectiveness of electrodialysis

Projects	Treatment effectiveness	Media
Magna Water Co., Salt Lake City, UT—Pilot electrodialysis reversal operated continuously for 4 days. The groundwater flow rate was approximately 7.4 gpm.	Influent 15–130 µg/L Effluent: 11–17 µg/L	Drinking water

5.5.2 Strengths and Limitations

Electrodialysis can remove perchlorate at low concentrations, but application is more effective as a polishing technique when coupled with IX. Table 5-11 notes specific strengths and limitations.

Table 5-11. Electrodialysis strengths and limitations

Strengths	Limitations
• Ability to manage water with a high TDS • Capable of high recovery (more product and less brine than IX) and a lack of effect by nonionic substances such as silica • Pretreatment with IX resin membranes when high TDS is a consideration	• Membrane fouling • Low selectivity of the permeable membrane for perchlorate • High electrical energy demands • Perchlorate that is removed forms a waste stream requiring management

5.5.3 Costs

Costs of this process are likely to exceed those of IX. A two-stage electrodialysis reverse system with averaged production flow rates of 3.45 mgd was tested in Salt Lake County, Utah. Capital costs were approximately $7,850,000. Annual O&M costs were $658,000, yielding a production cost of $1.16/1000 gal. Adding an IX process for polishing required additional capital costs of approximately $4,600,000 and annual O&M costs of $390,000.

5.6 Capacitive Deionization

Capacitive deionization is an electrochemical technology primarily for desalinating brackish water but can also be used to remove perchlorate ions. This technology separates ions from solution using an electric field applied between electrodes. The cations and anions are electrosorbed onto the cathode and anode, respectively, while treated water passes through. 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. Figure 5-7 illustrates the concept.

The method for making electrodes was an outgrowth of work conducted on making carbon aerogels from resorcinol formaldehyde resins. The basic method consists of impregnating a carbon paper support with a water-resorcinol-formaldehyde solution, polymerizing the resin into a gel, supercritically extracting the water to prevent the porous structure from collapsing, and heating the polymerized-resin/carbon paper structure to convert the resin to a microporous carbon aerogel supported by the carbon paper. The paper makes the structure strong, flexible, and highly conductive.

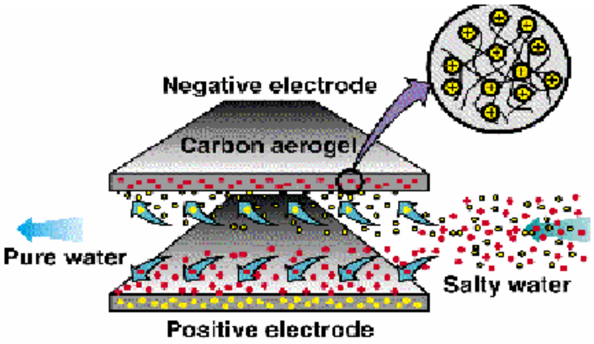


Figure 5-7. Capacitive deionization.

Another patented technology for capacitive deionization includes a different type of electrode designated as the “Flow-Through Capacitor.” This electrode is made of alternating electrodes with porous activated carbon. With application of small voltage, dissolved salts in the water moving through the capacitor are attracted to the high-surface-area carbon and removed. Once the capacitor is fully charged, the electrodes are shorted to regenerate the capacitor, causing absorbed contaminants to be released as a small volume of concentrated-liquid waste.

Eventually, the electrodes become saturated with ions and must be regenerated. Regeneration is accomplished by electrically discharging the electrodes. The applied electrical potential of the electrodes is removed, and since there is no longer any reason for the ions to remain attached to the electrodes, they are released and flushed from the system. Regeneration of the electrodes yields a concentrated brine. More than 80% of the influent emerges as fresh, deionized potable water, but the remainder is discharged as the concentrated brine.

Treatment Train. Capacitive deionization has been used as a stand-alone process, mainly to desalinate brackish water. The technology has not been used in conjunction with other perchlorate treatment alternatives.

Management of Residuals. Capacitive deionization is not destructive processes. Regeneration of the electrodes yields concentrated brine similar to IX and membrane processes. The concentrate solution requires further treatment before it can be discharged. Options for the brine treatment include catalytic treatment and biological reduction.

5.6.1 Applicability

Full-scale systems have not been placed in operation. Although not particularly for perchlorate removal, a pilot-scale system was tested to treat a drinking-water supply in Carlsbad, California, and the system remains in operation. Bench-scale testing has been researched. Table 5-12 notes the effectiveness of the method.

Table 5-12. Effectiveness of capacitive deionization

Projects	Treatment effectiveness	Media
Carbon aerogel—Bench/laboratory-scale test for treatment of synthesized perchlorate-contaminated waters. Data source: LLNL.	Influent 80 mg/L Effluent: 10 mg/L	Groundwater

5.6.2 Strengths and Limitations

The relatively low regeneration rate, combined with the high cost of carbon aerogel, makes it impractical at this time. Table 5-13 lists the strengths and limitations of the method.

Table 5-13. Capacitive deionization strengths and limitations

Strengths	Limitations
• No troublesome membranes • More energy-efficient than competing technologies, especially thermal processes • Uses less energy with lower operating pressures than reverse osmosis • Electrostatic regeneration of acids, bases, or salt solutions required by IX systems are not generated • Carbon aerogels have excellent stability in harsh chemical conditions and a very high specific surface area (600–1000 m^2/g of aerogel)	• Efficient only on low perchlorate concentrations • Small electrochemical energy limits capacity • Backflushing difficulties in which only 40%–60% regeneration is achieved • Perchlorate that is removed forms a waste stream requiring management • The sorption capacity of the carbon-aerogel anodes decreases with the size of the ion; in the case of perchlorate, a relatively large monovalent anion, the electrosorption capacity is less than the capacity for chloride

5.6.3 Costs

The primary advantage of this technology is its low operating cost, which is about one third that of its main competitor, RO. However, initial capital costs are higher than those of other perchlorate treatment alternatives. The current carbon-aerogel electrodes are very expensive. The main cost driver is the cost of the electrodes that are made from resorcinol, which is very expensive. Further research is under way to produce a less costly electrode. Ongoing work on improved electrodes will reduce costs by using carbon made from very inexpensive precursors.

5.7 Emerging and Innovative Technologies

Existing commercial technologies that either physically separate and concentrate perchlorate without destroying it (e.g., IX and activated carbon adsorption) or that use microorganisms to reduce perchlorate (e.g., biotreatment), produce water that requires further treatment. Both the public and private sectors are conducting research and development on emerging and innovative technologies for remediation of perchlorate. New technologies are in various stages of research and certification for acceptance in the environmental field.

5.7.1 Electrolysis

Electrolysis is the process of decomposing an electrolyte solution into positive and negative ions using electricity. The electrolysis of perchlorate-impacted groundwater occurs when an electrical charge, provided by an electrical power supply, is introduced and the water acts as an electrolyte. Electrolytes have positive or negative ions that conduct the electricity through water and produce the intermediate products of electrolysis for the treatment of pollutants in water. During the process, electricity splits up some of the water being treated into its atomic parts. This process is called “hydrolysis.” Electrons travel from anode to cathode where a solution is reduced or oxidized. Perchlorate is reduced at the cathode. Water can be collected in a treatment tank, where electrodes electrify the collected water with predetermined voltage and reduce the perchlorate and nitrates, and the clean water is discharged. Electrolysis is also used to produce commercial quantities of sodium perchlorate. The chloride ion in a liquid solution of sodium chloride can be oxidized through the sequence of hypochlorite (ClO), chlorite (ClO_2), chlorate (ClO_3), and finally perchlorate (ClO_4). There are questions concerning disposition of the perchlorate and residual salts.

Treatment Train. Electrolysis has been tested for removal of perchlorate as a stand-alone system for treatment of groundwater from municipal wells. Electrolysis has been used in water purification, with perchlorate being one of the removed impurities. Use in combination with other technologies has not been researched to date.

Management of Residuals. The chemical components of water are separated by an electrical charge into their two parts, hydrogen and oxygen. In this technique, hydrogen and oxygen atoms/ molecules are separated from perchlorate and nitrate molecules into harmless by-products and leave the water contaminant free. By-products can be oxygen, nitrogen, water, carbon dioxide, hydrogen and nontoxic salts. Perchlorate is a toxic salt rearranged to form nontoxic chemicals.

5.7.1.1 Applicability

Full-scale systems have not been placed in operation. One company claims an electrolytic water purification system has been developed that effectively destroys perchlorate and nitrate in water, leaving no residue besides harmless oxygen and nitrogen. A pilot-scale electrooxidation system was tested in California. The electrolysis process oxidized organic contaminants and reduced inorganics to their basic and harmless elements. Results from tests on a water supply well in San Martin, California showed a reduction of perchlorate from 10 µg/L to <4 µg/L and nitrates from 45 mg/L to 7.2–9.0 mg/L. The range of nitrate results was caused by different amounts of voltage applied to the water (EarthVision 2003).

5.7.1.2 Strengths and Limitations

The system must be reviewed and certified by NSF before the technology can be used for drinking-water treatment. The limitations as of this writing are significant, as Table 5-14 shows.

Table 5-14. Electrolysis strengths and limitations

Strengths	Limitations
• No brine or other waste stream	• Not certified • High electrical energy requirements • Limited research

5.7.2 Ultraviolet Laser Reduction

Ultraviolet (UV) laser reduction is an emerging technology shown to be effective for decomposing low levels (<100 µg/L) of perchlorate dissolved in water. The large tetrahedral structure of the perchlorate ion—four oxygen atoms surrounding the central, highly oxidized, chlorine(VII) atom—results in an ion with a highly disbursed, sterically hindered anionic charge. This provides for high solubility in many solvents. Despite its high oxidation potential, perchlorate is very slow to react due to its large activation energy. Thus, perchlorate is relatively stable, particularly under cold and dilute conditions. Chemical reactions that are kinetically rather than thermodynamically limited offer the possibility for rate enhancements by lowering or overcoming the activation energy barrier.

Photons can provide the activation energy necessary for some molecules in water solution, such as perchlorate, to react. Literature sources, including patent literature, report that UV light, such as that from a mercury-vapor lamp that emits a spectrum of UV light including a limited amount of 185 nm photons (the ClO_4^- UV absorption peak) in deoxygenated solutions in the presence of metallic-iron powder can provide the activation energy necessary for the chemical reduction of perchlorate to chloride. 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). However, the rate of perchlorate reaction resulting from mercury vapor lamp irradiation is low.

Treatment Train. Preliminary tests using UV laser reduction indicate that other common perchlorate co-contaminants such as chlorinated solvents and 1,4-dioxane can be decomposed along with perchlorate. Catalytic reduction destroys perchlorate in water through a chemical reaction involving zero-valent iron (ZVI) and UV radiation.

Management of Residuals. Due to the complete decomposition of perchlorate to chloride ions, no residuals are left to manage.

5.7.2.1 Applicability

Full-scale systems have not been placed in operation. Laboratory testing has successfully demonstrated that low concentrations of perchlorate dissolved in water can be completely decomposed to chloride ions by means of an UV laser without first removing dissolved oxygen and without any additives. An added advantage is that lower concentrations of perchlorate result in higher percentages of perchlorate removal. Concentrations of 10 mg/L perchlorate were converted completely to chloride using UV-laser photolysis. This technology is currently under testing and has not yet been commercialized.

5.7.2.2 Strengths and Limitations

Table 5-15 notes the strengths and limitations of ultraviolet laser reduction.

Table 5-15. Ultraviolet laser reduction strengths and limitations

Strengths	Limitations
• Complete decomposition at low concentrations • Surface water treatment • Catalytic reduction faster than biological reduction	• Not effective on high perchlorate concentrations • Limited research

5.7.3 ZVI Reduction with UV Radiation

Two innovative chemical processes using ZVI have been investigated to determine the feasibility of perchlorate removal from water: one with UV radiation and the other with phosphoric acid.

The first process involves the exposure of perchlorate simultaneously to metallic iron and UV light under anoxic conditions. Despite the concerns of many researchers regarding the high kinetic inertness of perchlorate, it was 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. UV light promotes the reaction, while metallic iron provides electrons for reduction of perchlorate. Both the concentration of metallic iron and dosage of UV affect the reaction rate significantly. More than 99% of perchlorate is reduced to Cl, with less than 1% reduced to ClO_3. It is believed the perchlorate ion is adsorbed on the surface of metallic iron and then undergoes an electron transfer process that is facilitated by UV excitation. It should be noted that perchlorate absorbs light at wavelengths shorter than 185 nm; however, the low-pressure mercury lamps used in this study generated light primarily at 254 nm (99%), with only 1% emitted at 185 nm. Thus, these lamps are not efficient for perchlorate excitement. Better results can be obtained by using lamps that emit primarily at the lower wavelength.

The approach taken to destroy perchlorate with commercially available ZVI particles and UV radiation proved to be a relatively slow process. Attempts were made to increase the rate of perchlorate destruction by increasing the concentration of ZVI and the intensity of UV radiation by reducing the pH of water and using four different reactor configurations. Higher temperature was not attempted because it was deemed impractical. Higher ZVI and UV intensity with slightly acidic pH in a thin-film reactor increased the first-order rate of reaction to 0.9/hour (i.e., 90% reduction of perchlorate was obtained within 2.5 hours). However, the reaction involved excessive release of ferrous iron, which resulted in large amounts of precipitate formation. Because of these operational problems, ZVI in conjunction with $NaBH_4$ is being investigated for destruction of perchlorate.

The second process involves the contact of perchlorate with the surfaces of metallic iron or an iron-oxide mineral (goethite) in the presence of phosphoric acid. The experimental results suggest that perchlorate can be removed up to almost 100% during the initial phases of the contact in the pH ranges of 2.0–2.5. This removal is believed to be due to formation of a complex between perchlorate and phosphoric acid that subsequently adsorbs to iron-particle surfaces. At higher pH values very little removal of perchlorate was observed. However, even at acidic pH, continuous contact with the surface—coupled with agitation and pH rise—seems to release the perchlorate back into solution. If this is to be used as a treatment method, particles must be separated from solution before perchlorate desorption occurs. Unfortunately, the requirement of very acidic conditions and subsequent neutralization for pH restoration might make this process too expensive for typical applications (Gurol and Kim 2000).

5.7.4 Nanoscale Bimetallic Particles

Nanoscale iron particles represent a new generation of environmental-remediation technologies that could provide cost-effective solutions. Nanoscale iron particles have large surface areas and high surface reactivity. Equally important, they provide enormous flexibility for in situ applications. Research has shown that nanoscale iron particles are very effective for the transformation and detoxification of a wide variety of common environmental contaminants, such as chlorinated organic solvents, organochlorine pesticides, and polychlorinated biphenyls

(PCBs). Modified iron nanoparticles, such as catalyzed and supported nanoparticles, have been synthesized to further enhance the speed and efficiency of remediation (Zhang 2003).

5.7.5 Titanium Reduction

It is known that titanous ions—Ti(III)—reduce perchlorate ions in acidic aqueous solutions, but that the reaction is quite slow, generally having a half-life of many hours to a few days. Laboratory research has identified reaction media in which this reaction [reduction of perchlorate to chloride by Ti(III)] takes place quite rapidly (half-life of minutes). The same group has also synthesized several new organic ligands that efficiently catalyze perchlorate reduction by titanous ions in ordinary acid-aqueous media. Further, they developed methods to bind such catalytic ligands to semisolid supports, which provide an appropriate reaction environment for rapid destruction of perchlorate by titanous species. These heterogeneous catalytic media can be used in flow or batch methods to efficiently and rapidly reduce perchlorate to chlorides. The ultimate products of the Ti(III)-perchlorate reaction are titanium dioxide (titania) and chloride salts, nontoxic and environmentally benign products. A patent describing these processes and the new chemical principles they involve is pending. 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. The reactant Ti(III) is inexpensive and readily available. The produced Ti(IV) can be reduced to Ti(III) by electrochemical or chemical means (Early, Amadei, and Tofan 2000).

5.7.6 Catalytic Hydrogen Gas Membrane

This technology, still in the research and development phase, involves hydrogen gas that works as a membrane to filter perchlorate from water. The system incorporates catalysts into porous membrane supports for deployment in the form of a continuous-flow reactor. A group of catalysts made of elements from the first, second, and third rows of the periodic table were synthesized and characterized with emphasis placed on the nonprecious metals, including Ni/W, Co/W, Ni/Mo, and Co/Mo. These catalysts were screened for their hydrogen and perchlorate adsorption capacity and catalytic hydrogen reduction of perchlorate. Commercially available catalysts were also screened.

A pressure reactor made of stainless steel was constructed and used for the molecular hydrogen system. A total of eight commercial catalysts and eight self-prepared catalysts were tested. Results indicated that both Raney-Ni 2800 (at hydrogen pressure of 4 atm and reaction time of 7 hours) and Pd (at hydrogen pressure of 2 atm and reaction time of 26 hours) were the best-performing catalysts with a greater than 20% perchlorate reduction. Overall, molecular hydrogen had rather low perchlorate reduction rate in the presence of the most powerful hydrogenation catalysts, such as Pt, Pd, and Raney-Ni.

A total of eight elemental metals were screened for their perchlorate-reduction capabilities in a direct elemental metal reduction system. Experiments were conducted in a batch reactor containing 60–100 mg/kg of hydrogen perchlorate. The specific rate constants were in the range of $3.8–90 \times 10^{-5}$ M/d/g-catalyst. Results indicated that transition metals could be excellent substitutes of precious metals for the reduction of perchlorate by hydrogen.

A total of six metals were tested in a monocatalytic membrane electrocatalytic system. Results indicated that atomic hydrogen is far more powerful than molecular hydrogen in reducing perchlorate.

An additional anion-specific membrane and electrostatic field were added to the monocatalytic membrane system as described above. The anion specific membrane and its electrostatic field enhance the transport of perchlorate anions toward the catalytic cathode membrane. A total of 18 catalysts were prepared from group of metals in the first, the second and the third row of the periodic table by coating directly onto the surface of membrane supports. It was shown that it is possible to reduce perchlorate to chloride in dilute aqueous solution at greater than 90% by atomic hydrogen in less than 6 hours using nonprecious metal catalysts such as Sc, Cr, Mo, and Cd (Huang 2005).

6. IN SITU BIOREMEDIATION OF PERCHLORATE IN GROUNDWATER

This chapter discusses in situ bioremediation of perchlorate in groundwater. Remedial technologies employed to stimulate in situ biological anaerobic degradation of perchlorate differ from the physical and ex situ processes discussed in other chapters in method of delivery and type of substrate/donor selected. The in situ nature of such technologies also presents challenges that are unique to the subsurface environment. Therefore, this chapter focuses on methods of delivery; describes substrates in use; briefly discusses other topics such as nutrient requirements and microcosm studies; and provides examples of bench-scale and pilot studies and full-scale remediation of perchlorate. This chapter is not intended to be a primer on in situ bioremediation; the focus of this chapter is in situ bioremediation of perchlorate. A general discussion of in situ bioremediation can be found in various other sources, some referenced in this chapter. In situ bioremediation of other contaminants such as chlorinated solvents is well documented in the literature. Appendix A includes a detailed in situ bioremediation case study for AMPAC, the parent corporation of the former Pepcon facility in Henderson, Nevada.

6.1 Technical Basis for Biological Reduction of Perchlorate

The success of in situ enhanced anaerobic bioremediation largely depends on the presence of appropriate perchlorate-reducing bacteria and the ability to stimulate sufficient growth in situ and activity to degrade perchlorate to the extent and rate that meets the intended remedial objectives. The ability to create the appropriate reducing conditions or to properly distribute the electron donor to maximize contact with the contaminant and the microbes are common issues when applying enhanced anaerobic bioremediation. Determining the potential for complete anaerobic biological reduction using substrate addition is perhaps the most difficult question to answer in the site-screening process.

Section 3.5.6 discusses the microbiology of perchlorate-reducing bacteria. Initially, a site can fall into one of three microbiological categories. For some sites, appropriate perchlorate-reducing microorganisms are present (generally believed to be widespread in the environment [Coates et al. 1999, Logan 2001]), geochemical conditions are appropriate for their growth, and evidence of anaerobic biological reduction is observed. In the second type of site, appropriate perchlorate-reducing microorganisms are present but at an insufficient level of activity, often due to an inadequate amount of substrate (electron donor) being present to support reduction of perchlorate. Because many aquifers are obligotrophic and aerobic, this scenario is very common in groundwater. A third type of site is also possible in which appropriate perchlorate-reducing bacteria are absent. However, this situation appears to be very uncommon based on laboratory studies and field experience (e.g., Hatziner 2005, Coates et al. 1999). In the first two cases, biostimulation alone (i.e., addition of an appropriate substrate) can often be applied with success. In the second case, more substrate may be required to reduce oxygen and nitrate in addition to perchlorate, but the likelihood of success is good as long as perchlorate-reducing strains are present. Substrate amendment and bioaugmentation would be necessary for in situ treatment of the third type of site. However, as previously noted, this scenario is uncommon due to the general ubiquity of perchlorate-reducing bacteria.

6.2 Biological Treatment Approaches

Enhanced in situ anaerobic bioremediation can be an effective method of degrading perchlorate in groundwater. Advantages of enhanced anaerobic bioremediation include complete mineralization of perchlorate in situ with little impact on infrastructure and relatively low cost compared to more active engineered remedial systems.

Enhanced in situ anaerobic bioremediation can be implemented to provide source area or dissolved plume treatment or containment, or a combination of source area and dissolved plume remediation can be used. Enhanced bioremediation will be subject to the same difficulties associated with mass transfer limitations of a continuing source and preferential flow paths in heterogeneous formations. The single largest difference between conventional remedial technologies and enhanced bioremediation may be that enhanced bioremediation, if properly implemented, can maintain effectiveness over a longer period of time at a lower overall cost. Typical system configurations and associated remedial action objectives that engineered anaerobic bioremediation may be used to address include the following:

- Source Zone Treatment. Remediation of source zones where good substrate/contaminant contact is possible.
- Plume Containment Using a Biologically Reactive Barrier. Reduction of mass flux from a source zone or across a specified boundary.
- Plume-wide Restoration. Total treatment of an entire dissolved plume. In some cases, several approaches may be combined. For example, a source area may be targeted for remediation using a grid configuration, combined with a linear barrier configuration upgradient from a downgradient point of compliance.

The appropriate application of in situ enhanced anaerobic bioremediation will be site-specific and based on a strategy that takes into account final remedial objectives, feasibility of the application, and regulatory issues. Implementation of in situ enhanced anaerobic bioremediation involves injection/addition of a substrate that causes profound changes to the subsurface environment, and the degree of success may be subject to hydrogeological, geochemical, and biological limitations. Some of these problems also affect other remedial techniques and are not necessarily unique to enhanced anaerobic bioremediation. Several issues that should be considered prior to applying enhanced anaerobic bioremediation in situ include, but are not limited to, the following:

- Site-Specific Limitations. Site-specific limitations may include low permeability or a high degree of heterogeneity that limits the ability to effectively distribute the substrate throughout the aquifer. The depth to which enhanced bioremediation can be applied is a function of drilling and cost and not necessarily a limitation of the bioremediation process. Other site-specific limitations may include high levels or influx of competing electron acceptors (e.g., dissolved oxygen, nitrate, or sulfate), climate (e.g., rainfall), and inhibitory geochemical conditions (e.g., pH). As a result, degradation may be limited. Enhanced in situ bioremediation also requires careful control of site-specific environmental characteristics (e.g., oxygen content, pH) to maintain optimal treatment conditions.
- Time Frame for Remediation. Enhanced bioremediation via anaerobic biological reduction is not an instantaneous process. The time required to develop the appropriate environmental conditions and to grow a microbial population capable of complete degradation might be on the order of several months to years at some sites. Therefore, the technology may require prolonged process monitoring and system maintenance.
- Water Quality. Free movement of microorganisms, electron donors, or treatment by-products in groundwater may impact downstream users of groundwater, requiring longer treatment time periods. Downstream monitoring wells, and capture and reinjection of treated water may be required.

There is an economic limit to the size of a plume that can be treated with a complete plume-wide application of enhanced bioremediation. For plume sizes greater than 10–20 acres, use of containment strategies (e.g., fixed biobarrier or biowall) combined with other remedial approaches may be more feasible. However, plume-wide approaches may still be applicable to address substantial portions of very large plumes.

There are a number of system and engineering design considerations for applying in situ enhanced anaerobic bioremediation: remedial objectives and suitable technical approaches, system configurations, substrate options, substrate delivery options, mixing and delivery systems, implementation constraints, and implementing bioaugmentation. The primary objective of a system design for in situ enhanced bioremediation is to effectively deliver the substrate throughout the subsurface environment at a rate that creates and maintains environmental conditions optimal for biological perchlorate reduction. Hydrogeology, groundwater geochemistry, and microbiology are site-specific conditions that may place constraints on system design and should be kept in mind throughout the design process. Different systems also vary in the amount of capital construction and O&M needed to implement them.

Table 6-1 lists in situ bioremediation technologies for perchlorate. As illustrated in the table, there are two general strategies for delivering amendments to the groundwater—mobile soluble amendments and fixed biobarriers. These two strategies can either be passive, where natural groundwater flow is used to distribute the amendments, or active, where remediation systems use extraction and reinjection wells to promote a vigorous and rapid distribution of the added substrate. Also as illustrated in the table, many names have been used to describe the two general strategies for amendment addition. Examples include "biobarrier," "biowall," and "radial biobarrier." These in situ bioremediation technologies designs are reactive and permeable. The distinction made between mobile soluble amendments and fixed biobarriers is that mobile amendment systems are characterized by injecting water-soluble amendments with low viscosity into the upgradient portion of a plume or source area. The amendment is allowed to move downgradient, treating the groundwater as it moves. Fixed biobarriers use solid or viscous amendments placed across the flow path of contaminated groundwater to form a permeable reactive barrier. Groundwater flows to, through, and past the fixed amendment.

Table 6-1. Examples of in situ bioremediation of perchlorate applied to date

Site/location	Configuration	Electron donor	Perchlorate (µg/L)		Status
			Initial	Final	
AMPAC, NV	Recirculation	Citric acid/ ethanol pilot and full scale	600,000	<1.5	Pilot study completed: full scale operational
Aerojet, NPL, CA	Recirculation	Acetate, lactate	8,000	<4	Completed
Aerojet, NPL, CA	600-ft active biobarrier	Ethanol	8,000	<4	Completed
Aerojet, NPL, CA	Recharge bioremediation	Ethanol, citrate	225	<4	Completed
Rocket manufacturer, CA	Radial biobarrier	Oleate	4,200	<4	Completed
Rocket manufacturer, CA	900-ft active biobarrier	Ethanol	2,200	<4	Completed
Rocket manufacturer, NV	Recirculation	Citrate	530	<4	Completed
Longhorn Army Ammunition Plant, TX	Semipassive biobarrier	Lactate	1,000	<4	Completed
Rocket manufacturer, AR	Direct injection	Corn syrup, edible oil	150,000	TBD	Ongoing
Naval Industrial Reserve Ordnance Plant, UT	Active biobarrier	Ethanol	350	TBD	Ongoing
Rocket manufacturer, CA	Vertical recirculation	Oleate, calcium magnesium acetate	150,000	TBD	Ongoing
NWIRP McGregor, TX	Biowall	Various solid substrates	13,000	<4	Ongoing
Naval Surface Warfare Center, Indian Head, MD	Recirculation cell	Lactate	170,000	<5	Pilot-scale field demo; completed
Los Alamos National Laboratory, NM	Biowall	Pecan shells and cottonseed			
Whittaker Bermite Facility, CA	Recirculation	Citric acid	300	<4	Pilot-scale field demo; completed
Rocket propellant manufacturer, MD	Permeable reactive biobarrier	Emulsified soybean oil with nutrients	9,000	<4	Pilot-scale field demo; completed

Mobile soluble amendments and fixed biobarriers are discussed in Sections 6.2.1 and 6.2.2. Consideration must be given to the organic substrate demand from by native inorganic electron acceptors, the demand to drive the microbial reduction of perchlorate, and a substantial safety factor recognizing the inherently inefficient distribution and use of substrate that may be added to stimulate bioremediation. When existing data are too marginal to support proceeding with bioremediation, a number of other screening tools may be used to collect additional information regarding the potential for enhanced bioremediation (see Chapter 3).

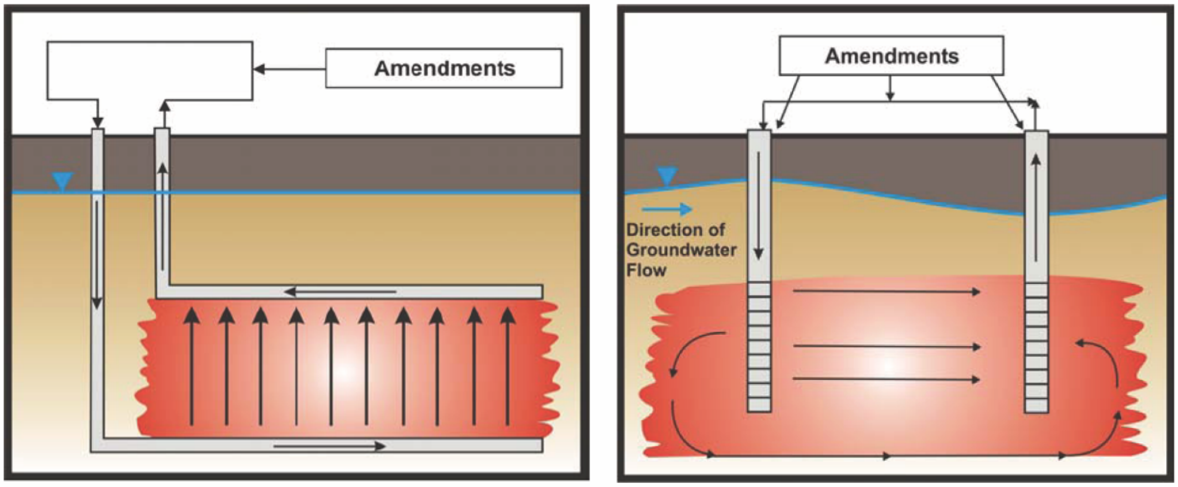
6.2.1 Mobile Amendments Systems

Mobile amendment systems for in situ enhanced anaerobic bioremediation are characterized by injecting water-soluble amendments with low viscosity into the upgradient portion of a plume or source area. The amendment is allowed to move downgradient, treating the groundwater as it moves. This technology can be implemented by direct-push injections or conventionally installed injection wells. Injection strategies dictate the need for passive or active treatment. Passive treatment requires no extraction or recirculation. Active treatment can employ groundwater extraction and reinjection wells to distribute substrates in the subsurface (Hatzinger 2005; Cramer et al. 2004; Cox, McMaster, and Neville 2001) or horizontal-flow treatment wells to mix and distribute electron donor in groundwater. A variety of soluble amendments can be used, including but not limited to lactate, ethanol, citric acid, acetate, molasses, and corn syrup.

In situ enhanced bioremediation systems may be configured to treat perchlorate across an entire contaminant plume. Creating an anaerobic reaction zone across broad areas of a plume is an aggressive approach that may reduce the overall time frame for remediation. Plume-wide delivery systems will typically be configured as a large injection grid or in multiple staggered rows throughout the entire contaminated portion of the aquifer. For larger plumes, a recirculation well field using a smaller number of wells may be employed to increase the effective area of substrate distribution via a forced gradient to influence a greater volume of the aquifer. Higher initial capital and operating costs of recirculation systems may be offset by shorter remedial time frames with lower monitoring and total long-term operating costs.

The most common recirculation systems are well systems consisting of a closed network of extraction and injection wells. Recirculation increases the retention time of contaminated groundwater in the treatment zone. The rate at which groundwater passes through the system depends on the rate of recirculation and the natural groundwater flux through the recirculation system. Therefore, design of recirculation systems must consider hydraulic conductivity, aquifer heterogeneity, and hydraulic gradient. A discussion of a number of recirculation configurations can be found in Chapter 2 of *Technical and Regulatory Requirements for Enhanced In Situ Bioremediation of Chlorinated Solvents in Groundwater* (ITRC 1998). Figure 6-1 provides schematic diagrams of a vertical circulation system using horizontal injection/extraction wells and a horizontal circulation system using vertical injection/extraction wells.

Substrate amendments applied in recirculation systems are more readily controlled and distributed throughout the treatment zone relative to passive systems. Recirculation systems also are capable of capturing a much greater volume of the aquifer, allowing much greater distances between wells. However, most small-scale recirculation pilot systems still use well spacings on the order of 3–10 feet, which is not practical for a full-scale system. Highly permeable and uniform lithologies are required to use well spacings on the order of 50–100 feet. Groundwater modeling and tracer testing are therefore highly recommended when designing large-scale recirculation systems.



A B

Figure 6-1. Schematics of (A) vertical and (B) horizontal recirculation systems.

Recirculation approaches may be the only effective method to achieve more uniform distribution of substrates and amendments at sites with difficult hydrogeological conditions (e.g., insufficient natural hydraulic gradient). Recirculation may also be considered for shorter-term applications that cannot be achieved through less aggressive, more passive methods. For example, recirculation may be useful to circulate groundwater from the greater contaminant plume through an established bioaugmented treatment zone.

Applications where substrate is delivered to the entire plume may be cost-prohibitive for very large plumes or cost-inefficient for low-level contaminant plumes. At sites where larger plumes are present (greater than several acres) or the depth of the plume makes installing injection wells difficult and expensive, multiple treatment lines can be established perpendicular to the direction of groundwater flow. A recirculation approach may not be practical or cost-effective at a large scale due to the significant volume of groundwater to be processed and ineffective in situ mixing in heterogeneous environments. Biofouling of recirculation wells is sometimes an issue, and operating plans may need to include well maintenance schedules. If substrate addition is done by some kind of multiple-point injection relying on natural groundwater flow for dispersion, this may require very close spacing of injection points and or it may not result in good mixing of substrate and perchlorate in situ.

The following are examples of mobile amendments to treat perchlorate in groundwater in situ:

- At Indian Head Division Naval Surface Warfare Center in Maryland, lactate was injected via wells using an active injection system. Water was pumped from two extraction wells at a rate of 1 gpm each. This water was subsequently amended with lactate and buffer and then reinjected. A buffer was also added to the aquifer to increase groundwater pH and enhance the kinetics of perchlorate reduction. Over a 20-week demonstration, the perchlorate concentration in groundwater declined by greater than 95% in eight of the nine monitoring wells in the field plot from an initial average of 170 mg/L, with five wells reaching <1 mg/L during the demonstration and two wells declining to below the minimum reporting level (MRL) for the study (5 µg/L) during this period (Cramer et al. 2004, Hatzinger 2005).

- At Aerojet-General Corp. in Rancho Cordova, California, several active and passive injection systems were evaluated. In one passive system, groundwater was extracted, amended with an electron donor (ethanol, lactate, and citric acid), and reinjected. An extensive active injection system used ethanol as the electron donor and consisted of groundwater extraction/ reinjection wells designed to capture a perchlorate plume approximately 600 feet wide. Perchlorate was reduced from 8 mg/L to <4 µg/L within 35 feet of the groundwater reinjection well. A horizontal flow treatment system using citrate was also installed to mix and distribute electron donors within a perchlorate-contaminated groundwater plume without bringing water to the surface.
- Bench-scale and pilot tests at the former Pepcon facility (parent corporation, AMPAC) in Henderson, Nevada, have successfully removed perchlorate to below the 18 µg/L Nevada provisional action level. The pilot study conducted in 2002 and 2003 resulted in a decline of perchlorate concentrations from 600,000 µg/L to below the laboratory quantitation limit for the study of 1.5 µg/L. Ethanol and then citric acid were used as electron donors during the pilot study. A full-scale in situ bioremediation system is currently operating (see Appendix A for a detailed case study discussion).

6.2.2 Fixed Biobarriers

Fixed biobarriers use solid or viscous amendments placed across the flow path of contaminated groundwater to form a permeable reactive barrier. Groundwater flows to, through, and past the fixed amendment. The fixed biobarrier approach can use engineered trenches or barriers containing solid-phase, slow-release substrates (Perlmutter et al. 2001) or viscous substrates placed crossgradient via direct-push injections (Zawtocki, Lieberman, and Birk 2004). A number of fixed biobarrier electron donors, including vegetable oil, pecan shells, chitin, Hydrogen-Release Compound (HRC™), and various compost materials have been observed to successfully support microbial reduction of perchlorate.

In situ enhanced bioremediation in the form of a fixed biobarrier is a suitable technology for large plumes having poorly defined, widely distributed, or inaccessible source areas. Fixed biobarrier systems can be used to intercept and treat contaminant plumes as a containment measure. Fixed biobarriers typically consist of a solid-substrate trench located perpendicular to the direction of groundwater flow. This configuration, as illustrated in Figure 6-2, is particularly suitable for low-permeability or highly heterogeneous formations, as the formation is physically removed and the biowall trench effectively exposes the contaminant plume to the solid substrate fill material.

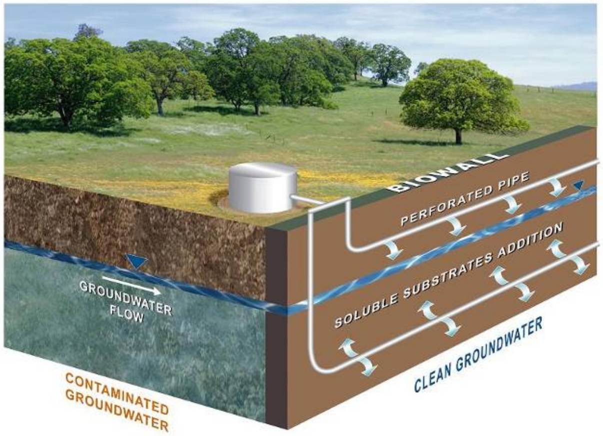


Figure 6-2. Schematic of a biowall using solid substrates. (*Source:* AFCEE 2004)

Fixed biobarrier systems rely on the migration of contaminated groundwater through the reactive zone created in situ. Therefore, key design parameters of fixed biobarriers include the following:

- a continuous reaction zone, typically oriented perpendicular to groundwater flow, that is of sufficient cross-sectional area to intercept the entire contaminant plume
- sufficient residence time within the reaction zone for the complete biological reduction of perchlorate in groundwater
- sufficient depth to capture the full thickness of the contamination
- maintained permeability to avoid groundwater flow around the barrier system

Capital and operating costs for a fixed biobarrier configuration are typically lower than for plume-wide configurations using mobile substrates (Section 6.2.1) because of a limited treatment area. Life-cycle costs could be significant if the source of the perchlorate upgradient of the biobarrier is not addressed. In addition, eventual replacement of slow-release substrates for biobarrier systems may still be required if the design life for remediation extends longer than the life span of the substrate.

Other variations of using solid substrates in flow-through fixed biobarrier configurations include surface amendment infiltration plots (GSI 2001, Haas et al. 2000), burial of mulch in excavations (ESTCP 2006a), and the recirculation of contaminated groundwater through mulch bioreactors (Parsons 2003). AFCEE is scheduled to release a protocol for biowall design and installation in early 2008.

The following are three examples of fixed biobarriers:

- A fixed barrier at NWIRP McGregor is the largest installation to date. It consists of a series of trenches (several thousand feet in combined length) that contain a mixture of mushroom compost, soybean oil, and wood chips as slow-release electron substrates. The shallow trenches (10–25 feet in depth) are cut into limestone and designed to capture groundwater and runoff water at the site. Influent perchlorate levels as high as 13,000 µg/L have been reduced to below detection in this biobarrier (Cowan 2000; Perlmutter et al. 2000, 2001; EnSafe, Inc. 2005).
- A fixed barrier system installed in Mortandad Canyon at LANL contains apatite, a phosphate mineral, to remove various radionuclides from groundwater, and a mixture of pecan shells and cottonseed as slow-release substrates for the reduction of perchlorate and nitrate (Strietelmeier et al. 2000).
- Another fixed biobarrier system example uses emulsified vegetable oil injected into a shallow, perchlorate-contaminated aquifer in Maryland. The in situ system creates a passive biobarrier (Zawtocki, Lieberman, and Birk 2004). Within 35 days of injection, perchlorate levels had declined from 9000 µg/L to <10 µg/L within 20 feet of the barrier.

6.3 Site Characterization Considerations

There are many considerations to take into account when selecting and designing an in situ enhanced bioremediation system, be it a mobile amendment application or a fixed biobarrier. Enhanced anaerobic bioremediation as a remediation technology may not be appropriate at all sites due to site-specific limitations (such as difficult hydrogeologic conditions, depth to groundwater, etc.). At some sites, it may have utility only when coupled with other remedial technologies.

Chapter 3 discusses site-screening criteria for evaluation when considering remedial options for perchlorate. When considering in situ enhanced anaerobic bioremediation, additional knowledge of the location of sensitive receptors, the site-specific hydrogeology, the plume dynamics, and groundwater biogeochemistry is essential. This information may be based on the CSM and qualitative and quantitative evaluations of the potential to stimulate and sustain anaerobic biological reduction of perchlorate over the lifetime of the remediation. Additional consideration must be given to the substrate demand from native inorganic electron acceptors, the demand to drive the biological reduction of perchlorate, and a substantial safety factor recognizing the inherently inefficient distribution and utilization of the substrate. When existing data are too marginal to support proceeding with bioremediation, a number of screening tools may be used to collect additional information regarding the potential for enhanced bioremediation.

Enhanced anaerobic bioremediation may be appropriate at sites with the following characteristics:

- Site-specific data indicate that perchlorate (including any co-contaminants present) can be readily degraded by native microbial populations under anaerobic conditions.
- Subsurface conditions (e.g., aquifer permeability) are conducive to adequate emplacement and distribution of a substrate, and creation of an in situ reactive zone conducive to anaerobic degradation of the targeted contaminants.
- A cost/benefit analysis indicates that the technology is cost-effective relative to other remedial measures (e.g., groundwater extraction).

A few conditions that may preclude the use of enhanced anaerobic bioremediation include the following:

- sites with impacted receptors or with short travel time or distance to potential discharge and/or exposure points
- sites with inaccessible sources
- difficult hydrogeologic conditions that may preclude cost-effective delivery of amendments, such as low permeability or a high degree of aquifer heterogeneity
- geochemical conditions (e.g., unusually low or high pH) that inhibit the desired in situ biodegradation

Additional site characterization, laboratory microcosm studies (Section 6.7.1), or small-scale field tests (Section 6.6.5) may be required as predesign steps before a field-scale system can be designed and a cost calculated for comparison to other remedial technologies. If a determination is made to proceed with enhanced bioremediation, site-specific factors will continue to influence the design of the remedial system and the interpretation of performance results.

6.4 Electron Donor Options

For in situ enhanced bioremediation of perchlorate in groundwater, using either mobile amendment systems or fixed biobarriers, there are many organic substrates that can be naturally degraded. Examples of easily biodegradable organic substrates include alcohols, low-molecular-weight fatty acids (e.g., lactate), carbohydrates, vegetable oils, and plant debris. Table 6-2 summarizes the attributes of several substrate types. These substrates are classified here as soluble substrates, viscous and low-viscosity fluids, solid substrates, and experimental substrates. The physical nature of the substrate dictates the frequency of addition, the addition technique, and potential system configurations.

Table 6-2. Substrates used for enhanced anaerobic bioremediation

Substrate	Typical delivery techniques	Form of application	Frequency of injection
Soluble substrates			
Lactate and citrate	Injection wells of circulation systems	Acids or salts diluted in water	Continuous to monthly
Methanol and ethanol	Injection wells of circulation systems	Dissolved in water	Continuous to monthly
Sodium benzoate	Injection wells of circulation systems	Dissolved in water	Continuous to monthly
Molasses, high-fructose corn syrup	Injection wells	Dissolved in water	Continuous to monthly
Viscous-fluid substrates			
HRC or HRC-X™	Direct injection	Straight injection	Annually to biannually for HRC (typical); every 3–5 years for HRC-X; potential for one-time application; follow-up injections as needed to rejuvenate
Vegetable oils (neat)	Direct injection or injection wells	Neat oil injection with water push, or high oil:water content (>45% oil) emulsions	Potential for one-time application (typical); follow-up injections as needed to rejuvenate
Low-viscosity fluid substrates			
Vegetable oil emulsions	Direct injection or injection wells	Concentrated emulsions diluted to 5%–20% in water before injection	Every 2–5 years (typical); potential for one-time application; longevity depends on initial loading
Solid substrates			
Mulch and compost	Trenching or excavation	Trenches, excavations, or surface amendments	One-time application (typical)
Experimental			
Whey (soluble)	Direct injection or injection wells	Dissolved in water or slurry	Monthly to annually
Chitin (solid)	Trenching or injection of a chitin slurry	Solid or slurry	Annually to biannually; potential for one-time application
Hydrogen (gas)	Biosparging wells	Gas injection	Pulsed injection (daily to weekly)
Humic acids (electron shuttles)	Direct injection or injection wells	Dissolved in water	Unknown; potentially semiannually to annually

The selected organic substrate should be suitable for the biogeochemical and hydrodynamic character of the aquifer to be treated. A common goal is to minimize overall project cost by minimizing the number of required injection points, the number of injection events, and substrate cost (Harkness 2000). The physical and chemical characteristics of the substrate (e.g., phase and solubility) may make certain substrates more suitable than others in particular applications. Combinations of various substrates are becoming more common.

6.5 Substrate Longevity

Substrate demand can be described in terms of the electron acceptor demand exerted by the following three categories:

- Contaminant Electron Acceptor Demand. Since perchlorate serves as an electron acceptor during biological reduction, there is a stoichiometric relationship for the electron donor required to satisfy the electron acceptor requirements.
- Native Electron Acceptor Supply. The flux of groundwater and minerals on the solid aquifer matrix include electron acceptors that in many cases are preferentially used over perchlorate. Therefore, their presence exerts a demand on the electron donor required to satisfy the removal of more energetically favorable electron acceptors, which must occur before conditions conducive to anaerobic biological reduction are established.
- Nonspecific Demand. One must expect that a large percentage of injected substrate, resultant organic acids, hydrogen, and other by-products will be used by opportunistic microbes for a myriad of life processes. In addition, numerous transformations of the solid mineral matrix may occur. Thus, there is a nonspecific substrate demand that is not practical to calculate.

In any system configuration, it is never possible to achieve a high efficiency for either substrate/ contaminant contact or substrate use. Practitioners typically include a substantial safety factor when determining substrate loading rates. The combined substrate demand must be met until a contaminant source is depleted or until remedial goals have been met. The practitioner should attempt to estimate the contaminant and electron acceptor demand using site characterization data. “Nonspecific” demands and the necessary safety factor can best be semiquantitatively estimated using information from field pilot tests.

The substrate should be applied at a rate sufficient to lower redox conditions and induce biological reduction but should not be consumed at such a high rate as to be rapidly depleted before migrating throughout the desired treatment area. Limiting the amount of substrate may result in large portions of the treatment area remaining too oxidizing for complete reduction. A limited area of excessive substrate may be acceptable to provide sufficient substrate after mixing with groundwater to maintain appropriate levels of organic carbon throughout the entire treatment zone.

Substrates that are rapidly depleted require more frequent injection to develop and sustain sufficiently reducing conditions. Hydrogen gas is the most bioavailable and rapidly used substrate, while soluble substrates such as ethanol are also considered to be readily bioavailable and are therefore depleted relatively quickly (within days to a couple of weeks). Table 6-3 lists the range of substrate concentrations typically used in field applications and the injection frequency and life span that can be anticipated with their use. The rate at which organic carbon is delivered to the aquifer (i.e., loading rate) depends on (1) the volume of substrate (or substrate mixture), (2) the concentration of the active ingredients in the substrate mixture, (3) the frequency of injection/addition, and (4) the degree of groundwater flux through the treatment zone and resulting rates of mixing and dilution. Substrate loading rates are typically reported as mass of substrate per unit volume of groundwater treated.

Table 6-3. Typical substrate loading rates, injection frequencies, and life spans of common organic substrates

Substrate	Injected form and concentration	Targeted concentration in formation	Typical injection frequency	Typical life span
Sodium lactate, potassium lactate, lactic acid	Diluted to 3%–30% by weight	50–300 mg/L	Continuous to bimonthly	7–60 days
Butyrate	Diluted to 3%–30% by weight	50–300 mg/L	Continuous to bimonthly	7–60 days
Methanol	Diluted to 3%–30% by weight	50–300 mg/L	Continuous to weekly	1–7 days
Ethanol	Diluted to 3%–30% by weight	50–300 mg/L	Continuous to weekly	1–7 days
Sodium benzoate	Diluted to 3%–30% by weight	50–300 mg/L	Continuous to weekly	1–7 days
Molasses	Diluted to 1%–10% by weight	50–300 mg/L	Daily to quarterly	70–90 days
High-fructose corn syrup	Diluted to 1%–10% by weight	50–300 mg/L	Daily to quarterly	70–90 days
Whey (fresh/ powdered)	Powdered form can be dissolved; fresh form can be injected as a slurry	50–300 mg/L	Monthly to annually	1–12 months
HRC	Pure product injected at 4–12 pounds per vertical foot of injection	100–500 mg/L	Annually to biennially for HRC and HRC-X (one-time injection may suffice in some cases; follow-up injections as needed to rejuvenate)	9–18 months for HRC; 3–5 years for HRC-X; longevity depends on initial loading
Vegetable oil (soybean oil) and vegetable oil emulsions	Oil-in-water emulsions with 45%–60% oil by volume or neat oil injection (source areas only); water push typical	100–500 mg/L	One-time emplacement (one-time injection may suffice in some cases; follow-up injections as needed to rejuvenate)	3–5 years; longevity depends on initial loading
Mulch and compost (cellulose)	Mixed with sand at 20%–60% mulch or compost by volume	100–1000 mg/L total organic carbon (TOC) within biowall reaction zone	One-time emplacement	Unknown; thought to be 5 years or more
Chitin	Powdered form injected as a slurry or bulk product in a trench	100–500 mg/L	One-time emplacement	Unknown; thought to be 5 years or more
Hydrogen gas	Pure hydrogen gas or less volatile mixtures with nitrogen		Continuous (permeable membranes) to weekly (pulsed gas sparging)	1–7 days

6.6 Substrate Delivery Options

As discussed in Sections 6.2.1 and 6.2.2 for mobile amendments and fixed biobarriers, there are a multitude of system configurations and delivery strategies that can be used to distribute organic substrates in the subsurface. Table 6-4 summarizes these delivery options according to substrate type and system configuration. Common delivery options include the direct injection or recirculation of mobile amendments, or emplacement of solid substrates in fixed biobarriers.

Table 6-4. Enhanced anaerobic bioremediation delivery options

Source	Barrier	Plume-wide
Periodic injection into source; recirculation across source	Periodic injections into linear injection well configurations oriented perpendicular to groundwater flow (substrate drift)	Periodic injections in grid arrays or multiple linear rows of wells; large-scale recirculation (extraction and injection)
Infrequent injection into source (may be one time for vegetable oils)	Infrequent injection into linear rows of injection points oriented perpendicular to groundwater flow (substrate sorbed)	Infrequent injection in grid arrays (may be one time)
One-time or very infrequent addition (e.g., placement in source area excavation)	One-time or very infrequent addition to linear trenches oriented perpendicular to groundwater flow (substrate sorbed)	May not be practical for large plumes; potential using combination of source and multiple barrier configurations
Biosparge injection into source (pulsed injection)	Biosparge injection in linear rows perpendicular to groundwater flow (continuous to semicontinuous)	May not be practical for large plumes

6.6.1 Small-Scale Pilot Tests and Substrate Use Tests

In evaluating the potential for applying enhanced anaerobic bioremediation of perchlorate at a site, small-scale pilot tests may determine microbial sufficiency, as well as provide predesign data on well spacing, substrate loading requirements, and injection frequency. In some instances, such field tests, which may comprise just a single injection well and a few monitoring wells, may preclude the need for laboratory studies. Field tests provide a greater level of confidence in estimating the in situ extent and rate of biological reduction and provide valuable engineering information for design purposes (e.g., injection pressures and ROI) than if no small-scale pilot test were conducted. Depending on the size of the field pilot test, the cost in time and money can be similar for laboratory and small pilot-scale efforts. In addition to small-scale pilot tests, “push-pull” tests may also be used to determine transport and mobility of solutes and substrates, biostimulation field degradation rates, and field-scale substrate use rates (Kim, Istok, and Semprini 2004).

6.6.2 Direct Injection

The most commonly used methods to deliver mobile amendments are installed injection wells or direct-push well points or direct injection through temporary direct-push probes. In other cases, direct-push technology (DPT) is used to install semipermanent well points having design lives of less than 3 or 4 years. This type of well is commonly used where injections will be required but the long-term need for more permanent wells is minimal.

Permanent injection wells are typically installed for use with soluble substrates where continuous or multiple injections of substrate or recirculation are required. Use of permanent injection wells is also necessary where depth or soil lithology make use of DPT impractical. Existing monitoring or extraction wells from previous investigation or remediation activities may be used when screened in appropriate horizons and located within appropriate portions of the plume.

6.6.3 Injection Well Location and Spacing

Injection well configuration includes injection well layout, injection intervals, and spacing. Injection wells are typically located in rows oriented perpendicular to the direction of groundwater flow; multiple rows of wells may be installed in a grid configuration or to construct multiline biobarriers. The depth and thickness of the targeted treatment zone impact selection of a drilling technique and the vertical spacing of well screen interval(s). The injection well screen should intercept the zone of contaminated groundwater that is to be treated. For thick treatment zones (>15–20 feet), multiple injection points installed in a cluster at each location and screened across different intervals are recommended. Alternatively, injection over thick intervals can be performed in a single well with multiple screens separated by packers.

Horizontal well spacing is primarily a function of the degree to which substrate can be distributed laterally in the vicinity of each injection well. An effective ROI should be calculated based on the volume and type of substrate used, taking into account the mixing and dispersion of the substrate that will occur with advective transport or through a recirculation system. Well spacing perpendicular to groundwater flow may range from 5 feet for passive systems in low-permeability silts and clays to 50 feet or more in high-permeability formations using recirculation techniques. More typically, horizontal well spacing for passive systems varies from 10–15 feet for viscous-fluid substrates to 20–30 feet for larger-volume soluble substrate systems. In a low-permeability aquifer, distribution of the substrate by advection will be limited, and the system may be diffusion dominated.

6.6.4 Application Using Fixed Biobarriers

Fixed biobarriers using solid substrates are typically constructed in a trench or excavation in a permeable reactive barrier configuration (e.g., biowall). This treatment method relies on the natural flow of groundwater through the biowall to promote contact with slowly soluble organic matter. Perforated pipe can be laid on the top and/or bottom of the fill material to amend the biowall material with liquid substrates or other amendments in the event the system needs to be modified to deliver more dissolved substrate mass or to alter geochemical conditions. Trenches or infiltration galleries may also be used for gravity flooding of dissolved substrates.

Biowall trenches may be installed using either continuous one-pass trenchers designed for installing subsurface utilities or hydraulic excavators (basically backhoes with extended booms). The type of equipment used, the stability of the formation, and the ability of the equipment to excavate the formation limit trench depths. Typically, trenches can be installed to 35 feet below ground surface, potentially to 45 feet below ground surface if using benching. Continuous trenching is not practical in hard, consolidated bedrock. If loose, noncohesive, unconsolidated sediments are present, a slurry may be used to keep the trench open during construction.

6.6.5 Nutrient and Amendments

Under natural conditions, the aquifer may contain suitable amounts of trace nutrients for microbial growth; however, the nutritional demand imposed by rapid microbial growth in response to addition of an organic substrate may exceed the capacity of the aquifer system (Chamberlain 2003). Substrate amendments may be used to provide additional nutrients for microbial growth. Substrate nutritional amendments generally include nitrogen, phosphorous, and trace elements.

Fermentation of complex substrates to metabolic acids and hydrochloric acid during anaerobic biological reduction of perchlorate may decrease the pH significantly. However, in some aquifers, reduction of iron may release OH^-, resulting in a slight increase in pH. Lowering of pH to below 5 may inhibit growth of sulfate reducers, methanogens, and some perchlorate-reducing microbes (Cramer et al. 2004). In groundwater systems with insufficient natural buffering capability, pH buffer amendments such as sodium bicarbonate may be required. Some other alkaline products such as NaOH or KOH have been tried, but generally in small doses. Other products specifically for use in aquifers are under development. As with all amendments, the effectiveness of a buffering agent is limited by the ability to distribute it away from the injection well and impact a more substantial portion of the aquifer.

6.7 Bioaugmentation

Bioaugmentation involves injecting a microbial amendment of organisms known to carry out biological reduction of perchlorate. It may be used when the presence of an appropriate population of perchlorate reducers is not present or sufficiently active to stimulate complete reduction. Bioaugmentation has not generally proven to be necessary in the field for perchlorate treatment. However, the topic is briefly addressed here for the small number of sites in which this approach may be required.

6.7.1 Laboratory Microcosms

Microcosms may be a useful tool to determine the optimal electron donor for a site and whether bioaugmentation can potentially be used to expedite complete biological reduction of perchlorate. Substrate loading and geochemical conditions can be carefully controlled in microcosms. In microcosms constructed of native soil and groundwater, bioaugmentation may indicate whether such a system modification may be warranted to reach remediation objectives. Findings in a microcosm do not always indicate what will occur in the field, as results can be influenced by a variety of systematic sampling problems. For example, field materials collected for microcosm may be a composite from several sampling locations at the site and as such is subject to variability in distribution of contaminants at the site. Microcosm results must be carefully evaluated and validated using field data.

In general, microcosms may be capable of answering the following questions:

- Are native microbial populations capable of achieving the desired rate of biological reduction of perchlorate, given sufficient organic substrate?

- What are the primary fermentation pathways used by native microbial populations for differing substrate types?
- Can bioaugmentation enhance the short-term rate or extent of biological reduction of perchlorate compared to the native microbial population? Microcosms may also be used to determine whether the introduced culture thrives in the native sediments and to compare bioaugmentation strains.

6.7.2 Molecular Screening Techniques

Molecular screening methods based on genetics have only recently been developed for application in the environmental field, and the number of microbial species and strains that can be positively identified is limited. Molecular screening methods are based on the detection of gene sequences unique to individual microorganism species. In particular, molecular identification targets the 16S rDNA gene because it contains conserved and highly variable sequences that can be used to identify groups and species of anaerobic microorganisms. The method consists of the following four steps:

DNA Extraction → Amplification → Sequencing (if necessary) → Identification

Table 6-5 summarizes the most common experimental methods using these steps to assess the presence of perchlorate-reducing species and available on a commercial basis. These include PCR, denaturing gradient gel electrophoresis, and an immunoprobe for the chlorite dismutase gene found in perchlorate-reducing bacteria (O'Connor and Coates 2002). Other analytical methods may be used by university researchers but are beyond the scope of this discussion. However, given that perchlorate-reducers are ubiquitous within the environment, the application of molecular screening techniques applied to in situ enhanced bioremediation of perchlorate in groundwater may not be frequently encountered.

Table 6-5. Molecular genetic identification methods

Test method	Description	Information provided	Usefulness	Information not provided
Polymerase chain reaction with gel electrophoresis	Qualitative amplification method for DNA sequencing and identification	Qualitative identification of microorganism species based on use of species-specific primers	High correlation between complete degradation of perchlorate and presence of perchlorate reducers; can screen multiple areas of site	Specific only for known perchlorate reducers, for which primers have been developed; may exclude other species or consortia known to have similar capabilities
Real-time polymerase chain reaction with gel electrophoresis	Quantitative amplification method for DNA sequencing and identification	Quantitative identification of microorganism species based on use of species-specific primers	Same as above; changes in concentration of known perchlorate reducers over time indicate that growth of the targeted species has been stimulated	Same as above

Test method	Description	Information provided	Usefulness	Information not provided
Denaturing gradient gel electrophoresis	Analysis provides determination of the types of organisms present and their general physiological status	Qualitative identification of multiple species based on use of "universal primers"	Provides detailed information on microbial community; can identify perchlorate reducers whose extracted 16S rDNA genetic sequence is established in a genetic database	Specific only for known perchlorate reducers; excludes other species that have not yet been identified
Immunoprobes	Immunoprobe based on the chlorite dismutase gene to detect perchlorate-reducing bacteria in environmental samples	Highly specific and sensitive immunoprobe used assess dissimilatory (per)chlorate-reducing populations in environmental samples regardless of phylogenetic affiliations	Is a rapid, inexpensive, simple, and sensitive function probe with no culture biases as sometimes experienced with culture-based methods	Is not applicable to soil or sediment samples; there is a potential for false positives

6.8 Strengths and Limitations

When selecting enhanced anaerobic bioremediation relative to other technologies, one should evaluate both the advantages and limitations of this approach.

6.8.1 Advantages

Remediation of perchlorate in the subsurface is difficult and sometimes technically infeasible due to aquifer heterogeneity, depth to groundwater, and plume size. Highly engineered remedial techniques such as P&T are costly due to inherent mass transfer limitations, capital expenditures, the need for treatment of secondary waste streams, energy consumption, and long-term O&M requirements. Conversely, enhanced in situ anaerobic bioremediation may in some cases offer the following advantages:

- Lower Capital and Maintenance Costs. Lower capital costs often are realized because substrate addition can be easily accomplished using conventional well installations, the use of DPT, or other traditional installation technologies. Mobile amendments or mobile/ fermentation products of slow-release substrates can potentially migrate into and disperse within heterogeneous lithologies via advection and diffusion. Carbon sources demonstrated to date as electron donors are relatively inexpensive. Systems used to mix and inject substrates can be readily designed and installed by environmental engineers. O&M is generally routine.
- Destruction of Contaminants In Situ. Perchlorate has the great potential of being completely mineralized or destroyed. Destruction of contaminants in situ is highly beneficial because contaminant mass is not transferred to another phase, there is no secondary waste stream to treat, potential risks from co-contaminants related to exposure during remediation are

limited, and there is minimal impact on site infrastructure. Land above ground is available for use during the treatment period. Indigenous microorganisms that are already resident in the groundwater can generally drive the biologically mediated reactions involved.

- Perchlorate Reducers Are Naturally Occurring. There is an apparent abundance of naturally occurring perchlorate-reducing microorganisms in the environment (Coates et al. 1999). It has also been shown that perchlorate degrades relatively quickly in situ and enhanced anaerobic bioremediation works even at low concentrations of perchlorate.
- Potential Application to a Variety of Contaminants. In addition to perchlorate, the technology may be applicable to a variety of other contaminants that may be present with the perchlorate in groundwater (e.g., chlorinated solvents, RDX, nitrate). Enhanced anaerobic bioremediation has the potential to treat any contaminant that can be made less toxic or less mobile through reduction reactions.
- Treatment Train Options. Enhanced anaerobic bioremediation can be used in tandem with existing or alternative remediation systems to optimize performance (e.g., source removal). Alternatively, in situ enhanced bioremediation can be used to treat soil hot spots that would prevent subsequent contamination of groundwater.

6.8.2 Potential Adverse Impacts

Application of enhanced anaerobic bioremediation can cause profound changes in the distribution of contaminants and the geochemistry of the treated aquifer. The potential for adverse impacts should be considered during the site screening process. While some site conditions may exacerbate these adverse impacts, in most cases they can be mitigated by design alternatives. This requires an understanding of the biogeochemical and hydrogeologic conditions of the aquifer system to be treated and of the potential impacts that may occur.

6.8.2.1 Secondary Water Quality Considerations

Several changes in water quality may occur during anaerobic bioremediation. These changes occur primarily within the anaerobic treatment zone and may be of concern if drinking water aquifers are present and primary/secondary drinking water standards are enforced. Increased concentrations of by-products of anaerobic biodegradation may result from anaerobic dechlorination of commingled contaminant plumes. TDS and sulfides that affect taste and odor are necessarily elevated in the anaerobic reactive zone due to biodegradation of the substrate. Generation of reduced sulfur compounds (e.g., thiols or mercaptans) or alcohols (e.g., 2-butanol or isopropanol) may occur under extreme fermentation conditions. Some mobilized inorganics may be precipitated/immobilized downgradient of the reactive zone when the conditions return to a more oxidizing state. Section 3.5.4 provides additional discussion of water quality issues.

6.8.2.2 Mobilization of Metals

The formation of an active reducing environment by the addition of substrate can result in the mobilization of some formerly insoluble forms of metals that occur naturally in the aquifer matrix (e.g., iron, manganese, and arsenic). This is not always problematic. In some cases, migration of metals such as arsenic may be retarded by adsorption to the aquifer matrix. But, if conditions exist where the mobilized metals can daylight into a receiving stream or surface water body, there is the potential to visibly and adversely impact the surface water quality. Thus, in selecting a location for in situ treatment, it is necessary to consider conditions and receptors immediately downgradient of the reactive zone and allow groundwater travel time outside of the reactive zone to reestablish native conditions and groundwater quality. Section 3.5.4 provides additional discussion of the mobilization of metals.

6.9 Costs

Advantages of enhanced anaerobic bioremediation include complete mineralization of perchlorate in situ with little impact on infrastructure and relatively low cost compared to more active engineered remedial systems. Discussed here are the general costs incurred for the addition of mobile amendments and fixed biobarriers to address perchlorate in groundwater.

For mobile amendment systems, costs are typically associated with the installation of extraction and injection wells, capital and operating of recirculation systems (if applied), the cost of the amendment, and monitoring and reporting. Table 6-6 shows example mobile amendment costs. The overall cost to install fixed biobarriers ranges $100–1000 per linear foot depending on the length and depth of the fixed biobarrier. The single most expensive item for biobarrier construction is trenching. Mobilization costs alone may range $20,000–60,000. Thus, due to the large cost of mobilization, there is an economy of scale in trenching costs. Figure 6-3 illustrates cost per linear foot for continuous chain trenching at a hypothetical site.

Table 6-6. Example typical costs of mobile amendments

Mobile amendment	Bulk price per pound (dollars)
Sodium lactate	1.00–2.00
Propionate, butyrate	2.00–3.00
Methanol, ethanol	0.10, 0.20–0.25
Molasses	0.25–0.35
Refined sugars (high-fructose corn syrup)	0.25–0.30
HRC	5.00–7.00*
Vegetable oil/commercial emulsion products	0.20–0.40/2.00–4.00

* Cost includes other services unique to the product provider
Source: AFCEE 2004.

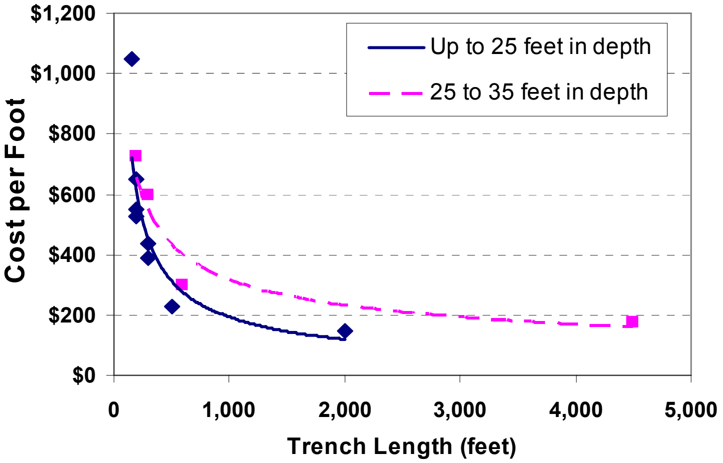


Figure 6-3. Example fixed biobarrier trenching costs.

Operational costs for fixed biobarriers are primarily for annual groundwater monitoring. If the substrate in the fixed biobarrier needs to be recharged, there may be additional costs associated with the recharge events. A rough order-of-magnitude cost for such an event may be around $20,000. Modifications/contingencies to a fixed biobarrier system will also increase costs.

7. EX SITU BIOLOGICAL PROCESSES FOR WATER

7.1 Introduction

The efficiency (i.e., volumetric removal rate of contaminant) of any ex situ biological treatment process is dependent on maintaining a high active biomass concentration in the reactor. Biological reactors are classified according to the nature of their growth. Those in which the active biomass is suspended as free organisms or microbial aggregates are classified as suspended-growth reactors (i.e., continuously stirred tank reactors [CSTRs]), whereas those in which growth occurs on or within a solid medium or a biomass granule or pellet are termed supported-growth or fixed-film reactors (i.e., FBRs and packed-bed reactors [PBRs]). References on reactor design and operation are included in Chapter 11.

Perchlorate biotreatment principles (Sutton 2006) imply the ideal bioreactor configuration for treatment of the contaminant at low and medium concentration levels (i.e., 100–500 ppm perchlorate) will have the following characteristics:

- able to operate efficiently at a high perchlorate volumetric removal rate while achieving a long solid-retention time by maintaining high biomass concentration in a controlled fashion
- designed to achieve plug-flow hydraulic conditions
- designed to promote the treatment mechanism of physical-chemical adsorption

A key step in the design of any biological process is the selection of the appropriate reactor configuration. Operational factors to consider in reactor selection include the following:

- reaction kinetics of the treatment process
- construction and O&M costs
- characteristics of the wastewater to be treated
- other local environmental conditions (site, sizing, etc.)

Two common reactor configurations used to treat perchlorate are CSTR and plug-flow reactor. The CSTR is a suspended-growth system well suited for treatment of high-strength wastewaters (tens to thousands of ppm) at low flow (Hatzinger 2005). In contrast, the plug-flow systems, including the PBR and the FBR, are well suited for the treatment of lower-strength perchlorate streams (50 ppb–500 ppm) at higher flows, as required for groundwater or drinking water treatment. Table 7-1 summarizes, compares, and contrasts the systems discussed in this chapter.

Table 7-1. Summary and comparison of ex situ biological systems

System	Description	Volume and flow	Perchlorate concentration	Cost	Start-up time	Full scale	Pilot test
Fluidized-bed reactor	Plug flow through bottom which "fluidizes" suspends the bed increasing surface area	Can support high-volume flows for groundwater and drinking water (up to 5500 gpm)	From ppb range to 500 ppm; concentration must not fluctuate widely	Capital cost vary: $350,000 for smaller systems; O&M $0.16–1.10/1000 gal	Weeks to months for bed growth, optimization and stabilization	Yes	Yes
Packed-bed reactor	Plug flow can be up flow or down flow	Can support low to higher volumes of groundwater and drinking water (1–2 gpm currently operating)	Lower concentrations of perchlorate; can tolerate fluctuations of perchlorate and nitrate	NA	Weeks to months for bed growth, optimization and stabilization	No	Yes
Continuously stirred tank reactor	Continuously stirred mix suspended and not attached to a substrate, can remediate mixed contaminant waste streams from industrial operations	Continuous flow or batch flow	Higher concentrations of perchlorate (100–4000 ppm) and mixed wastes	Approximate total cost per kg of perchlorate reduced is $2.00	Several days	Yes	Yes

7.2 Fluidized-Bed Reactors

7.2.1 General Process Description

The FBR is a reactor column that fosters the growth of microorganisms on a hydraulically fluidized bed of media, usually sand or activated carbon (see Figure 7-1). The fluidized medium selected provides a large surface area on which a film of microorganisms can grow, thus producing a large inventory of biomass in a small reactor volume. The result is a system capable of high degradative performance for target contaminants in a relatively small and economical reactor volume. The FBR can be controlled to operate under aerobic, anaerobic, or anoxic conditions, depending upon the nature of the target compounds. The choice of media for the FBR bed depends on the specifics of the treatment required. Sand is often selected for higher mass flow rates of contaminants where the yield of biomass is expected to be relatively high, i.e., high biofilm growth. Carbon is often selected for greatest assurance of producing low-concentration effluent (i.e., ppb levels). The following sections describe the FBR process, the microbiology involved, and the specific advantages associated with the FBR perchlorate treatment system.

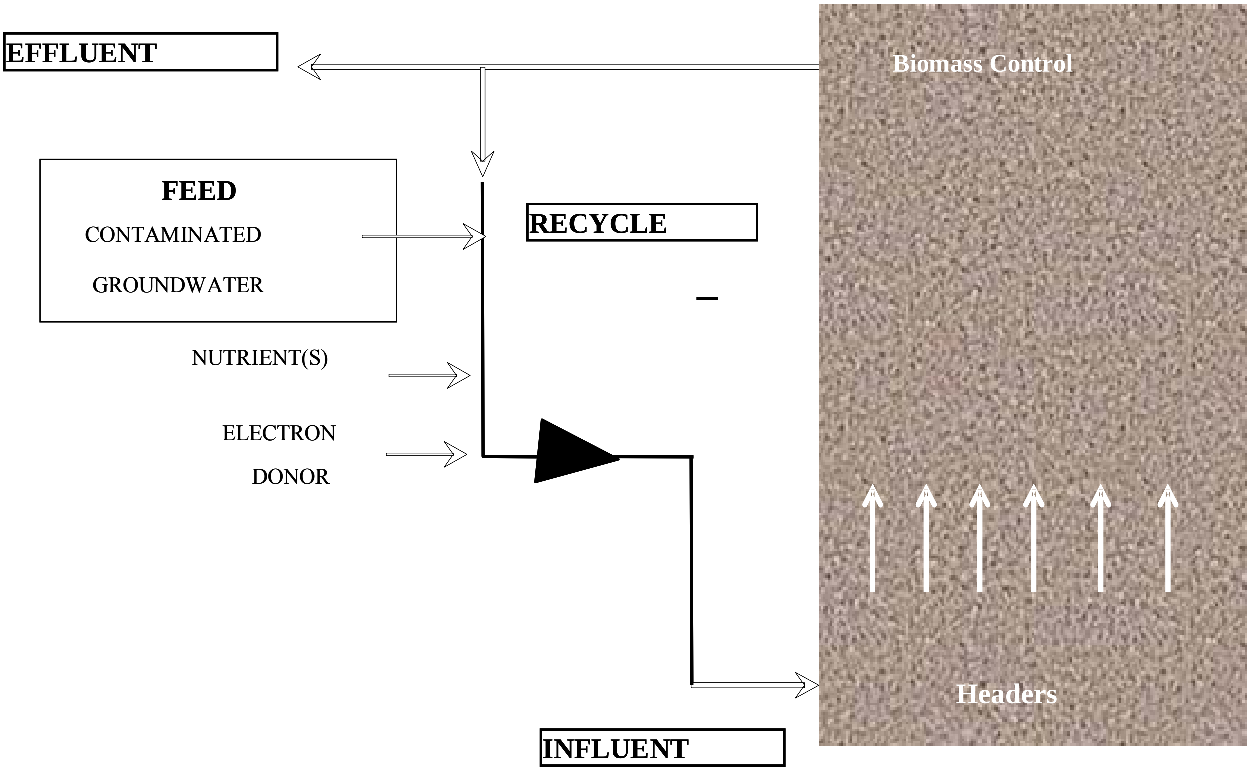


Figure 7-1. Fluidized-bed reactor schematic.

The FBR treatment system, consisting of a cylindrical tank containing a medium for growth of attached microorganisms, is designed to create the necessary environment for microbial growth. Flow is distributed at the bottom of the reactor and collected at the top. A header and lateral system distributes the flow evenly across the bottom of the reactor. Typically, the flow distribution nozzles are closely spaced and securely attached to the main header and laterals. As the water travels up through the media, the bed is hydraulically expanded and fluidized for uniform dispersion of the water within the microorganism population.

After the reactor is "seeded" with microorganisms, natural growth and reproduction occur in the presence of adequate perchlorate, electron-donor substrate (organic carbon source), and necessary nutrients. Under these conditions, the microorganisms will attach to the rough surfaces of the medium and begin to develop a layer of biomass that over time will cover the entire particle surfaces. This attached-growth process allows the reactor to develop much higher concentrations of microorganisms than would normally be possible in a typical, continuous, suspended-growth process treating the same flow rate. The medium serves as a dynamic anchor that helps to keep the biomass from floating out of the reactor with the process flow.

When operated under anoxic conditions, the resident microorganisms reduce perchlorate molecules (ClO_4) to the innocuous products chloride and water through normal metabolic activities. Facultative anaerobic microorganisms first consume the available oxygen in the feed water. After the dissolved oxygen has been depleted, perchlorate-degrading microorganisms reduce the perchlorate.

If the feed water source is not expected to have sufficient organic substrate or nutrients to support biological activity within the FBR, a chemical feed system must supplement it. An organic substrate and a specially blended nutrient solution (primarily nitrogen and phosphorous) are added to provide the necessary nutrients for healthy microbial growth and reproduction. Additionally, the system has a sensor, controller, chemical feed pump, and tank, should they be required to stabilize the operating pH.

When provided substrate and nutrients, microorganisms continue to grow and colonize the medium particles until excess biomass passively sloughs off the particles or is mechanically removed through agitation/sheer imparted with the FBR bed height control system. Excess biomass increases the particle size and reduces the overall density of the media. If the biomass growth is uncontrolled, the buoyancy of the particles will increase sufficiently to carry them to the top of the reactor where they may escape from the reactor with the effluent. An internal bed height control system collects medium particles which begin to rise in the reactor, scours the biomass from the particles, and returns them to the reactor. As the microorganism population ages or during periods of high growth rates, excess biomass will either be sloughed off the medium due to the energy of fluidization or will be automatically removed by the bed height control system. The FBR effluent and biomass concentrate (from the biomass separation system) are typically passed through a medium capture tank as a redundant precaution against loss of medium. Accumulation in the media capture tank is monitored, and accumulated medium is automatically returned to the reactor. The FBR effluent and biomass concentrate streams flow out of the medium capture tank by gravity to the site treatment system. The perchlorate treatment system sizing is based on flow and concentration of perchlorate, nitrate, and oxygen.

Perchlorate reduction occurs under anoxic conditions. Given sufficient organic substrate, the microbial population first consumes any dissolved oxygen present in the feed wastewater while feeding on the organic carbon. Under this anoxic condition, the perchlorate-degrading microorganisms biologically reduce the perchlorate molecules to water and chloride ions.

7.2.2 Effluent Treatment

Treated effluent from the FBR is collected through submerged headers and directed as discharged effluent or recycled. The headers are submerged to minimize turbulence within the effluent collection system that could reintroduce dissolved oxygen into the recycle stream. The recycle nozzle is set lower than the effluent nozzle to allow 100% recycle flow without the loss of volume. Treated effluent discharge may or may not require local government or state permits such as NPDES. Chapter 4 reviews the discharge permit requirements for both Kerr McGee (Tronox) and Aerojet.

7.2.3 Strengths and Limitations

The FBR system can remove low to moderately high concentrations of perchlorate from the environment. The final effluent concentrations below the EPA and California guidelines can be achieved. The system has a relatively small footprint if piping and other infrastructure from pumping wells are buried. Once the system is optimized and operates effectively, it requires minimal operator attention.

The FBR system can take several months following start-up for system optimization and operation and may involve the addition of other treatment technologies, such as GAC, sand filters, and hydrogen peroxide as part of an overall treatment train (see discussion on Kerr McGee [Tronox] FBR system). Naturally occurring compounds such as nitrate and chlorate also biodegrade before or concurrent with perchlorate as in the case of the FBR system at the Tronox facility. Sulfate reduction is minimized by controlling the level of electron donor.

The cost of an FBR system depends on the concentration and volume treated. For higher concentrations of perchlorate, the overall cost following initial capital cost can be considerably less than that of an IX system (see Appendix A, Aerojet Case Study).

7.2.4 Applicability

The range of water quality and contaminant levels appropriate for use of the FBR system is site specific. The FBR can handle a wide range of flow rates and concentrations. Flow rates for full-scale FBR systems range 5–5500 gpm. For higher-flow-rate applications, multiple FBRs are usually specified. Similarly, the perchlorate and nitrate concentrations have ranged from 50 ppb up to and over 400 ppm and from 2 ppm to over 200 ppm, respectively.

7.2.5 Commercial Full-Scale Applications

7.2.5.1 Aerojet Facility

The GenCorp Aerojet Facility in Sacramento, California, is the site of the world's first groundwater treatment system for perchlorate in groundwater. The $5 million facility is designed to treat up to 4000 gpm of groundwater using four FBRs. The concentration of perchlorate in the groundwater to be treated is up to 8 mg/L (ppm). The original design treatment goal was an effluent with less than 18 µg/L (ppb) perchlorate. The system began treating water in the spring of 1999 and has consistently produced effluent with less than 4 ppb perchlorate, the detection limit, since its start-up. It has been processing >5000 gpm, exceeding its design throughput, since the fall of 2000.

Aerojet evaluated several treatment strategies for perchlorate in groundwater, beginning in 1993, including IX resins and biological reduction. The current system design was selected following the performance of field pilot studies using an FBR (Figure 7-2). The pilot system treated a groundwater flow of 30 gpm, and data generated from the study were used for the design basis of the full-scale system. Annual operating costs for this system were estimated by Aerojet to range $0.16–0.22 per 1000 gal depending on flow and concentration treated. A detailed description and case study is presented in Appendix A of this report.

Figure 7-2. Aerojet FBR.

7.2.5.2 Longhorn Army Ammunition Plant

The Longhorn Army Ammunition Plant (LHAAP) in Texas has groundwater contaminated with VOCs and perchlorate from past operations. The groundwater was previously remediated by pumping the water to the surface, removing the VOCs in an ex situ treatment process, and then discharging the treated water to a nearby stream. In early 2000, USACE, which oversees the operation of the groundwater treatment plant, took steps to supplement the existing treatment process with a biological FBR (Figure 7-3) to remove (degrade) the perchlorate prior to surface water discharge. After preliminary FBR sizing and costing information was obtained, a laboratory treatability program was conducted to confirm the system design assumptions and to confirm the effectiveness of the FBR process. Both acetic acid and ethanol were investigated as growth (i.e., electron donor) substrates. Influent concentrations varied 11,000–23,000 ppb of perchlorate. The target effluent perchlorate concentration was 350 ppb. For the majority of the test, effluent perchlorate concentrations were below the quantitation limit of 5 ppb, except when the FBR was operated at a low substrate load to determine the point of treatment failure.

Figure 7-3. LHAAP FBR system.

Based on the success of the laboratory test, a full-scale FBR system with the capacity to treat 50 gpm was installed at the groundwater treatment plant. System start-up was initiated in the first quarter of 2001. Since then the FBR system has been treating up to 50 gpm of groundwater with perchlorate concentrations as high at 35,000 ppb of perchlorate.

The cost for the FBR and its ancillary equipment was $366,000. Annual operating costs have been in the $0.30–1.10/1000 gal, depending on flow and concentration treated. The system has been operating for more than five years with effluent perchlorate concentrations <4 ppb.

7.2.5.3 Naval Weapons Industrial Reserve Plant McGregor

McGregor NWIRP in Texas has groundwater contaminated with perchlorate from past operations at the site. The Navy installed a biowall at the site and also tested several ex situ technologies for use in conjunction with the biowall. These technologies included IX, a fixed-bed bioreactor, and the FBR. In January 2002, a full-size FBR was installed. The reactor is 7.5 feet in diameter and 22 feet high (Figure 7-4). Prior to the preliminary design, a field pilot demonstration of the FBR was conducted to ascertain design parameters and the cost/technical effectiveness of the FBR system. It is currently treating 100–400 gpm of groundwater with 1–20 ppm of perchlorate in the influent. The effluent has been below 4 ppb since March 11, 2002. See Appendix A of this report for detailed case study.

Figure 7-4. McGregor Naval Weapons Industrial Reserve Plant FBR.

7.2.5.4 Tronox (formerly Kerr McGee) Facility

The Kerr McGee facility, in operation 1944–1998, produced various chlorates and perchlorates for sale to commercial and government customers. The Kerr McGee (Tronox) facility began treating groundwater for perchlorate in 1998 using an IX system. In 2001, the former Kerr McGee (Tronox) installed additional wells and additional IX at the main plant. Although effective, this method was costly, and in December 2002, Kerr McGee (Tronox) contracted the design, fabrication, and installation of an FBR system (Figure 7-5) to treat 1000 gpm of groundwater. The FBR system at Kerr McGee (Tronox) reportedly consists of eight 14-foot-diameter FBRs that treat an influent of up to 400 ppm of perchlorate, 500 ppm of chlorate, and 50 ppm of nitrate.

Figure 7-5. Kerr-McGee (Tronox) FBR System.

The design and construction phase for the Kerr-McGee (Tronox) FBR system was completed in December 2003, followed by process conditioning in January–March 2004. System start-up and optimization phase occurred in March–November 2004. The FBR system was completely operational following the October–November 2004 performance test, where an effluent quality of <18 ppb perchlorate was maintained for more than 30 consecutive days.

FBR process conditioning of the sand and carbon substrate for optimal bacterial acclimation and growth involved pumping initial feed water into the FBR system with relatively low concentrations of nitrate, chlorate, and perchlorate. Several species of bacteria were added to the FBR and allowed to compete during the initial conditioning and growth phase. The system start-up phase was initiated in March 2004 once good conditions were achieved. During system start-up and initial system operations, the concentration of electron donor and other nutrients were adjusted to compensate for increased chemical loading composed of high concentrations of nitrate, chlorate, perchlorate, and sulfate and to achieve NPDES permit requirements of <18 ppb perchlorate in the effluent discharged to the Las Vegas Wash.

During the start-up phase, effluent water quality exhibited foaming, sulfide odor, solid precipitates, and unwanted bacterial growth at various times. The following additional processes were added as part of overall treatment train and/or optimized to improve effluent quality during and following system start-up:

- A static mixer was added to the flow following the secondary bioreactors and prior to the dissolved air floatation system.
- Hydrogen peroxide was injected near the static mixer to shut down the bioprocess and prevent formation of sulfide in the effluent.
- Several antifoaming agents were tested and one selected that demonstrated optimal results.
- Several coagulants and flocculants were tested, and those demonstrating optimal results were selected for long-term use.

Additionally, surge tanks were added to the influent process flow to allow for equalization of flow and chemical loading. Influent water from all well fields and collection systems is blended in a series of large on-site equalization tanks (surge tanks), enabling a constant chemical load to be provided to the FBR system. This equalization of flow and chemical loading prevents shocks to bacterial growth within the FBR system due to changes in influent chemical loading or surges in flow from the collection systems.

7.3 Packed-Bed Reactors

7.3.1 General Process Description

As with the FBR, the PBR is a fixed film–based bioreactor in which the sand, carbon, or plastic media is stationary. As in the FBR, the microorganisms attach to the media in the reactor. Unlike the FBR, PBRs can be designed in either upflow or downflow configurations. The nutrients and electron donor are added to the inlet stream as needed. PBRs are once-through reactors usually requiring more residence time (larger reactors) than the FBR but with less pumping required. PBRs produce high-quality effluent (perchlorate below EPA and California suggested limits), destroy the perchlorate, and have conditional regulatory acceptance to produce drinking water quality. Unlike the FBR, there are no full-scale PBRs in operation today on perchlorate water streams. However, the use of PBRs for low-concentration contaminant remediation has been applied for years on other contaminants. Coupled with several promising perchlorate pilot tests, PBRs must be included when examining ex situ perchlorate treatment options.

7.3.2 Field and/or Pilot Applications

7.3.2.1 Castaic Lake Water Agency (CLWA)

The fixed-bed biological pilot test results for the CLWA are summarized as follows:

- Perchlorate was consistently reduced from 50 ppb to <4 ppb in empty bed contact times of 15 minutes even with dissolved oxygen and nitrate concentrations of 7 and 15 ppm, respectively.
- Generally, nondetect TOC concentrations in the effluent were present; sulfate and pH did not significantly impact the PBR.
- Effluent turbidity was approximately 0.6 nephelometric turbidity units.
- Extended shutdown of the PBR did not affect perchlorate removal.
- Intermittent electron donor feed did not affect perchlorate reduction.
- The PBR could tolerate fluctuations of perchlorate (50–300 ppb) and nitrate (15–to 23 ppm).
- Backwash was required but did not affect perchlorate in the effluent.

7.3.2.2 City of Redlands

In Redlands, California, two PBRs were tested in parallel. One contained sand media for microbe growth attachment and the other plastic media for microbe attachment. In the sand, PBR perchlorate was reduced from 75 ppb to <4 ppb at a hydraulic loading of 1–2 gpm/square foot of reactor area when the reactor was backwashed weekly. The plastic media produced the most consistent effluent at 1 gpm/square foot.

7.3.2.3 Naval Weapons Industrial Reserve Plant McGregor

A 5-foot-diameter by 18-foot-high PBR was tested at the McGregor NWIRP in McGregor, Texas (Xu et al. 2003). The reactor treated up to 20 gpm of groundwater with 7–20 ppm perchlorate. The results are described as meeting the site perchlorate analytical limit of 20 ppb with an electron donor ratio of 5:1 acetate to perchlorate. The full-scale remedial solution selected for this site was the FBR.

7.4 Ex Situ CSTR Treatment Technology

7.4.1 Process Description

The CSTR perchlorate biodegradation is a complete-mix, suspended-growth process, which means that the biomass is suspended in the treated water and not attached to the media surfaces to keep them in the reactor. The biomass continually reproduces at a high rate (doubling in number every 20–60 minutes) so that a constant population is maintained. CSTRs can be configured in series and sized to give the desired hydraulic residence time required for complete perchlorate reduction. An external carbon source is added at a ratio determined by the type of carbon source and the amount of oxygen-containing compounds (nitrate and perchlorate) requiring reduction. A variety of carbon sources including sugars, starches, alcohols and waste food products have been shown to support perchlorate reduction in CSTR systems.

Bench-scale studies were undertaken for the U.S. Air Force that led to the development of a CSTR-based biological treatment system for perchlorate reduction. In addition, it was demonstrated that the CSTR culture could destroy perchlorate in the presence of other energetic compounds, including nitroglycerin, nitramines, stabilizers, and plasticizers.

Recent work has focused on increasing the salt tolerance of the CSTR process with the addition of a membrane system. The membrane allows the efficient return of biomass to the CSTR and also cleans the effluent stream allowing for possible reuse of the brine stream effluent. The ability to reduce nitrate and perchlorate in brine streams generated by IX processes offers a solution for the disposal of these waste streams and also significant cost savings if the brine streams can be reused.

Reactor temperature is typically maintained at 20°C or higher to maintain bacteria growth and performance. The pH is monitored in the reactors, and caustic is added, as required, to maintain neutral pH. Rigorous mixing is not necessary, so reactor mixing can be accomplished with fixed mixers or with a low-power pump and eductor. Figure 7-6 is a simple process flow diagram illustrating the main components of the CSTR perchlorate biodegradation process. Two reactors are configured in series with gravity flow from the first reactor to the second and finally to discharge. However, the systems are designed with the ability to be configured in series, parallel, or independent operation as required.

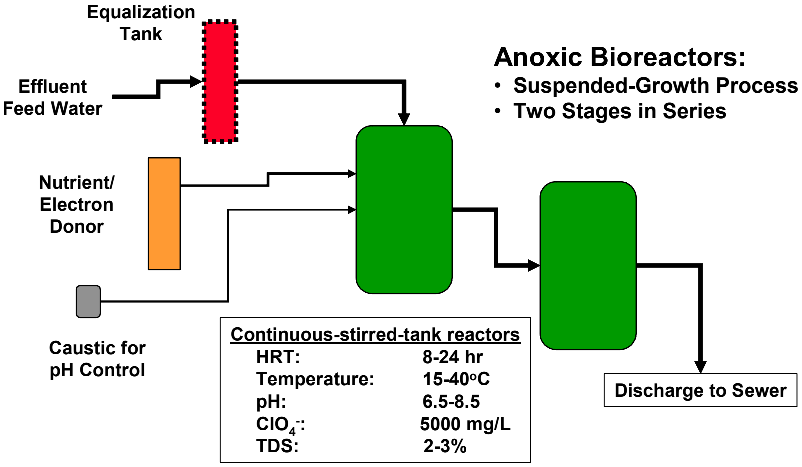


Figure 7-6. CSTR biodegradation schematic.

7.4.2 Applicability and Treatment Capability

One of the advantages of the CSTR system is the flexibility to treat both low- and high-concentration waste streams, due to the complete mix characteristics of the process. The CSTR process can operate in either continuous flow or batch mode. These two characteristics result in a treatment process that is flexible, with a wide range of capabilities and possible applications. The process has been tested in various configurations—at bench, pilot, and full scale—and on a variety of perchlorate-contaminated waste streams. Applications of this process range from demilitarization of existing perchlorate-contaminated munitions and propellants; the destruction of production effluents from new insensitive munitions such as PAX-21 and AFX-757; and the destruction of perchlorate-contaminated residuals from separation and concentration technologies such as IX and RO. Figure 7-6 shows the range of key operating parameters for current treatment systems. Perchlorate and TDS values listed are upper limits for wastewater delivered to the first stage reactor. In one system, nearly saturated effluent streams (>100,000 mg/L) are fed to the reactor and simultaneously diluted with water to less than the levels indicated. While perchlorate concentrations treated range 100–4000 mg/L, recycling biomass to the reactors by means of a clarifier or membrane system can efficiently expand both the perchlorate and TDS treatment ranges.

7.4.3 Treatment Cost

The CSTR biodegradation process is the least expensive treatment process for effluents containing high perchlorate concentrations for several reasons. First, this process uses a very inexpensive nutrient, desugared molasses, which is essentially a waste by-product from sugar beet processing. Also, pumping and mixing cost are minimal. Reactors require minimal power for mixing and are configured to operate by gravity flow. Treatment system automation reduces operator labor to routine O&M checks. Treated effluent contains no detectable levels of perchlorate, chlorate, nitrate, or nitrated energetic materials and can be discharged to sewage treatment systems for little additional cost.

Table 7-2 summarizes O&M costs for a full-scale treatment system as a percentage of the total cost. Treatment cost is represented by normalizing to \$/kg of perchlorate anion reduced to chloride. The O&M cost of \$2/kg of perchlorate reduced is applicable over a broad range of perchlorate concentrations (100–5000 ppm) and flow rates (2–200 gpm). O&M costs include nutrient (condensed separator bottoms [CSB] at \$115/ton), caustic for pH control (NaOH at \$0.15/pound), micronutrients, maintenance, and electricity. Micronutrient supplement depends on effluent water quality and perchlorate concentration. The primary components of the micronutrients are phosphate (phosphoric acid at \$0.50/pound) and iron. Maintenance appears to be a disproportionately large fraction of O&M cost because the other cost components are low, not because maintenance costs are high. Labor is not included because labor costs are not proportional to the volume of water treated or to the amount of perchlorate reduced. The CSTR systems in operation require a part-time technician approximately 10 hours/week to monitor performance, sample, analyze, log operational data, calibrate pH probes, and maintain nutrients.

Table 7-2. O&M cost summary

Cost component	Percentage of O&M cost*
Nutrient (CSB)	55%
Caustic (NaOH)	6%
Micronutrients	6%
Electricity	8%
Maintenance	25%

*Total O&M cost = \$2/kg of ClO_4^- reduced (2008 \$US).

7.4.4 Commercial Applications

7.4.4.1 Aliant Techsystems (ATK) Thiokol Propulsion

Optimization studies performed in 1996 led to the first industrial application of a perchlorate biodegradation process. Through a Cooperative Research and Development Agreement between the Air Force and Thiokol Corporation, Defense and Launch Vehicle Division, the Air Force pilot system was modified and integrated into existing waste treatment processes at Thiokol's production facility near Brigham City, Utah. The prototype system was designed to treat perchlorate wastewater containing salts, corrosion inhibitors consisting of nitrate and nitrite, and other contaminants. In 1997 the pilot-scale system was disassembled and shipped to ATK-Thiokol, in Brigham City, Utah, where it was reassembled and placed in operation. The system was inoculated in December 1997 and has been in continuous operation since that time. The prototype system was modified in 2001 to increase treatment capacity, enable the simultaneous biodegradation of three different effluent streams (ammonium perchlorate, potassium perchlorate, and nitrate), and provide for metering desugared molasses nutrient to the bioreactors.

The first operational prototype treatment system began operation at ATK-Thiokol's facility near Promontory, Utah, in December 1997. Currently the system is treating approximately 1 million gal/year or 2000 pounds/month of perchlorate, on average. The system at Thiokol was installed to treat perchlorate solutions from ammonium perchlorate and potassium perchlorate recovery operations at the site. Typical brines at Thiokol had TDS concentrations of 15%–30% and perchlorate concentrations ranging 2,800–41,000 mg/L. These solutions are diluted to an acceptable range and fed to the biological treatment system (Figure 7-7).

Figure 7-7. Thiokol biodegradation system.

The original Thiokol system consists of a pair of anoxic CSTRs, configured to operate either in parallel or in series. The volumes of the original reactor were 1600 and 720 gallons, and hydraulic residence times could be controlled from 12 to 30 hours. The treatment system also includes facilities to mix and deliver nutrient solutions to the bioreactors, equipment for dilution and feed of the influent brine solutions, and programmable logic controls for variables such as pH and temperature. The influent to the bioreactors is initially maintained at 2%–3% TDS, with up to 5000 mg/L of perchlorate. The system at Thiokol was initially maintained 35º–40ºC during normal operation. Since start-up the system has been operated at temperatures down to 20ºC without sacrificing performance. Inhibited biological activity and perchlorate reduction was observed at temperatures in excess of 43ºC. To sustain the biological process, it is necessary to supplement the process with an electron donor nutrient. Initially, dried brewers yeast was the nutrient; however, it was expensive. The Thiokol process was converted to CSB in May of 1999, which reduced nutrient cost more than 90%. In 2001–2002 a modification increased the perchlorate treatment capacity from 2000 to 8000 pounds/month, permitting the simultaneous treatment of three different effluent streams composed of ammonium perchlorate, potassium perchlorate brine, and nitrate.

7.4.4.2 Hodgdon Powder Company, Pyrodex Plant

In 2003, a CSTR-based perchlorate treatment system installed in the Hodgdon Powder Company at the Pyrodex plant located near Herington, Kansas. The system was designed to treat industrial wastewater generated from the production of clean-burning black-powder substitutes, containing relatively high concentrations of nitrate, perchlorate, and other proprietary constituents. Since start-up in May 2003, the biodegradation system at the Pyrodex Plant has successfully treated more than 2 million gallons of wastewater. Periodic sampling and analysis required by the Kansas Department of Health and environment confirmed the perchlorate reduction for below the detection limits of EPA Method 314.0.

The perchlorate biodegradation treatment system installed at the Pyrodex plant is a simpler version of the Thiokol system. Wastewater containing high concentrations of nitrate and perchlorate is generated during the manufacturing of a black powder substitute. The wastewater is collected in two holding ponds and then pumped to the treatment system. Water from the pond enters the equalization tank, which provides the necessary residence time for equalization of feed water and provides a means for preheating water during cold-weather months.

Process water is fed from the equalization tank to two CSTRs in series (Figure 7-8), providing adequate residence time, process redundancy, and process control to optimize performance and operability of the system and provide complete perchlorate destruction. Nitrate and 95%–100% of the perchlorate are reduced in the first-stage reactor. Caustic is added, if necessary, to maintain pH at 7.5 in both reactors. Table 7-3 shows overall system operating and design conditions. The system is capable of operating over a wide range of conditions within the limits specified. Perchlorate feed concentration is maintained in the reactor by the addition of dilution water when necessary.

Figure 7-8. Pyrodex biodegradation system.

Table 7-3. Pyrodex operating and design conditions

Design parameters	Min.	Max.	Design
Perchlorate concentration, mg/L	<1000	5000	3000
Temperature, ^{o}F (^{o}C)	60 (15)	105 (40)	77 (25)
Reactor 1, pH	7.0	8.5	7.5
Reactor 2, pH	6.5	8.0	7.0
Reactor working volume, gal each	2500	2500	2500
Hydraulic residence time, hours	8	30	16
Feed flow rate, gpm	<1.4	5.2	2.6

After treatment, the effluent from the system is held in external storage tanks for analysis and subsequent discharge to a local publicly owned treatment works (POTW). The Kansas Department of Health and Environment (KDHE) permitted the process with a 100 ppb discharge limit, taking into account the dilution that will occur in the POTW. Since start-up in April of 2003 the system has filled, tested, and discharged 110 effluent tanks (>2 million gallons), all below the 20 ppb MDL for this wastewater and well below the 100 ppb discharge limit. A number of effluent tanks have been analyzed using the more sensitive LC/MS method, and these samples were below the 2 ppb detection limit, indicating that complete perchlorate reduction does occur in the system. Due to the success of the treatment process, KDHE has recently reduced sampling and analysis requirements from every tank to every fourth tank. In addition, the Pyrodex plant also won the 2004 Kansas Water Environment Association award for an industrial wastewater pretreatment plant.

Currently, the Thiokol and Hodgdon plants are both using CSB and desugared molasses as the external nutrient source. CSB is a by-product of sugar beet processing that is readily available in large quantities and is relatively inexpensive ($115/ton delivered to Herington, Kansas). A mix of macro- and micronutrients are also added to the system to assist in maintaining proper biological activity and perchlorate reduction.

7.4.4.3 Tyndall AFB Pilot Study

The results of these laboratory studies were used to design and construct a pilot-scale CSTR biodegradation system to demonstrate the operability of the process using actual effluent from the washout of a Minuteman Stage 2 propellant. The modular, skid-mounted system was delivered to Tyndall AFB in October 1994 on three trailers and completely assembled in seven days. In May 1995, the pilot-scale system was operated continuously for over 1500 hours, reducing a 3000 ppm perchlorate feed stream to less than detectable limits at residence times as short as 12 hours.

8. IN SITU AND EX SITU REMEDIATION FOR SOIL

Perchlorate remaining in the vadose zone may represent a major continuing source of perchlorate to the groundwater (Newman et al. 2005). Such residual contamination can increase the operating time frame and associated costs for hydraulic containment (P&T) and in situ groundwater treatment systems.

Because perchlorate is extremely soluble in water, precipitation may quickly reduce the contaminant mass present in soils (source area). Sufficient rainfall will eventually transport these contaminants, as dissolved salts, away from the source area. Thus, the basis for suspecting soil contamination by perchlorate will depend on site-specific details such as the amount of suspected residual contaminant mass at the ground surface, whether the source area is an active or continuous problem, the surface topography and geology, and the climatic conditions (DOD 2007).

Although perchlorate does not adhere to soil particles, dissolved perchlorate can be trapped within the soil pores by capillary forces and surface tension (molecular attraction) or become trapped in dead-end pore spaces. Source investigations have found that perchlorate can be retained in some propellant matrices and distributed in soil. This perchlorate does not dissolve quickly, particularly in areas with low precipitation. In most cases, the perchlorate sources have been directly released to the soil through disposal or training activities. Another potential source of perchlorate-contaminated soil is the accumulation of perchlorate at the ground surface in areas that are subject to evaporation or to evapotranspiration, or where perchlorate-laden groundwater discharges at the surface. The perchlorate can precipitate as salts or bioaccumulate in plant matter.

Dissolved perchlorate can be held between soil particles if the specific retention capacity of the soil matrix is high. Within the vadose zone, for example, retention capacity ranges from 0.01% for granite, to 3% for sand, to 48% for clay (DOD 2007). Under most circumstances, soil columns with high specific retention capacities should be considered as media of concern for perchlorate.

In arid environments, the transport of perchlorate to groundwater is limited by the net infiltration from precipitation. When evapotranspiration is high, dissolved perchlorate may migrate only a short distance through the soils before the water bearing it evaporates. The precipitated perchlorate may accumulate at shallow depths within subsurface caliche deposits or be held within the soil matrix. Typically, there will be little adsorption of the perchlorate in the soil. Perchlorate in soils will remain either as precipitated salts that are present between the soil particles or as dissolved perchlorate in the interstitial pore water. Perchlorate in soil should be considered at sites with any of the following conditions (DOD 2007):

- Large quantities of perchlorate have been used, disposed of, or burned at the site in the past.
- A perchlorate source is likely to be present, and the soils and vadose zone matrix have an affinity to retain interstitial water.
- The climatic conditions result in high evapotranspiration rates.
- Perchlorate-laden groundwater or surface water can discharge to the ground surface and be subject to high evaporation rates.
- A perchlorate source is ongoing because of on-site testing, use, or disposal.
- Groundwater contamination is elevated and suggests the presence of ongoing soil contamination emanating from an unknown source area.

8.1 Source Area Remediation

All site closure strategies ultimately have to address contaminant sources. Without source treatment and accompanying reduction of mass flux from the source area, groundwater treatment strategies that treat only dissolved contaminants may require operation for an indefinite period of time. Source area treatment is often employed in situations where downgradient migration of the dissolved contaminant plume is being adequately controlled by natural attenuation processes or, more likely with perchlorate, by another remediation process, such as a biobarrier or hydraulic containment.

Near-surface contamination can generally be treated in place or excavated and treated on site by bioremediation methods such as composting or intrinsic bioremediation (Cox et al. 2000; Cox and Scott 2003; Kastner et al. 2001; Nzengung, Das, and Kastner 2001; O'Niell and Nzengung 2003a, 2003b). Excavated soils may also be treated using thermal desorption (Gangopadhyay et al. 2005). Phytoremediation shows promise to treat both vadose zone soils and groundwater.

However, cost-effective treatment of deeper contamination represents an important challenge, because there are many perchlorate sites with deep contamination over relatively large areas (O'Niell and Nzengung 2003a, 2003b). In situ bioremediation may be effective. The technical challenge is to cost-effectively deliver electron donors to the areas where perchlorate may remain in the vadose zone and to maintain sufficient control of the environmental conditions within the vadose zone to enhance the activities of the perchlorate-reducing bacteria.

This chapter discusses several remedial options available to address perchlorate in the vadose zone:

- in situ bioremediation
- ex situ bioremediation
- ex situ thermal treatment

8.2 In Situ Bioremediation of Vadose Zone Soils

8.2.1 Basis

As described in Chapter 6, enhanced anaerobic bioremediation is able to mineralize perchlorate to innocuous by-products. Biodegradation of perchlorate in soils by ubiquitous natural bacteria will occur rapidly under suitable field conditions, which include pH, redox conditions, moisture content, and electron donors. Vadose zones are often aerobic because gaseous diffusion can provide more oxygen than water. Even in deeper soils and geologic strata, reductive processes like perchlorate degradation will often be severely limited by the low supply and availability of electron donors. As a result, perchlorate in the vadose zone can be persistent and a source for long-term groundwater contamination. However, if electron donors can be supplied, bioremediation of the vadose zone contamination can be very effective in reducing the longevity of the groundwater contamination and ensuring long-term groundwater security (Nzengung, Das, and Kastner 2001).

Perchlorate degraders are widespread in soils as well as groundwaters, and the process appears to occur under a wide range of environmental conditions (Coates et al. 1999). The challenge at most sites, therefore, is primarily one of cost-effectively delivering electron donors in a usable form to the locations where perchlorate remains in the deeper vadose zone materials. Liquid and gaseous delivery systems offer the two general approaches of supplying donors to the vadose zone.

8.2.2 Liquid Delivery

Electron donors are often injected into the groundwater, and similar solutions can be directly applied to the vadose zone. Application methods could include sprinkler irrigation (O'Niell and Nzengung 2003a, 2003b), direct injection, or periodic flooding via infiltration galleries. One method, known as Surface Application and Mobilization of Nutrient Amendments (SAMNAS), has been studied at the bench, pilot and field scale (Kastner et al. 2001; Nzengung, Das, and Kastner 2001; O'Niell and Nzengung 2003a, 2003b). In this approach, liquid and solid amendments are mixed in with surface soils (0–3 feet) and controllably mobilized with water to greater depths to stimulate perchlorate biodegradation. The liquid and solid amendments evaluated include ethanol, acetate, molasses, mushroom compost "tea," mushroom compost, cow and horse manure, and chicken manure. 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 (O'Niell and Nzengung 2003a, 2003b).

Dilute aqueous solutions of ethanol applied as irrigation water to the surface of perchlorate-contaminated clay-rich soils and mobilized to greater depths were used to stimulate vadose zone biodegradation of perchlorate at depths of up to 3–4 feet (Kastner et al. 2001). To design infiltration systems for different soils types, the partition coefficient of the electron/carbon donor offers a valuable tool to directly estimate the amount of organic carbon that would be transported to defined depths based on application rates. In bench-scale soil column tests conducted with silty clay soils from LHAAP that were contaminated with perchlorate, Nzengung, Das, and Kastner (2001) observed that even at very low infiltration rates, complete breakthrough of ethanol was achieved in 3–4 days. This outcome indicated that the soil had a very low capacity to hold organic carbon, as confirmed by the experimentally determined partition coefficient (K^d) of 3.1×10^{-5} L/kg (0.03 mL carbon/kg soil). These data and parameters should serve as useful design parameters when developing full-scale remediation strategies.

The application of aqueous substrates used for groundwater to bioremediate perchlorate in soil is being studied (ESTCP 2007a). In one project, two application approaches are being tested. In the first, an infiltration gallery will be designed to deliver and distribute the electron donor (mixed with extracted groundwater) to the perchlorate-contaminated vadose zone soils. An injection well also may be used to supply the donor to deeper vadose zone soils. In the second approach electron donor agents will be mixed with the top 2–3 feet of soil and then watered regularly to deliver electron donor agents to the contaminated soils. Both liquid and solid donor amendments will be evaluated in the second approach. For both application methods, the most effective electron donor will be determined using site-specific column studies.

To intercept and treat any mobilized contaminant mass in sensitive situations, it may be desirable to establish a reaction zone downgradient of a source area prior to implementing substrate. This decision should be based on the relative strength of the source and the nature of the downgradient buffer zone. The greater the source strength, the higher concentration of added substrate, and the more sensitive or shorter the downgradient buffer zone is, the greater the need to control the potential impacts from source treatment.

8.2.3 Gaseous Delivery

Some donors (such as hydrogen and carbon dioxide, low-molecular-weight organic acids, and alkanes) are sufficiently volatile that they can be supplied as gases, similar to bioventing with oxygen (see Figure 8-1). This "anaerobic bioventing" has been used for other contaminants resistant to aerobic biodegradation, including DDT, RDX, and PCE (Shah et al. 2001, Mihopoulos et al. 2002, EPA 2006).

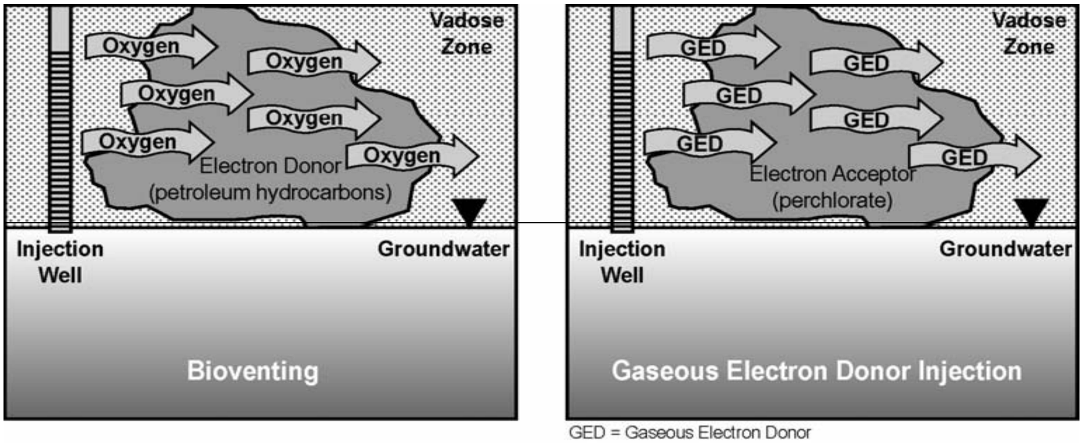


Figure 8-1. Schematics comparing gaseous electron donor injection and aerobic bioventing.

Anaerobic bioventing is an attractive option for vadose zone remediation because gases can disperse farther into the unsaturated materials than liquids. Gases can also potentially diffuse more thoroughly through the subsurface, to some extent minimizing the problems of preferential flow pathways that are more common with liquid flow (Mihopoulos et al. 2002). Additionally, gaseous electron donor technology does not require the capture and treatment of infiltrated liquids that could otherwise adversely impact groundwater. However, gaseous injection may cause soils to lose moisture to levels that do not support biodegradation.

The technology can be implemented in one of two general configurations—gas injection or soil vapor extraction (SVE), amendment, and reinjection. In the gas injection configuration, nitrogen from a generator or a liquid nitrogen supply is amended with gaseous electron donor and then injected into the perchlorate-impacted vadose zone. The presence of nitrogen serves to flush oxygen from the soil gas, enhancing conditions for the degradation of perchlorate. In the SVE configuration, soil vapor is extracted, amended with gaseous electron donor, and then injected back into the perchlorate-impacted vadose zone. As the reductive degradation of perchlorate progresses, the oxygen content of the extracted soil is reduced, thereby facilitating further perchlorate degradation. Well spacing for both of the configurations depends on the pneumatic ROI and the specific gaseous electron donor selected for use (Evans 2006a).

8.3 Ex Situ Bioremediation of Shallow Vadose Zone Soils

Soil excavation and aboveground biological treatment allow for pretreatment and better process control than in situ bioremediation. Composting has been used at several sites to treat perchlorate-contaminated soils. As with other waste, composting of perchlorate-contaminated soil involves mixing with bulking agents and organic amendments such as wood chips, hay, manure, and vegetative wastes. Appropriate amendments provide sufficient porosity and a balance of carbon and nitrogen to allow thermophilic microbial activity. Monitoring of moisture content and temperature is done to optimize contaminant degradation (EPA 2005b, Cox et al. 2000).

In one composting application, at the Aerojet California site, soil had been excavated and screened to remove rocks and cobbles >2 inches. The screened soil was mixed with water, glycerin, and diammonium phosphate in a pug mill. The rate of amendments was determined in a treatability study. Amended soil was placed in either Ag-Bag™ containment cells (traditionally used for agricultural operations such as silage composting and storage) or in concrete block treatment cells covered with plastic. Indigenous anaerobic bacteria reduced perchlorate to chloride. Initial average perchlorate concentrations ranged 600–5400 µg/kg. Full-scale results demonstrate that perchlorate is reduced to nondetectable concentrations (<20 µg/kg) within one month and typically in 2 weeks (Evans and Sharma 2006).

8.4 Status

The infiltration of electron donors and nutrient amendments to biostimulate the degradation of perchlorate in vadose zone soils has been demonstrated at the field scale as a proprietary technology. A current ESTCP project (ER-0435) is testing the addition of electron donors via irrigation and infiltration galleries to develop cost and performance data under field conditions. Gaseous delivery is also being tested under field conditions (ER-0511). Results are not yet available, though laboratory testing for the field demonstration showed that hydrogen and propane would be most effective at the site to stimulate rapid perchlorate biodegradation. Hexane was also shown to be effective (Evans 2006a). Other studies have shown that several gaseous electron donors (such as hydrogen, ethyl acetate, propane and 1-hexene) can result in perchlorate biodegradation (Brennan et al. 2006, Evans and Trute 2006).

8.5 Advantages and Limitations

The primary advantage of vadose zone bioremediation is that it can remove much of the source of continuing groundwater contamination in a far more cost-effective manner than excavation or thermal treatment, for example. Bioremediation can completely degrade the perchlorate to innocuous chloride. There is no secondary waste generation, and little infrastructure required or disruption of any ongoing site activities. It is also applicable to other reducible contaminants that may occur with perchlorate, notably many of the chlorinated solvents.

All methods of vadose zone bioremediation are limited by the ability to distribute the electron donors within the subsurface. Delivery limitations can be particularly difficult at sites with deep vadose zone contamination, low permeabilities, or highly heterogeneous geological conditions. Establishing and maintaining sufficiently reducing conditions can be difficult, especially in shallower zones, due to the migration of oxygen from the surface. However, anaerobic reduction of perchlorate takes place under only slightly reducing conditions (see Figure 3-4). Some of the donor sources, particularly the gaseous ones, may pose health and safety concerns due to flammability. Injection of aqueous donor sources may require capture and treatment of liquids to prevent adverse impacts to groundwater. Finally, geochemical limitations on perchlorate reducers, such as acidic or highly alkaline pH, presence of nitrate or other competitive ions, or toxicity due to metal concentrations, may be very difficult to overcome within the vadose zone.

8.6 Perchlorate-Contaminated Soil Bioremediation Projects

One full-scale and three pilot-scale demonstrations of anaerobic composting for treatment of perchlorate in soil have been identified. Three demonstrations of in situ bioremediation of perchlorate-contaminated vadose zone soils have been performed. Table 8-1 summarizes these examples, and several applications are discussed in more detail below.

Table 8-1. Summary of vadose zone bioremediation projects

Location	Scale and technology	Design and operation	Performance summary	Source
Longhorn Army Ammunition Plant, Texas	Pilot in situ bioremediation Surface Application and Mobilization of Nutrient Amendments (SAMNAS)	Based on the results of batch and laboratory column tests that evaluated the ability of different nutrient amendments to stimulate perchlorate degradation by naturally occurring bacteria. The tested nutrient amendments included cow manure, chicken manure, methanol, ethanol, acetate, molasses, and cotton gin waste. Six 15- by 9-foot treatment plots were treated in duplicate with ethanol, horse manure, and chicken litter, respectively, with one plot used as untreated control. The plots were hydraulically isolated with 12-inch-deep plastic-lined trenches. For the plots treated with solid nutrient amendments, the soil inside each plot was mixed with the amendment and tilled to approximately 12 inches below ground surface (bgs). Water was added to achieve saturation within the top 12 inches, and subsequently down to 24 and 36 inches, respectively. Ethanol was added as a dilute solution in the applied water. Soil moisture content at depth was monitored with tensiometers, and oxidation-reduction potentials were measured at a number of locations and depths in each plot. The plots were covered periodically to prevent growth of vegetation. The targeted treatment depth was 3 feet bgs, and the soil type was silty clay.	Period of performance: 10/7/2000–8/27/2001. Follow-up monitoring after 31 months. Perchlorate concentrations at all depths in soils treated with ethanol decreased from 300 mg/kg to below the treatment level of 40 μg/kg in 10 months. The solid amendments stimulated perchlorate biodegradation in the clay-rich soils, with highest removal within the top foot, but the treatment goal was not achieved in 10 months. Removal of perchlorate continued after 31 months in the treated plots, but not in the control plots. The concentration of perchlorate in plant tissues after treatment confirmed the reduction of perchlorate from soils and a significant reduction of ecological risk. The decrease of perchlorate observed in the control plot occurred mostly during the 10-month active treatment period and was attributed to the redistribution of perchlorate that occurred when the soil was tilled, rather than to biodegradation. The concentration of perchlorate monitored in the groundwater below did not increase and provided evidence that perchlorate was not mobilized or leached into the groundwater.	Kastner et al. 2001 Nzengung, Das, and Kastner 2001
Longhorn Army Ammunition Plant, Texas, Site 17, trenches used for burning bulk TNT,	Pilot in situ bioremediation Surface Application and Mobilization of Nutrient Amendments	Perchlorate ranging 8.2–480 mg/kg, 1,3,5-trinitrobenzene (1,400 mg/kg), 2,4-dinitrotoluene (10,000 mg/kg), 2,4-dinitrotoluene (9,000 mg/kg), 2,6-dinitrotoluene (3,700 mg/kg), 2-amino-4,6-dinitrotoluene (7.5 mg/kg), 4-amino-2,6-dinitrotoluene (130 mg/kg), 2-nitrotoluene (11 mg/kg), 4-nitrotoluene (9.5 mg/kg), were treated with mushroom compost and cow manure on a 1-acre site to the water table at 7 feet	Period of performance: May 2003 to March 2004. Active treatment was 10 months with follow-up soil monitoring in spring 2005. After eight months of active treatment the mass of perchlorate decreasing from 78 kg in soil to 16 kg—about 80% (± 9%) of the estimated initial mass of perchlorate had	O'Niell and Nzengung 2003a

Location	Scale and technology	Design and operation	Performance summary	Source
photo, flash powder, and reject material	(SAMNAS)	bgs. The shallow groundwater contained perchlorate at 230 mg/L and other co-contaminants such as chlorinated organic solvents, including PCE and its reductive dechlorination products. The site was subdivided into three sections: 2/3 of the southern section was treated with 600 yd^3 of mushroom compost; 1/3 of northern portion of the plot separated into a northeast section (1/6 of the total area) was treated with 125 yd^3 of cow manure compost only, while the remaining 1/6 of the northwest portion of the plot was treated with 125 yd^3 of cow manure compost and perchlorate-degrading bacteria. The top 3 feet of the vadose zone soils (silts and clays) were tilled with the amendments and irrigated with water via an installed irrigation system. Additionally, mushroom compost tea and ethanol were occasionally added to the irrigation water to achieve faster biostimulation of explosives and perchlorate degradation in the vadose zone soil and groundwater. The wetness of the soil was monitored using clusters of tensiometers installed at different depths.	been removed. The biostimulation of biodegradation in the site groundwater was confirmed by the decrease in concentrations of perchlorate and chlorinated solvents during the demonstration test. Total explosives decreased by three orders of magnitude in 8 months with TNT decreasing from about 3400 mg/kg to 62 mg/kg. The concentrations of total explosives and perchlorate in the vadose zone soils were below detection levels when Site 17 was last monitored in spring 2005. The concentration of perchlorate in plant tissues growing on the bioremediated soils was below detection limit in spring 2005.	
Longhorn Army Ammunition Plant, Texas, Building 43-X, 90-days temporary storage area	Pilot in situ bioremediation Surface Application and Mobilization of Nutrient Amendments (SAMNAS)	Perchlorate-contaminated soil consisted of 12–15 inches of sand underlain by clay-rich soils, with perchlorate concentrations of 6.7 mg/kg. The 110 ft^2 of contaminated soil was completely homogenized with cow and composted chicken manure and water added as needed intermittently. This project posed unique challenges because (1) the perchlorate contamination occurred in the vadose zone soils in a confined space, Building 43-X; (2) the top 12–15 inches of soil in this building consisted entirely of sand underlain by clay-rich soils; and (3) the topsoil had been exposed to creosote, an antibacterial agent.	Period of performance: August 2002 to July 2003. Perchlorate concentrations in soil were bioremediated from 6700 µg/kg to below 40 µg/kg down to a depth of 30 inches bgs in 10 months. The site was completely restored and closed out in only 10 months.	Corrigan 2004
Aerojet General Corp. Superfund Site, Rancho Cordova,	Pilot composting	Anaerobic composting was used to treat soil from the former perchlorate burn area. Approximately 20 cubic yards of soil was treated with manure initially placed on top of perchlorate hot spots. Compost was later tilled into soil to enhance perchlorate destruction 2–3	Period of performance: June 2001 to October 2002. The maximum initial soil perchlorate concentration of 4200 mg/kg was treated to	Cox et al. 2000

Location	Scale and technology	Design and operation	Performance summary	Source
California		inches below the surface.	an average concentration of 0.1–23 mg/kg following seven days of treatment.	
Edwards Air Force Base, California	Pilot composting	Anaerobic composting of perchlorate-contaminated soil treated with horse stable compost in 55-gal drums.	Period of performance: Not available. Initial concentration of perchlorate decreased from 57 mg/kg to the remedial goal of 7.8 mg/kg.	ITRC 2005
UTC Site, San Jose, California	Pilot composting	Anaerobic composting perchlorate-contaminated soil piled 5 feet high with 7 feet diameter at the bottom. A plastic liner was placed underneath the pile, and soil berms were constructed around the circumference of the pile to prevent migration of leachate, if any. A plastic sheet was used to cover the top of the compost pile.	Period of performance: Not available. The average initial concentration of 170 mg/kg was treated to <0.64 mg/kg in less than 38 days.	Cox and Scott 2003
Naval Weapons Industrial Reserve Plant, McGregor, Texas	Full composting	The perchlorate-contaminated soil was excavated and transported to an on-site treatment cell. This engineered treatment cell was lined with a 30-mil high-density polyethylene (HDPE) liner. The cell was approximately 6 feet deep with a 500- × 30-foot bottom. Perchlorate-contaminated soil was placed approximately 2.5 feet deep in the cell. Prior to placing soil in the treatment cell, it was mixed with citric acid (carbon source), nitrate and phosphate-fertilizers (micronutrients), and soda-ash (buffer). Soil was saturated as it was placed in the treatment cell. Approximately 2 inches of water was maintained above the soil to foster anaerobic conditions. The cell was covered with a 6-mil HDPE liner.	Period of performance: October 1999 to April 2000. Influent perchlorate concentration in soil was 500 mg/kg. Perchlorate concentrations in the treated soil sampled at six different locations was <100 mg/kg.	Roote 2001

8.6.1 Aerojet Rocket Engine Testing and Manufacturing Company, Cavitt Ranch Area 41

Background. Three variations of ex situ bioremediation were applied at the Aerojet General Corporation site, which covers 5900 acres near Rancho Cordova, 15 miles east of Sacramento, California. Since 1953, Aerojet and its subsidiaries have manufactured liquid and solid propellant rocket engines for military and commercial applications and have formulated a number of chemicals, including rocket propellant agents, agricultural, pharmaceutical, and other industrial chemicals. In addition, the Cordova Chemical Company operated chemical manufacturing facilities on the Aerojet complex 1974–1979. Both companies disposed of unknown quantities of hazardous waste chemicals, including TCE and other chemicals associated with rocket propellants, as well as various chemical-processing wastes. Some wastes were disposed of in surface impoundments, landfills, deep injection wells, leachate fields, and some were disposed of by open burning. Under the site are 40- to 100-foot-deep dredge tailings, left from past gold mining operations (EPA Region 9 2007).

While Aerojet was investigating, evaluating, and implementing treatment methods for removing perchlorate from extracted groundwater, the firm also evaluated methods for removing perchlorate from soil, including biodegradation. One piece of property impacted by perchlorate was Area 41, or Cavitt Ranch, which was remote from the Aerojet site and used for disposal and destruction of spent solvents and solid rocket propellant. Soils at Cavitt Ranch were no more than 3 feet thick overlying fractured bedrock. TCE and perchlorate were present in both soils and groundwater at high concentrations. Isolated areas of metals above remedial goals were also found in spots where laboratory wastes were taken for destruction.

Early column studies of heap leaching of soils to remove the perchlorate showed that leaching of perchlorate was very efficient even when the infiltration proceeded more slowly than anticipated. However, the heap leaching process produced brine that would require treatment or another disposal alternative.

In early 1999 bench-scale biotreatability tests were performed on perchlorate-impacted soils from Cavitt Ranch. The tests included both composting and anaerobic slurry treatment of the soils. In the composting study, the soils were bulked with manure, alfalfa, and sawdust with moisture added to make the piles approximately 50% moisture. A second treatment added liquid food waste to the bulking mixture. The bench-scale composting of soils found that 30 mg/kg of perchlorate in soil was reduced to <2 mg/kg within several weeks, producing perchlorate half-lives of 3–4 days. Use of the liquid food waste did not appear to change the results as the native soils had sufficient bacteria of the appropriate kind to provide for perchlorate reduction. The anaerobic slurry was made using saturated soils and a variety of electron donors—ethanol, manure, food waste, vinegar, and molasses. Perchlorate biodegradation in the anaerobic slurry occurred after an acclimation period of up to 40 days, after which it proceeded rapidly, regardless of which electron donor was used, even at initial concentrations of up to 10,000 mg/L (Borch and Neville 2000).

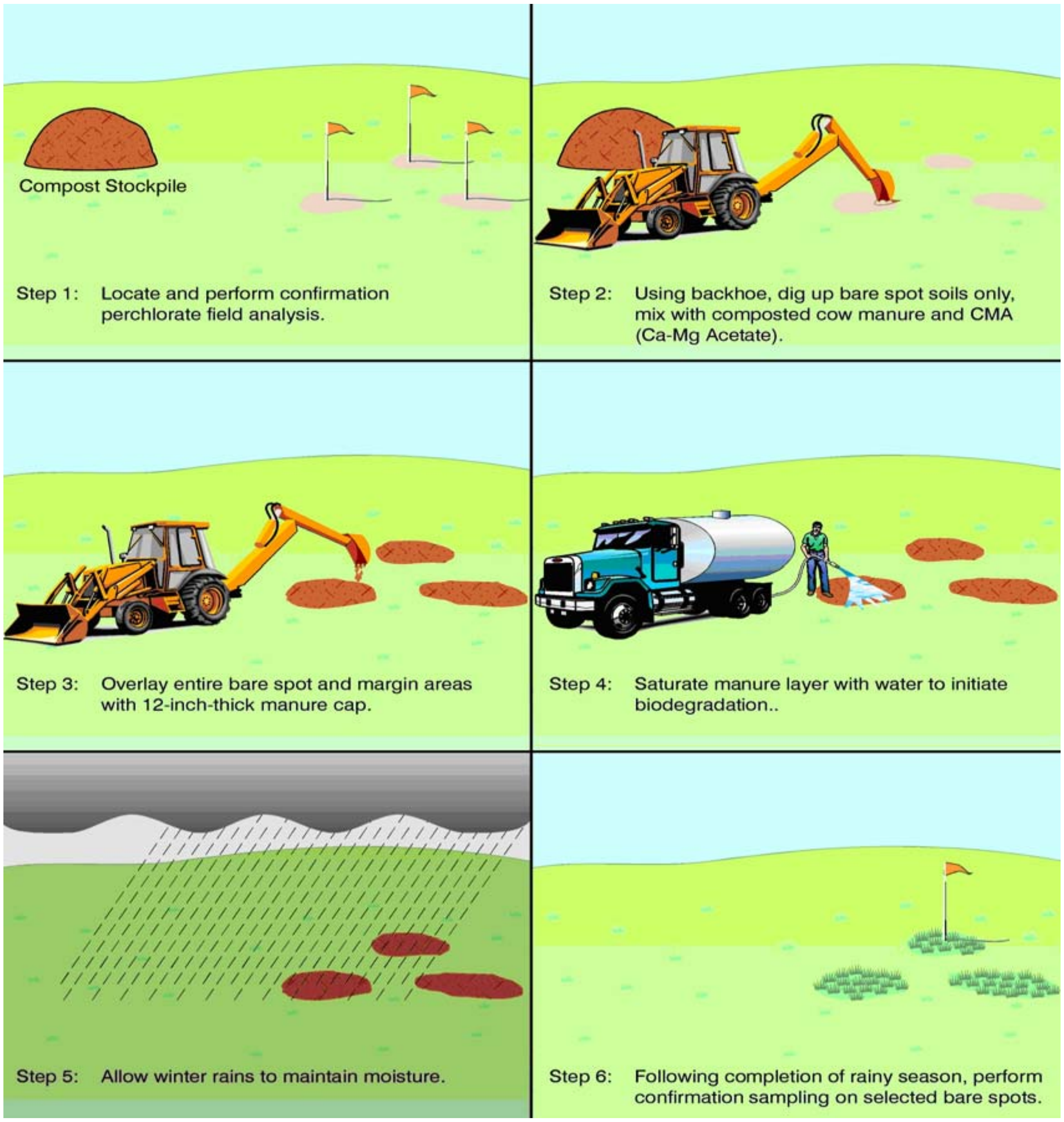
Following this successful bench-scale testing, a pilot test of composting was performed for perchlorate-impacted soils at Cavitt Ranch. Two soil compost piles were constructed, one on bare ground with suction lysimeters placed to evaluate potential leaching of perchlorate during the composting trial, and one on plastic liner with a simple leachate collection system. Two to three cubic yards of perchlorate-impacted soils were used for each pile. Initial perchlorate concentrations were 200–500 mg/kg. Soils were amended so that the piles consisted of approximately 35% soil, 25% manure, 20% sawdust or wood chips, and 20% alfalfa. Clean water was added to maintain moisture content of 35%–45% by volume. Temperature and moisture conditions were monitored within the piles. Perchlorate destruction was rapid as the concentrations of perchlorate during the 30-day test were reduced to <0.1 mg/kg in internal soil samples and 2 mg/kg in surface samples.

The successful application of bioremediation of perchlorate in compost piles led Aerojet to conduct treatability studies at sites 56B and 49B at Cavitt Ranch that involved applying manure to the surface over perchlorate-contaminated soils. If this approach were successful, it would save cost and time over constructing and monitoring compost piles. In October 1999 manure was applied at 3–4 inches (49B) and 12 inches (56B) at the two test plots. Water was applied to the test plots to maintain sufficient moisture to promote biodegradation. During the first month, surface concentrations of 1100, 4600, and 1500 mg/kg had been reduced to 15, 12, and 7.9 mg/kg, respectively, at the 56B test plot and surface concentrations of 2000, 1800, and 470 mg/kg were reduced to 172, 98, and 1.2 mg/kg, respectively, at the 49B test plot. The lower layers below the upper 1–2 inches did not appear to be affected within the first month and remained dry as no rainfall occurred during the first month.

To accelerate the degradation of perchlorate at the deeper depths, Aerojet aerated the soils in a section of each of the test plots to a depth of 4–5 inches using a tine aerator. During the next seven weeks significant rainfall occurred saturating the entire soil profile and weather bedrock with manure leachate. No differences in performance were seen between the tilled and untilled sections. At the 56B test plot where soils were thinner, only low levels of perchlorate (maximum 16 mg/kg) remained after 18 weeks that originally had up to 4600 mg/kg. At test plot 49B, with the thinner manure layer and deeper soil layer, concentrations had decreased from 2000 mg/kg to 62 mg/kg in the upper 2 inches and from 560 to 180 mg/kg in the deeper soils. It was estimated that during the end of the rainy season the test plots will dry out and the perchlorate will be wicked upward by capillary action (observed at other locations). The perchlorate will then be in the biologically active soil/manure layer where perchlorate degradation would occur until the soil became dry. Aerojet concluded that simply applying a layer of manure would be effective in remediating the perchlorate in the shallow soils at Cavitt Ranch. The study concluded that a thicker manure layer overlay is best as it provides a higher organic loading rate and increased water content for release to the underlying soil.

Aerojet expanded the field application at Cavitt Ranch in April and May 2001. At 10 areas with high levels (50–11,000 mg/kg) of perchlorate, soil was excavated, amended with cow manure and calcium magnesium acetate, placed back in the excavation, and covered with a 6–12-inch layer of composted cow manure. An additional 65 bare areas (due to burning during rocket propellant destruction) with low concentrations of perchlorate were treated by a simple overlay of composted manure. One year later, the soil was resampled and the average perchlorate concentration at the monitoring locations had decreased from 452 mg/kg to 1.4 mg/kg. Figures 8-2 and 8.3 illustrate the hot-spot soil treatment approach used at Cavitt Ranch Area 1.

Figure 8-2. Hot-spot treatment at Cavitt Ranch Area 41. (*Source:* Geosyntec Consultants)



Step 1: Locate and perform confirmation perchlorate field analysis.

Step 2: Using backhoe, dig up bare spot soils only, mix with composted cow manure and CMA (Ca-Mg Acetate).

Step 3: Overlay entire bare spot and margin areas with 12-inch-thick manure cap.

Step 4: Saturate manure layer with water to initiate biodegradation..

Step 5: Allow winter rains to maintain moisture.

Step 6: Following completion of rainy season, perform confirmation sampling on selected bare spots.

Figure 8-3. Hot-spot soil treatment using composted manure.

8.6.2 Hodgdon Powder Explosives Manufacturer, Kansas

Soils at explosives manufacturers may be contaminated with perchlorate. Biotreatment of these perchlorate-contaminated soils has proven successful. At Hodgdon Powder in Kansas, three large (16,000 yd^3) cells were constructed and tested using two different carbon sources. In one cell calcium/magnesium acetate was applied, and in two of the cells manure was tilled into the soil followed by wastewater from a nearby waste treatment plant. After four months all three cells showed a 95% reduction in perchlorate. Perchlorate concentrations were as high as 45 mg/kg.

8.6.3 Longhorn Army Ammunition Plant

Both laboratory and field treatability studies were conducted to identify suitable carbon sources for the cleanup of perchlorate-contaminated soils at LHAAP in Karnack, Texas. In the laboratory studies several carbon sources were tested, including poultry manure, cow manure, horse manure, cotton waste, methanol and ethanol. In the field pilot tests three carbon sources were tested: ethanol and horse and chicken manure. The perchlorate concentration was 400 mg/kg as the field demonstration started in October 2000. Six identical treatment plots (4.57 × 2.74 m) and one control cell (5.5 × 5.5 m) were constructed using plastic liners (Figure 8-4). Duplicate cells were treated with the same predetermined concentration of each amendment, and no amendment was added to the control cell. Water was applied to all seven plots to achieve complete saturation only down to the desired treatment depths below ground surface. Results after 10 months showed complete removal of perchlorate in the surface soils and varied reduction in the deeper layers. Horse manure and ethanol were the superior carbon amendments.

Figure 8-4. Soil treatment pilot cells at Longhorn Army Ammunition Plant.
(*Source:* Nzengung, Das, and Kastner 2001)

8.6.4 Former Munitions Manufacturing Site in California

Another ex situ bioremediation application has been conducted at a private industrial facility in Los Angeles County, California. Soils containing PCE and TCE are being treated in Ag-Bag and cement bunkers. The key treatment issues at this site were to design an economical system to address PCE and potentially TCE and address large soil volumes in a reasonable time frame. The facility was used to produce munitions and explosives, including rocket motors, gas generators, and missile main charges. Site investigations have identified several contaminants of concern, including perchlorate, metals, and VOCs, that may be a threat to future on-site residents and/or groundwater. Remediation alternatives were evaluated for the near-surface soils that include excavation and remediation by combinations of ex situ anaerobic bioremediation, ex situ soil washing, and ex situ chemical oxidation. Extensive pilot testing was conducted for the candidate ex situ soils remediation technologies in support of the project Feasibility Study and Remedial Action Plan.

Soil is currently being treated using ex situ anaerobic bioremediation. Soil is excavated and screened to remove rocks and cobbles >2 inches. The screened soil is then mixed with water, glycerin, and diammonium phosphate in a pug mill at a rate of up to 300 tons per hour. Amended soil is then placed either in Ag-Bag containment cells or in concrete block-lined treatment cells that are covered with plastic. Indigenous anaerobic perchlorate-reducing bacteria then reduce perchlorate to chloride. Figures 8-5 and 8-6 show filling and staging of the Ag-Bag at the site. Figure 8-7 shows the concrete-lined treatment cells. Initial average perchlorate concentrations ranged 600–5400 µg/kg. Full-scale results demonstrate that perchlorate is reduced to nondetectable concentrations (<20 µg/kg) within one month and typically in two weeks.

Figure 8-5. Ag-Bag being filled with soil. (Courtesy CDM Corp.)

Figure 8-6. Staged Ag-Bags filled with soil. (Courtesy CDM Corp.)

Figure 8-7. Cement-lined treatment cells. (Courtesy CDM Corp.)

8.7 Thermal Processes

8.7.1 Introduction

Thermal desorption systems generally rely on volatilization or evaporation mechanisms a part of the destruction process. In general, this process can be applied to soil contaminated with perchlorate. The thermal desorption system uses heat to separate contaminants from the soil and then thermally destroys them (see the process flowchart in Figure 8-8). Once rocks and other debris are removed, the soil is fed into the primary treatment unit. Inside this rotating drum, soil is heated to 500–1100°F. These 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 (http://groundwaterprogram.army.mil/community/facts/thermal_desorption.html).

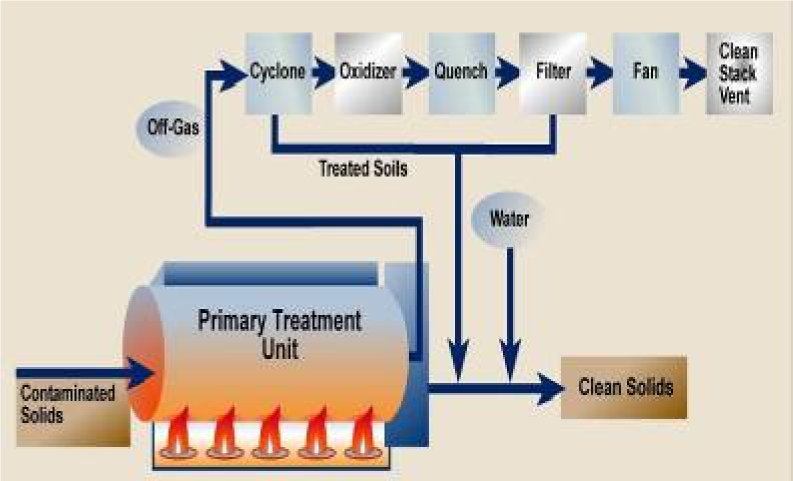


Figure 8-8. Thermal desorption process flowchart.

Continuous tumbling ensures all of the soil is exposed to the heat for the appropriate time period. While contaminants are captured in the off-gas, treated soil is discharged from the primary treatment unit and rehydrated with clean water to reduce the soil temperature and control dust emissions. Treatment of the contaminants continues as the off-gas flows through the air pollution control system. As it spins through the cyclone, the soil particles caught in the off-gas are removed before the off-gas moves into the thermal oxidizer. Using temperatures of up to 2000°F, the oxidizer destroys any remaining contaminants, transforming them into nitrogen, water, and carbon dioxide.

In the quench or cooling chamber, clean water cools the off-gas to a temperature that can be handled by the filtering system. The air pollution control system then uses air filters to pull any remaining treated particles of soil out of the air. A sonic pulse is used to periodically disengage the collected particles from the filter and deposit them in the treated soil stream. The filtered off-gas is then discharged.

Conceptually, thermal destruction using kilns followed by an afterburner, such as cement or cement rotary kilns, can work to destroy perchlorate-impacted soils. Lime and cement kilns can operate at temperatures up to 3200°, while typical hazardous waste incinerators can operate in the range 1400–2500°F (Corwin 1998). However, inorganic and elemental end products following incineration can disturb the process.

Thermal desorption systems can be of two general types, indirect and direct fired, with a further classification into high- and low-temperature operations. The low-temperature process is generally not considered an incinerator, even if an afterburner is incorporated into the design, because the kiln is operated below the ignition temperatures of typical contaminants and combustion may be suppressed by firing under low excess air conditions. Combustion is essentially complete in the burner used to provide a hot carrier gas or radiant heat source before the moisture is completely evaporated from the wet soils. The naturally occurring organic materials in the soils decompose to a carbonaceous form, depending on the operating temperature.

Another thermal process is supercritical wet oxidation (SCWO), or hydrothermal oxidation. This process uses water above its critical temperature and pressure (373.976°C and 220.55 bar, respectively) as a medium for thermal oxidation of compounds found in hazardous liquid or sludge waste. For most wastes, conditions in the reactor achieve 99.9% destruction efficiency. Organic compounds are oxidized to carbon dioxide, water, and nitrogen gas. Inorganic wastes such as nitrates or ammonia can similarly be destroyed by the addition of oxidizing or reducing agents (Frisch 1998). SCWO systems using liners fabricated from titanium alloy can provide protection against corrosion from salts that may precipitate out of the waste feed if present.

Additional thermal methods applicable to liquid wastes (as well as some solids) that can achieve high destruction efficiency include plasma systems. Application of plasma-arc systems involves generation of plasma with an electrical discharge through a gas. Plasma-arc systems produce extremely high temperatures and destruction efficiency (Lee and Huffman 1998).

Thermal desorption has been used as a stand-alone system for destruction of perchlorate-impacted soil ands wastewater. Thermal treatment of spent GAC and IX resins has also been conducted. Table 8-2 includes some example projects and shows how effective thermal desorption has been.

Table 8-2. Thermal desorption treatment effectiveness

Projects	Treatment effectiveness	Media
Environmental Chemical Corp (ECC), Burlingame, California, bench-scale program—Direct-fired thermal desorption process was tested for the destruction of perchlorate and explosive powders. Preliminary tests on candidate contaminated soils indicated that a portion of the perchlorate sublimed into an inert carrier gas steam after the soils dried and heated up above 725°F.	100 µg/kg and 100 mg/kg initial soil concentrations were used for testing (native soils were spiked with an aqueous solution). A post-treatment concentration <4 µg/kg was obtained at a residence time of 10 minutes at 775ºF (100 µg/kg) and 900°F (100 mg/kg) in a laboratory-scale rotary kiln.	Soil
MMR, Camp Edwards, Cape Cod, Massachusetts, ECC, full scale, summer 2004—Operating temperature for the full-scale system (based on the bench-scale program above) was approximately 850°F+ with explosives (e.g., RDX, HMX) and perchlorate-impacted soils. The higher temperature was required to allow the wet soils to dry in the kiln and reach the desired destruction temperature within the (fixed) residence time. Approximately half the 10-minute residence time was needed simply to dry the wet feed soils. Spiking tests indicated that even higher temperatures (up to 925°F) would be required at initial concentrations above 100 mg/kg, in this kiln. The required temperature conditions were predictable and repeatable (Gangopadhyay et al. 2005).	Reduction from 100 mg/kg to <4 µg/kg during demonstration. Approximately 60,000 tons of soil were treated below remediation goal of 4 µg/kg during full-scale operations.	Soil
AWWARF—Destruction of perchlorate brine from water treatment plant.		Wastewater and brine
General Atomics, Thiokol, Brigham City, Utah, bench-scale SCWO—The concentration of ammonium perchlorate in propellant was 10.8%. Two pilot tests using 25 and 800 pounds. The critical point of water was 705°F.	99% effective but unclear whether <1 µg/kg is achievable.	Soil

8.7.2 Management of Residuals

Thermal desorption processes volatilize the contaminants from soil without oxidation after the moisture has been evaporated. Liquid and semivolatile organic contaminants may steam-distill from the soils during this drying process but will leave a residual which must be thermally removed to reach typical compliance goals (Kuhlman and Osgerby 2003, Baker and Kulman 2002). The desorbed contaminants are transferred to a carrier gas phase and must be further treated either by condensation and filtration or combustion in an afterburner.

8.7.3 Applicability

Perchlorate is a relatively stable inorganic salt, and about 35% undergoes sublimation at approximately 725°F. Perchlorate will decompose above this temperature.

8.7.4 Strengths and Limitations

To be effective, any thermal process selected to destroy perchlorate must achieve high soil temperatures for a minimum residence time in addition to high destruction and removal efficiencies. The operating conditions should be developed on soils to be remediated, and although initial values can be derived from small-scale kilns as was done for MMR soils, the soils should be evaluated in preliminary tests using the full-scale kiln.

The exhaust created by this process is collected by an air pollution control system and heated to temperatures of 1400–2000°F to destroy the contaminants. The exhaust is then filtered to remove any remaining dust particles from the air stream. Air permitting regulations would be required on an operating remediation system to ensure all emissions meet state requirements.

Destruction efficiency should be demonstrated in preliminary (performance and operability) tests on any perchlorate-contaminated media. Certification of the thermal destruction would be required for the treated media. Discharged soil is sampled to confirm that treatment is effective. Once sample results confirm that cleanup goals have been met, soil cleaned through this process can be used for backfill in site restoration. Table 8-3 lists the strengths and limitations of thermal desorption.

Table 8-3. Thermal desorption strengths and limitations

Strengths	Limitations
• Achieves complete destruction of perchlorate media (e.g., soil, resins, and wastewater). • Enables treatment with co-contaminants.	• High temperature and energy requirements. • An afterburner is essential to eliminate the sublimed portion of the perchlorate crystals and explosive powders of co-contaminants. • Constraints of a minimum temperature and residence time are expected to apply to this process since fine particulates may tend to short-circuit the treatment train. • Salts with high melting points can become sticky and plug up the system (Corwin 1998)

8.7.5 Costs

Capital costs for a system using the electrolysis process depend on system size. Operating costs depend on electrical needs, maintenance requirements, and the length of time the system is functioning. Because of cost, thermal treatment should be considered only based on ability to reliably demonstrate achievement of treatment objectives, economies of scale due to large soil volumes, and regulatory concerns with other alternatives. The thermal destruction process becomes most viable when perchlorate-impacted soils to be remediated are mixed with other hazardous and toxic substances such as explosives and/or recalcitrant semivolatile organic compounds (Gangopadhyay et al. 2005).

9. PHYTOREMEDIATION AND CONSTRUCTED WETLANDS

9.1 Phytoremediation

9.1.1 Introduction

Phytoremediation is the use of plants to remove contaminants from soil and groundwater. Evidence obtained from a growing number of bench-scale tests shows the potential effectiveness of phytoremediation of perchlorate-contaminated soils, surface, and groundwater (Susarla et al. 1999a, b, c; Nzengung, Wang, and Harvey 1999; Nzengung and McCutcheon 2003). Research on phytoremediation of perchlorate has been conducted by the University of Georgia; the EPA National Exposure Research Laboratory in Athens, Georgia; the U.S. Air Force; and possibly others. This work has involved testing with several wetland species, including *Typha latifolia* (cattail), *Spirodela polyrhiza* (L.) Shield (duck weed), microbial mats, and *Myriophyllum aquaticum* (parrot feather), as well as several terrestrial plants, including black willow (*Salix nigraand, Salix caroliniana*), eastern cottonwood (*Populus deltoides*), eucalyptus (*Eucalyptus cinerea*), loblolly pine (*Pinus taeda*), French tarragon (*Artemisia dracunculus*), and spinach *(Spinacia oleracea)* (Nzengung, Wang, and Harvey 1999; Nzengung et al. 1999; Nzengung, Penning, and O'Niell 2004; Nzengung and Wang 2000; Nzengung and McCutcheon 2003; Susarla et al. 1999a, b, c). Other studies have been conducted by the University of Iowa with poplar trees (Van Aken and Schnoor 2002), Texas Tech University on upflow constructed treatment wetlands (Kui et al. 2004), and Lawrence Livermore Laboratory on pilot-scale constructed treatment wetlands (Krauter 2001, Krauter et al. 2005). Much of the data and concepts contained in this chapter are based on the work of Valentine Nzengung, who has conducted research at the University of Georgia.

9.1.2 Mechanisms

The published literature contains multiple studies focusing on mechanisms for phytoremediation of perchlorate (Nzengung, Wang, and Harvey 1999; Van Aken and Schnoor 2002; Nzengung and McCutcheon 2003; Nzengung, Penning, and O'Niell 2004). Bench-scale studies have identified the predominant mechanisms of phytoremediation of perchlorate (Figure 9-1) as (1) uptake and phytodegradation, (2) uptake and phytoaccumulation by some plant species, and (3) rapid rhizodegradation (Nzengung et al. 1999). Because uptake and phytodegradation is a slower process, it poses ecological risk resulting from the temporal phytoaccumulation of some fraction of the perchlorate taken up and transported mainly to plant leaves. For example, 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. However, the rapid degradation of perchlorate in the root zone of plants by perchlorate-degrading microorganisms minimizes the uptake and potential accumulation in the plant tissues (Yifru 2006).

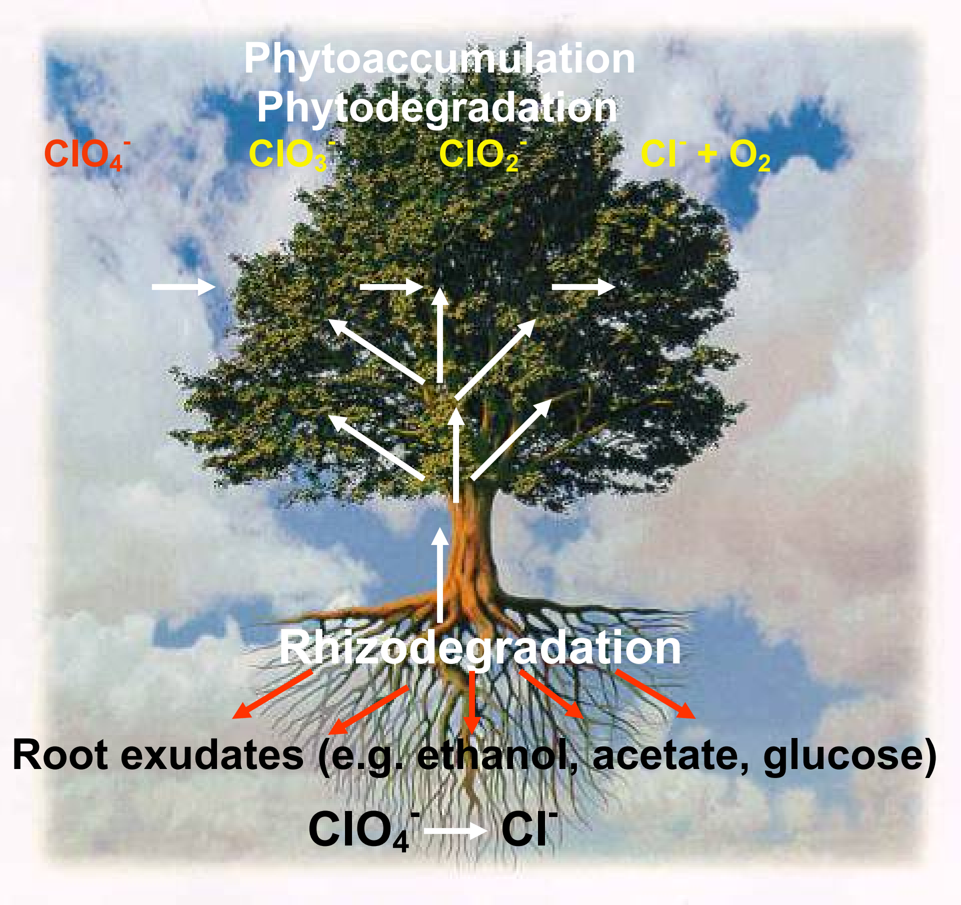


Figure 9-1. Mechanisms of phytoremediation of perchlorate.

Other studies have focused on influences of co-contaminants on phytoremediation mechanisms of perchlorate, including nitrate (Nzengung et al. 1999, Krauter 2001, Krauter et al. 2005); NDMA (Yifru and Nzengung 2007a, b; Mbuya and Nzengung 2006); and TCE (Nzengung 2002).

9.1.3 Uptake and Phytodegradation

The uptake of perchlorate by plants has been observed to be highest under predominantly aerobic and high nitrate concentrations in the root zone, as the latter conditions are not favorable for rapid rhizodegradation of perchlorate (Figure 9-2). Also, the amount of perchlorate taken up by a plant has been observed to increase with the perchlorate concentration in the growth media, soils, and water. In bench-scale tests, uptake may account for the removal of 5%–25% of the perchlorate present in the root zone of plants, with the least uptake observed under favorable rhizodegradation conditions. The duration of the uptake dominated phase is determined by the availability of electron donors and suitable redox conditions in the plant root zone.

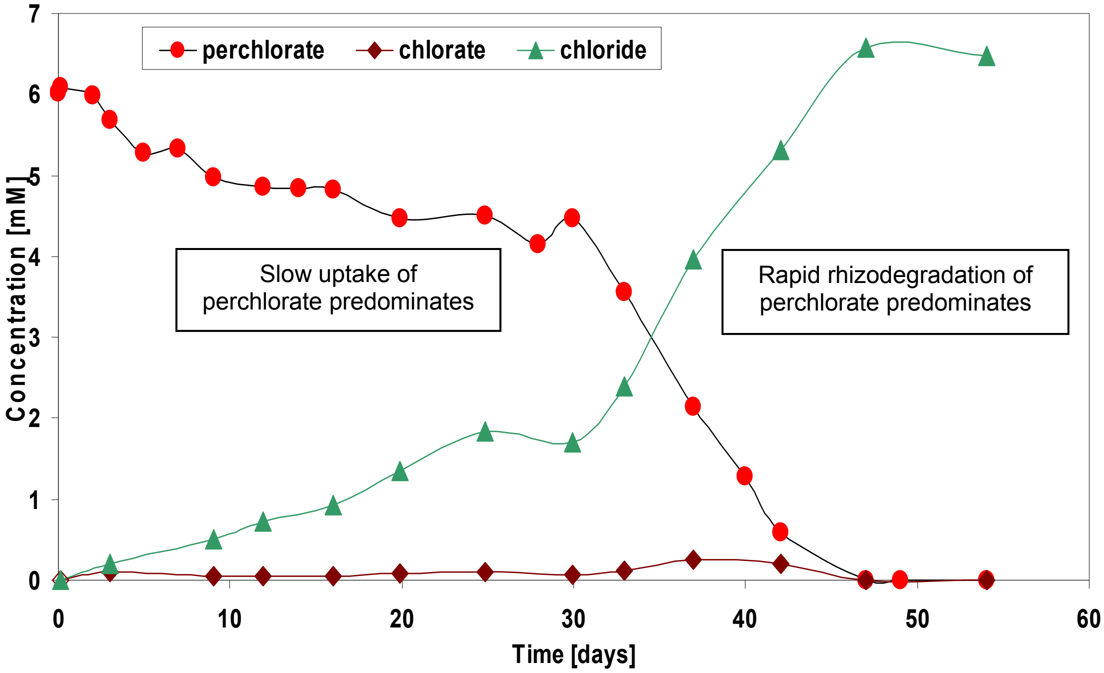


Figure 9-2. Phytoremediation degradation rate.

Analysis of tissues harvested from laboratory and field plants (cottonwood, pine, and willow trees) growing on perchlorate-contaminated media indicates that perchlorate taken up into plants is not simply hyperaccumulated (phytoaccumulated) in plant leaves, but phytodegraded, and that the capacity to phytodegrade perchlorate within leaves can vary with the plant species (Sursarla et al. 2000, Van Aken and Schnoor 2002). Pure plant-mediated processes that contribute to perchlorate reduction to chloride have been investigated in bench-scale tests (Van Aken and Schnoor 2002). Direct evidence of phytodegradation of perchlorate in leaf tissue of willows and poplar trees has been obtained in laboratory studies conducted with ^{36}Cl-labeled perchlorate (Van Aken and Schnoor 2002; Nzengung and McCutcheon 2003; Nzengung, Penning, and O'Niell 2004). Additionally, plant-mediated degradation of perchlorate was observed in aqueous suspensions of minced and fresh extracts of French tarragon (*Artemisia dracunculus*) and spinach *(Spinacia oleracea)* (Nzengung and Wang 2000). The latter studies suggest the presence of enzymes or enzyme cofactors in some plant leaves capable of catalyzing the degradation of perchlorate to chloride with the formation of various proportions of reduced metabolites (i.e., ClO_3^-, ClO_2^-, and Cl^-). The identified metabolites inside the plant tissues suggest a stepwise reduction of perchlorate to chloride, through a pathway similar to the reductive microbial metabolism. Therefore, uptake and phytodegradation could potentially be an important component of phytoremediation of perchlorate for plant species with high rates of phytodegradation.

Bench and field tests have confirmed the accumulation of some fraction of perchlorate taken up by plants. The phytoaccumulated perchlorate represents some fraction of the total perchlorate taken up and transported mainly to plant leaves, where phytodegradation occurs. Because phytodegradation is a relatively slower process than uptake, a significant fraction of the perchlorate remains stored in the senescenced (oldest) leaves or harvested plant tissues (Yifru 2006; Nzengung and McCutcheon 2003; Smith et al. 2001, 2004).

The amount of perchlorate taken up and phytoaccumulated tends to vary with the plant species. If the perchlorate taken up by field plants is not completely phytodegraded by the fall season, it is recycled when the plants age. Field data gathered by researchers at the University of Georgia identify salt cedar (*Tamarix sp.*) growing in the Las Vegas Wash and Bermuda grass harvested from LHAAP as plant species that significantly mine and phytoaccumulate (hyperaccumulate) perchlorate from contaminated soil and water (Yifru 2006). It was observed that plant litter and topsoil below salt cedar growing in Las Vegas Wash contained relatively higher concentrations of perchlorate than the fresh plant tissue (Smith et al. 2004, Yifru 2006, Urbansky et al. 2000). Meanwhile, phreatophytes (willows and poplars) commonly used in phytoremediation at hazardous waste sites tend to accumulate relatively moderate levels of perchlorate. There is strong evidence from research published in the peer-reviewed literature indicating the ability to minimize uptake and phytoaccumulation of perchlorate by biostimulating and enhancing rhizodegradation processes.

9.1.4 Rhizodegradation

Plant-microbe symbioses are ubiquitous in vegetated soils and have been shown in laboratory and field tests to contribute significantly to the rapid mineralization of perchlorate. Degradation of perchlorate in the root zone of plants (rhizodegradation) involves anoxic and anaerobic microbes using plant exudates/enzymes in the root zone to rapidly degrade ClO_4^- to innocuous Cl^-. For plants growing at most field sites, uptake and phytodegradation of perchlorate generally predominate over rhizodegradation because the amount of dissolved organic carbon exuded by the plants is not sufficient to sustain rapid rhizodegradation of perchlorate. In the presence of nitrate, rhizodegradation of perchlorate is significantly reduced, and a higher fraction uptake of perchlorate by plants is observed. The competitive effect of nitrate is overcome by supplying high concentrations of organic carbon and electron sources to the root zone (Nzengung et al. 1999; Nzengung and Wang 2000; Yifru and Nzengung 2007a, b; Yifru 2006).

In completed bench-scale tests conducted at the University of Georgia and the University of Iowa, biostimulation of rapid degradation of perchlorate in the root zone of plants has been achieved by supplying common carbon and electron sources consisting of plant exudates, compost extracts and synthetic electron donors (Shrout et al. 2006, Yifru 2006, Yifru and Nzengung 2007a, Nzengung et al. 1999). Shrout and co-workers used plant exudates to biostimulate rhizodegradation of perchlorate, while Nzengung et al. (1999) and Yifru and Nzengung (2007a) used acetate and compost extracts as electron donors and nutrient amendments to enhance rapid rhizoremediation of perchlorate in hydroponics and soil bioreactor experiments. The applications involved providing the selected root zone amendments (plant nutrients plus carbon and electron sources) in solution in the irrigation water (along with trace elements needed for plant growth) or mixed in with the soils during planting.

For hydroponically grown willow trees dosed with 25–40 mg/L perchlorate, the rate of perchlorate removal from solution increased from 0.25/day (first order) in control planted bioreactors (i.e., not supplied with an external dissolved organic carbon [DOC] source) to about

4.0 mg L^{-1} day^{-1} (zero order) in planted bioreactors amended with 500 mg/L DOC. In 5-gal willow planted soil bioreactors treated with 300 mg/L DOC, the rate of perchlorate removal by rhizodegradation was two orders of magnitude faster (24 mg L^{-1} day^{-1} per tree) than in the planted controls (0.35 mg L^{-1} day^{-1} per tree) that received no DOC treatment. The results of these bench-scale tests suggest that the rate limiting factor during phytoremediation of perchlorate appears to be the lack of an adequate supply of DOC used as carbon and electron sources by ubiquitous perchlorate-respiring microbes in the rhizosphere during rhizodegradation. Maintaining the concentration of DOC at an order of magnitude higher than the concentration of perchlorate tends to sustain high rates of rhizodegradation.

In bench-scale studies, the perchlorate concentrations measured in leaves harvested from DOC-amended soil buckets (simulating enhanced rhizodegradation) were an order of magnitude less than in leaves harvested from trees grown in control bioreactors. The ecological significance of biostimulation and enhancement of rhizodegradation is minimization of (1) the undesirable uptake and phytoaccumulation of perchlorate in plant leaves, (2) concentration of perchlorate in the food chain, and (3) possible recycling of perchlorate into the ecosystem.

9.1.5 Effect of Nitrate and Other Co-Contaminants

For environments having higher concentrations of competing terminal electron acceptors, such as oxygen and nitrate, the rhizodegradation of perchlorate is inhibited. The removal of perchlorate from soil and water by plants is dominated by uptake in aerobic and high nitrate conditions. Hydroponics studies have estimated rhizodegradation of 96.1% ± 4.5% (± 95% CI) of initial perchlorate in the absence of nitrate compared to 76% ± 14% (± 95% CI) in the presence of nitrate, a competing terminal electron acceptor (Nzengung and McCutcheon 2003). Scientists at the University of Georgia successfully achieved rapid rhizodegradation of perchlorate in the presence of high oxygen or nitrate concentrations by increasing the supply of electron donors supplied as DOC to the root zone.

Results of bench-scale tests indicate that willows, cottonwoods, and potentially other plant species are effective at treating mixed contaminants in groundwater containing either nitrate, chlorinated organic solvents, or NDMA and perchlorate. Thus, phyto-based treatment of mixed contaminant plumes is possible (Nzengung 2002, Yifru and Nzengung 2006). In greenhouse tests, no competitive removal of perchlorate and PCE or TCE was observed (Nzengung 2002). Removal of the chlorinated compounds from solution was dominated by plant uptake, while perchlorate was mostly biodegraded to chloride in the root zone. Phreatophytes, such as willows and poplars, passively absorb (take up) and mainly phytovolatilize NDMA; there is yet no evidence of rhizodegradation. A strong linear correlation between the mass of NDMA removed from solution and the incremental volume of transpired water was observed (Yifru and Nzengung 2006).

9.1.6 Phytotoxicity of Perchlorate

The effect of perchlorate concentration on rhizodegradation and plant uptake has been studied in hydroponics and soil bioreactors planted with willows (*Salix babylonica*) under greenhouse conditions (Mbuya and Nzengung 2006). In both hydroponic and soil bioreactors, the aqueous and soil media were dosed with DOC extracted from cow manure at approximately 300 mg/L and one of three perchlorate concentrations in the ranges: low (50–150 mg/L), high (100–700 mg/L), and very high (1,000–10,000 mg/ L). Nonplanted controls were handled in parallel.

At the low perchlorate (50–150 mg/L range) concentrations, complete perchlorate removal was reached within 5–8 days in both planted and nonplanted bioreactors. At high perchlorate (100–700 mg/L) concentrations, a significant difference in perchlorate removal rate was observed between planted and nonplanted bioreactors. The planted bioreactors dosed with high concentrations of perchlorate had similar results to the low concentration experiment in which all of the perchlorate was removed within 6–11 days. Meanwhile, the nonplanted controls dosed with high perchlorate concentrations retained substantial amounts of perchlorate in solution when the experiment was terminated at day 11 (4.52%, 9.68%, 17.89%, and 61.07% of the initial concentrations for 100, 300, 500 and 700 mg/L, respectively). The hydroponic bioreactors dosed with very high perchlorate concentrations (1,000–10,000 mg/L) and supplied with excess electron donors as DOC showed visible signs of phytotoxicity after 2 days. Willow plants dosed with 2000 mg/L of perchlorate or more did shed all their leaves by the fourth day.

For willow-planted soil bioreactors dosed with 1,000; 5,000; and 10,000 mg/L perchlorate, it was observed that willow plants in the DOC-treated bioreactors dosed with 5,000 and 10,000 mg/L perchlorate started to dry up within 12 hours. By day 2, the plants were dead and had shed all their leaves. The corresponding no-DOC treatments of 5,000 and 10,000 mg/L started to show signs of phytotoxicity at approximately 24 hours. Four days later all plants without DOC started to shed their leaves. Treatments that received 1,000 mg/L perchlorate had less intense and slow phytotoxic reaction. Mbuya and Nzengung (2006) concluded that young willow plants exhibited signs of phytotoxicity at perchlorate concentrations of about 1000 mg/L or higher.

9.1.7 Advantages and Limitations

Phytoremediation of perchlorate-contaminated soils and water is expected to have many of the same advantages of phytoremediation of other degradable contaminants. These advantages include the following:

- low cost—phytotechnologies generally compare favorably with costs for aboveground treatment technologies
- high public acceptance
- no secondary waste production if phytoremediation is engineered to enhance rhizodegradation
- minimum disturbance to the environment or any on-site operations
- can help meet other land-use goals as well (such as open-land quotas, wetland acreage, or canopy coverage) and can improve a site's aesthetic appeal
- can also treat other common co-contaminants, such as chlorinated solvents, explosives, including N-nitrosodimethylamine (Yifru and Nzengung 2006)

The limitations of phytoremediation of perchlorate include the following:

- depth and climate restrictions

- potential for transfer of contaminants from soil and groundwater into the food chain because the perchlorate taken up into the plant tissues remains an ecological risk until completely phytodegraded
- relatively slow process if phytoremediation is not engineered to achieve rhizodegradation enhancement—directly impacts sustainability and time-effective risk mitigation
- subject to seasonal variations, so often many plants spread over a large area will be needed for adequate capture and treatment
- dominance of the uptake and phytodegradation mechanism leading to transfer of contaminants into the leaf tissue (potentially resulting in plant biomass disposal or redeposition issues
- selecting a plant species suitable for achieving treatment goals is important because perchlorate might exert a toxic effect on certain species
- climatic changes can significantly impact plant growth, thus requiring variation in the treatment period
- the relatively immature stage of the technology, without cost and performance data and greater regulatory comfort, making it difficult for site managers to select and obtain approval for phytoremediation of perchlorate

9.1.8 Conclusion—Phytoremediation

Perchlorate remediation by plants and root zone microorganisms has been investigated mainly at the bench scale with limited field-scale demonstrations. It is clearly understood that the predominant mechanisms of phytoremediation of perchlorate are rapid degradation to innocuous chloride by ubiquitous perchlorate degraders in the root zone (rhizodegradation) and relatively slow uptake and degradation in plant leaves (phytodegradation), which leads to the accumulation of a significant fraction of perchlorate in the leaf tissue (phytoaccumulation). The uptake of perchlorate by plants increases under aerobic and high nitrate concentrations in the root zone as the contribution of rhizodegradation, a more efficient process for decontaminating perchlorate-contaminated soils and water, is not favored.

The results of bench-scale tests indicate that the rate-limiting factor during phytoremediation of perchlorate is the lack of an adequate supply of DOC used as carbon and electron sources by ubiquitous perchlorate-respiring microbes in the rhizosphere during rhizodegradation. Researchers at the Universities of Georgia and Iowa have successfully engineered phytoremediation of perchlorate at the bench scale. The process involves biostimulation and enhancement of rhizodegradation (“rhizoremediation”) by providing electron donors to the rhizosphere in synthetic or natural DOC

Phytoremediation of Groundwater at Longhorn Army Ammunition Plant

A pilot-scale application of phytoremediation of perchlorate-contaminated groundwater has been conducted at LHAAP in Karnack, Texas, by the University of Iowa (Schnoor et al. 2002, Schnoor et al. 2004). The field demonstration was conducted on a 0.7-acre site planted with 425 hybrid poplars in March 2003. In March 2004, one year after the trees were planted, the initial perchlorate concentration of 34 mg/L in the groundwater decreased to 23 mg/L. The mass of perchlorate taken up by the poplar trees and/or degraded within the rhizosphere was estimated as 0.114 ± 0.016 kg/day. The investigators estimated that 52 kg of perchlorate was removed from the groundwater by the hybrid poplar trees and/or the microbes that grow in the root zone between April 2003 and September 2004 (Schnoor et al. 2004).

forms. The ecological significance of rhizodegradation is that it minimizes the undesirable uptake and phytoaccumulation of perchlorate in plant tissues and food chain and possible recycling of perchlorate into the ecosystem.

Because the slow buildup of DOC in the rhizosphere by root exudation and natural soil organic matter decomposition is insufficient to sustain rhizoremediation, an optimum design of phytoremediation of perchlorate should include enhancement of rhizoremediation by supplying sufficient and sustained external DOC to the plant root zone. This technology is anticipated to be most applicable to vadose zone source areas in soil, groundwater, or surface runoff. Field-scale application of phytoremediation would require adequate space to establish the plants, and they may need special handling afterwards, if rhizodegradation is not enhanced and perchlorate salts accumulate in the plant tissues. The rate at which the plants become established and rhizodegradation occurs may also be a consideration.

9.2 Constructed Wetlands

9.2.1 Introduction

Constructed wetlands have been used for decades for the management and treatment of many wastewaters, including municipal, acid mine drainage, agriculture, petrochemical and textile industries, and storm water (Kadlec and Knight 1996, Moshiri 1994, Hammer 1990). Increasingly, however, constructed wetlands are being used for the remediation of groundwater or surface water impacted by industrial chemicals and wastes such as landfill leachate (Mulamoottil, McBean, and Rovers 1998) and explosives such as TNT or RDX. The trend toward increased use of constructed wetland technology relates to the low capital and O&M costs associated with this mostly passive technology. Recent successful trials of small-scale wetland reactors (Dondero 2001, Krauter 2001, Nzengung 2002, Kui et al. 2004) suggest that full-scale use of constructed wetlands could be a cost-effective method to deal with large volumes of perchlorate-contaminated water sources such as groundwater.

9.2.2 Mechanisms

Two main mechanisms are responsible for the treatment of perchlorate in wetlands: (1) microbial-mediated degradation reactions that occur in the sediment/soil, water column, biofilms, and rhizosphere and (2) uptake, accumulation, and/or transformation by plants. Plant uptake of perchlorate has been well documented, and recent studies using pureed crude extracts of edible plants (spinach and French tarragon) provided direct evidence of phytodegradation of perchlorate (Nzengung and Wang 2000). The transformation of perchlorate into innocuous products addresses some of the concern of bioaccumulation of perchlorate in the food chain where plants are employed as a cleanup tool. Unfortunately, phytodegradation is a relatively slow process, and as a result, a fraction of the perchlorate taken up by plants is phytoaccumulated. Phytoaccumulation of perchlorate poses potential ecological risks due to the accumulation of perchlorate in the ecosystem.

Wetland plants, while contributing to perchlorate removal through uptake and transformation, would most likely contribute to perchlorate removal primarily through rhizodegradation, or microbial-mediated processes in the vicinity of plant roots (the rhizosphere). In the presence of nitrates, experiments with ^{36}Cl-labeled perchlorate have shown that removal is dominated by plant uptake and transformation mechanisms, but in nitrate-limiting conditions (<200 mg/L) rhizodegradation becomes the dominant removal mechanism (Nzengung and Wang 2000, Nzengung and McCutcheon 2003). Furthermore, removal of perchlorate under anaerobic, low-nitrate conditions proceeded more rapidly than removal by plant uptake and transformation in these experiments (Kui et al. 2004). Thus, in the absence of the competing substrate nitrate and under anaerobic conditions, rhizodegradation can efficiently remove perchlorate from water. Such conditions are readily achieved in constructed wetland systems.

A complex web of interactions develops in the rhizosphere between the various microbial populations, plants and microbes, their metabolites, and dissolved contaminants and other substances in the soil and pore water within reach of the organisms in the rhizosphere. These interactions result in the ability of the microbe/plant consortia to degrade contaminants that might normally degrade very slowly. Perchlorate is a contaminant whose degradation is accelerated by the synergism of the rhizosphere environment. Although studies have shown that microbial-mediated degradation of perchlorate can also occur at reasonable rates in the absence of plant roots, plants in a wetland system provide other functions such as nutrient turnover (dissolved carbon source required for bacterial perchlorate reduction), enhanced porosity of media, and uptake/transformation, among others.

Reducing conditions are common to wetland soil/sediment, as are a variety of dissolved organic carbon sources (e.g., decomposing organic matter and root exudates). Nitrates are typically found at low levels in a wetland since plants and algae rapidly consume them, or they are converted by denitrifying bacteria in the sediment. The conditions in many wetlands are therefore ideal for perchlorate reduction. Furthermore, the ubiquitous perchlorate-biodegrading bacteria have been identified from many sources, including wetlands and subsurface environments (Coates et al. 1999). Constructed wetlands have the additional advantage over naturally occurring wetlands that they can be designed to optimize perchlorate degradation mechanisms and/or uptake and transformation. One such approach is through the reinforcement of the constructed treatment wetland with microbial mats (O’Niell and Nzengung 2003b).

9.2.3 Applications

Constructed wetlands can be broadly categorized into two types: surface-flow (SF) wetlands and subsurface-flow (SSF) wetlands.

SF Wetlands. SF wetlands are wetlands with shallow water pooled on the ground surface, typically having emergent vegetation such as cattail and bulrush. Water flowing through SF wetlands contacts microbes on surfaces of detritus, plant stems/leaves, and surface soil/sediment, where nutrient uptake and/or contaminant degradation takes place. Settling, volatilization, and phytodegradation are some of the other important mechanisms of removal in SF wetlands, though biological processes are dominant in perchlorate removal. The anaerobic conditions of the wetland sediment/soil, where the bulk of perchlorate-reducing bacteria are present, can be permeated by the water flowing through the wetland, though this is the less preferential path. Most water in a SF wetland flows through the free water column, and unless the wetland is large relative to the volume of water flowing through it (i.e., the hydraulic residence time [HRT] is sufficient), all of the perchlorate may not come in contact with perchlorate-reducing bacterial populations in the sediment before the water exits the wetland.

SSF Wetlands. SSF wetlands, where water flows beneath the surface of a bed of porous medium such as gravel, are potentially more suitable for perchlorate treatment on an equivalent area basis compared to SF wetlands. Water in a SSF wetland is required to flow through the media, which develops a thick biofilm, rich in bacteria, in a reducing environment. SSF wetlands are often costlier to construct and are more sensitive to design/construction issues such as media size but provide more treatment on a per unit area than their SF counterparts. Anaerobic vertical flow constructed wetlands would seem ideally suited to treat perchlorate-contaminated water.

Laboratory and field research has shown that phytoremediation processes can uptake and, in many cases, transform perchlorate to environmentally acceptable end products. In one study, upflow columns were used to demonstrate that upflow natural wetlands have the potential to treat perchlorate-contaminated waters (Kui et al. 2004). The wetland columns were planted with and without Bulrush (*Scirpus sp.*). In the absence of nitrate (NO_3^--N <1 mg/L), wetland columns were capable of removing ClO_4^- to levels below the detection limit (<4 µg/L) for a series of influent ClO_4^- concentrations (4, 8, 16, and 32 mg/L). At an influent ClO_4^- concentration of 32 mg/L, ClO_4^- breakthrough was observed with the increase in nitrate concentration. Perchlorate and nitrate degradation rate constants were determined using a 1-D transport model with dispersion. Plant uptake was directly linked with ClO_4^- concentration in the rhizosphere, and the stem bioconcentration factor was estimated to be 57. A mass balance indicated plant uptake accounted for 0%–14.3% of initial ClO_4^- input. Microbial degradation played a more important role than plant uptake in ClO_4^- degradation in this wetland system. Perchlorate degradation in the upflow wetland system was limited by nitrate concentration, organic substrate availability, and reoxygenation zone near the surface.

Meanwhile, Dondero (2001) used wetland bioreactors consisting of 55-gal drums planted with a mixture of wetland plants and terrestrial plants, respectively, in a layered sand and compost substrate to treat high concentrations (250 µg/L) of perchlorate applied at the surface. The media quickly developed reducing conditions, and drums containing wetland plants showed the highest removal rates for perchlorate (half-lives about 1.5–4 days), though unplanted control drums also showed similar removal half-lives. Other studies have shown that algae and microbial mats can stimulate reducing conditions in surface waters, resulting in anaerobic degradation of perchlorate in these systems. Both algae and microbial mat bioreactors and ebb-and-flow bioreactors were shown to degrade perchlorate at concentrations up to 300 mg/L, with perchlorate half-lives of 1.2–25 days (O'Niell and Nzengung 2003b). The microbial mats outperformed the algal mats (perchlorate half-life of 1.2 days) and were also more resilient to upset conditions as compared to algal mats.

In another flow-through study, a wetland bioreactor system consisting of four small tanks of coarse aquarium gravel planted with wetland plants was shown to remove perchlorate at 100 µg/L from nitrate-contaminated groundwater (68 mg/L), with acetate as a carbon source (Krauter 2001). The HRT required to remove perchlorate to below the detection limit was 0.5 days under these conditions. Significantly higher HRTs of 4 days were required in the absence of a carbon source. These results suggest that denitrifying bacteria are responsible for

Constructed Treatment Wetland at LLNL

An ongoing full-scale application of containerized constructed treatment wetlands to remediate perchlorate-contaminated groundwater is being implemented at the DOE's LLNL. The containerized wetlands bioreactor system was started in November 2000. Groundwater was allowed to circulate through the bioreactor for three weeks to acclimate the wetland plants and to build a biofilm from indigenous flora (Krauter 2001, Krauter et al. 2005, Dibley and Krauter 2004). Treatability studies showed that the addition of organic carbon provided as dilute acetic acid solutions enhanced microbial denitrification and perchlorate mineralization without inoculation. The indigenous chlorate-respiring bacteria effectively degraded perchlorate into innocuous oxygen and chloride when supplied with electron donors (Krauter 2001).

The treated groundwater contains VOCs, nitrate (48 mg/L) and perchlorate (14–27 µg/L) as co-contaminants. Groundwater from Site 300 (known as Building 854) is pumped into GAC canisters to remove VOCs using solar energy. The VOCs-treated groundwater containing approximately 48 mg/L of nitrate and an average of 13 µg/L of perchlorate is gravity fed continuously into two parallel series of two 1900 L and two 4200 L constructed wetland tank bioreactors. Each bioreactor contains coarse, aquarium-grade gravel and locally obtained plant species such as cattails (*Typha* spp.), sedges (*Cyperus* spp.), and indigenous denitrifying microorganisms. An active flow rate of 3.8 L/min is set to provide a minimum reactor HRT of 17–20 hours, which should increase as the plants mature and organic matter and rootlets accumulate in the bioreactors.

Results obtained to date show that degradation of perchlorate and nitrate to their detection limits of 4 µg/L and <5 mg/L, without an added carbon source, required an HRT of 4 days and 20 hours, respectively. When provided an electron source (0.25 g/L solution of sodium acetate), the HRT decreased to 0.5 days. In about two years, the system processed over 3,463,000 L of groundwater and treated more than 38 g of perchlorate and 148 kg of nitrate. The fecal coliform count for the treated water was <2 Most Probable Number/100 mL), acetic acid was below detection level (<5 mg/L), ammonia –N was <0.03 mg/L in the treated effluent water.

perchlorate removal in the containerized wetland system (a carbon source is obligatory for nitrate reduction). The key benefits listed for the system were as follows:

- low cost because it is a largely passive system, solar-driven, and easy to construct
- low O&M
- environmentally friendly technology
- self-sustaining because it provides microbial habitats and sources of organic carbon for bacterial processes
- no creation of wetland habitats that require permits
- accurate hydraulic control

Potential shortfalls of this system include sensitivity to water and heat stress, requirement of low flow through small containers, and degradation rates that may fluctuate with the seasons.

9.2.4 Advantages and Limitations

The benefits and limits to the use of wetlands to treat ground and surface water are discussed in the previous chapter on phytoremediation.

9.2.5 Conclusion—Constructed Wetlands

Based on the success of bioremediation and phytoremediation trials for perchlorate in groundwater and soils, constructed wetlands appear to be a logical combination of treatment mechanisms to achieve cost-effective remediation of perchlorate-impacted groundwater and surface water. Treatment of perchlorate by constructed wetlands is a potentially effective remediation method due to the reducing conditions of wetland soil/sediment, the high biological activity of wetland soil/sediment in terms of microbial diversity and numbers, the availability of a variety of dissolved carbon sources, the ability of plants to uptake and transform perchlorate, and the ubiquity of bacteria which degrade perchlorate. Biological methods such as constructed wetlands treatment are particularly attractive since they have the potential to cost-effectively destroy many contaminants, perchlorate included, instead of transferring them to another medium (e.g., impacted resin or brine).

Design of the wetland system to treat perchlorate-contaminated water should be guided by the site-specific conditions such as perchlorate contamination level, nitrate concentration, heterogeneity of soil medium, long-term organic substrate supply, hydraulic loading, flow regime, and cost. Contaminated groundwater and surface water may be pumped and treated in constructed wetlands and then recharged to the aquifer through percolation ponds. The use of phytoremediation and bioremediation processes in constructed wetlands has potential to provide a robust, natural, and low-cost remedial alternative to treat perchlorate-impacted water.

10. STAKEHOLDER CONCERNS

10.1 Definition of Stakeholder

"Stakeholder" is a broadly defined term that includes all individuals or groups that are directly or indirectly affected by perchlorate contamination and the associated investigation and remedial activities. The stakeholder is affected by the potential risk (economic and health related) associated with an environmental exposure of a contaminant. Examples of stakeholders include community members, business owners, employees, local governments and tribes, local utilities, developers, and realtors. These are individuals and groups that have the potential to be negatively impacted by the potential health risk or inconvenienced through the investigation and remediation process.

Community stakeholders are diverse. They may be concerned about the following:

- health effects
- property values
- water costs
- jobs, tax revenues, profits
- traffic
- noise
- odor
- length of time required for remediation

Where there is significant community interest, environmental decision makers may find it useful to go beyond one-time or occasional community meetings and create a community advisory board with representatives from each segment of the community. Such boards have improved community relations at numerous perchlorate sites as well as hundreds of other contamination sites across the country.

Community advisory boards often provide decision makers with "one-stop shopping" for community input. That is, instead of guessing which community interest represents the public, they rely on the advisory group to work out differences among community members. In turn, community representatives act as liaisons to the community at large. Even if communities do not achieve consensus, advisory group discussions usually define the major issues.

Finally, well-designed community involvement programs build trust by providing community members with information in a timely way and by addressing their concerns. Sometimes this means the careful explanation of findings and proposals; sometimes it means altering proposals to resolve issues raised by community members. Community acceptance is in most cases a required consideration in the selection of cleanup remedies, and the foremost factor in achieving community acceptance is whether the public trusts the people making the decisions. Regular meetings foster respect between the community members and the decision makers.

10.2 Background

The discussion of stakeholder concerns in this text will concentrate on the proven commercially available technologies; however the majority of stakeholder concerns are global in nature and also apply to other emerging technologies.

The federal government, states, and sovereign tribal nations regulate and or mandate the participation of stakeholders in the investigation and remediation process. Not only do releases of hazardous substances pose public health risks, but frequently the investigative and remedial processes generate noise and other inconveniences. When government responds to environmental contamination, various environmental statutes require coordination with stakeholders and require that the public be given an opportunity for meaningful involvement in the process.

Over the past several years, the presence of perchlorate in soil, water resources, and drinking water supplies has been a sensitive issue, especially in the West, where widespread perchlorate contamination has received extensive attention from the press, environmental organizations, and elected officials. It is particularly important, therefore, that environmental decision makers carefully design community involvement programs to involve the public early, often, and on a continuing basis.

At locations where perchlorate impacts local drinking water, community members have sought balance between source remediation and drinking water protection. For example, the Perchlorate Community Advisory Group in San Martin has helped the Olin Corporation, California's Central Coast Water Quality Control Board, and the Santa Clara Valley Water District develop a strategy to implement both in situ and ex situ treatment at the source while providing alternative water to the owners of downgradient contaminated private wells (see the Olin case study in Appendix A).

10.3 Remediation and Stakeholder Concerns

10.3.1 Concerns Common to Most Technologies

Concerns common to all stakeholders typically relate to health issues, economic or monetary issues, inconvenience, and natural resource issues. Issues related to health and risks are discussed in the stakeholder forum during the remedial investigation phase of the project. At Aerojet's Rancho Cordova facility, members of the Community Advisory Group questioned the location of a treatment plant. They were concerned that the site was too close to the local water supply system, and they didn't want treated water to be delivered directly to area homes.

Monetary issues are often related to the type of tax revenue being used to address the remediation of the site. Are state, federal, or tribal dollars involved in the cleanup? Stakeholders are frequently grass root organizations that have not had the opportunity to ask questions related to the organizational structure and funding of regulatory agencies. This is an opportunity for regulatory leaders to inform the public about monetary issues. Education builds consensus in the stakeholder process.

Stakeholders will be concerned about the effect that investigation and remediation have on business. Will customers and employees be inconvenienced by the ongoing investigation and remedial activities? Will long-term property values be affected by the remediation activities? It is important for regulators and industry to acknowledge these concerns and work to minimize impact to stakeholders. It is also important that project personnel reinforce that the remediation of the soil and/or groundwater may result in a long-term improvement in property value and revitalize business development in the area surrounding remedial activities.

Natural resource issues that are common to most stakeholder groups relate to the consumption of power and water. Stakeholders may be concerned that the power requirements of the remedial processes will affect delivery to other customers or affect the overall price of power. Stakeholders will want assurances that surface water and or groundwater remediation will not deplete these resources. Stakeholders may be concerned that the remediated water is not reused in the most beneficial manner.

Stakeholder groups may also be concerned that the remediated water contains other contaminants that should not be returned to the environment. Many of the older perchlorate plumes were caused or exacerbated when chlorinated compounds or metals were remediated in ex situ treatment and then reinjected for groundwater recharge or as a hydraulic barrier. These remedial activities were done without realizing perchlorate was present, or they were prior to regulatory guidance developed to minimize health risk to perchlorate. Perchlorate is an example showing how emerging contaminants can add to the overall remediation time frame and cleanup costs.

In situ and ex situ soil treatment technologies generally consume less water than do water treatment technologies, but stakeholder perception will be similar, and efforts should be made to quantify the consumption and demonstrate the value. Stakeholders will be particularly concerned about water consumption in an area of rapid population growth. In the arid South and West where growth and sustainable yield are important issues, competition for water will be an important concern for most stakeholders. Municipalities, developers, agriculture, and business will all compete for diminishing natural resources.

10.3.2 Concerns Related to Specific Treatment Systems

Drinking water exposure has been given the greatest amount of attention related to perchlorate contamination. However, recent data from the sampling of milk and food products have indicated a need for greater attention to nondrinking water–related sources. The majority of remediation technologies address treatment of groundwater and drinking water for perchlorate. The large scale of the surface water contamination of the Colorado River and Lake Mead may require new technologies. Stakeholder concerns related to commercially available treatment technologies are described below.

10.3.2.1 Ion Exchange

IX is a reversible chemical reaction caused when an ion from solution is exchanged with a similarly charged ion from an immobile solid. Stakeholder concerns related to IX include location of the treatment facility, facility size, potential odors, and noise generation associated with the treatment facility. Additional concerns include treatment or disposal of the residual perchlorate brine following IX resin regeneration. Some types of resin regeneration are most cost-effective when done off site. This is currently the case with ferrous chloride treatment of regenerant waste.

Fixed-bed systems are composed of a treatment train with a series of aboveground canisters 10–20 feet tall and approximately 10 feet in diameter. It would be difficult to construct a fixed-bed system that could be hidden for aesthetic purposes. This is a closed system and would not present any significant concern related to odor. The contents of the canisters are periodically replaced and taken off site for disposal or regeneration. There are no significant noise issues related to the system operation other than pump noise. The amount of pump noise depends on the flow design of the remediation system. Traffic and noise may be a concern during construction and decommissioning of the treatment system. Once the facility has been constructed, operation should not be a significant issue to stakeholders, although periodic changeout of the resin will be required.

Older, regenerable moving-bed IX treatment systems were very large and required a significantly larger footprint than fixed-bed systems. Newer, regenerable fixed-bed systems are not as imposing and are very close in size to traditional, fixed-bed nonregenerable systems. During operation and maintenance, traffic to and from the location should be minimal. There are no significant noise issues related to the system operation other than pump noise. The amount of pump noise again depends on the flow design of the remediation system. This type of remediation system is also closed and does not present any odor issues.

10.3.2.2 Phytoremediation and Constructed Wetlands

In general, members of the public favor phytoremediation and constructed wetlands remedies as “natural,” at least where pilot studies show that the particular remedy is both effective and efficient. Because of the widespread concern that perchlorate easily enters the food chain, stakeholders are likely to seek assurances that remediation will not lead to the spread of contamination. In particular, they will want proof that perchlorate is being degraded and not just accumulated. In ecologically sensitive locations, people may express concerns about the introduction of nonnative species, as well as soil disturbance caused during construction. Finally, the public will likely insist on measures to prevent or reduce nuisances sometimes associated with phytoremediation and constructed wetlands, such as unwanted insects, odor, pollen and other allergens, damage to foundations and underground utilities, and the obstruction of views.

10.3.2.3 Biological Treatment

Some regulatory agencies have expressed concern that the public might be nervous about the biotreatment of perchlorate-contaminated drinking water supplies. However, the record thus far is that the public likes bioremediation if it is shown to be effective. Still, because some stakeholders might fear the presence of treatment bacteria at the tap, it's important to explain that such biotreatment will be implemented only as part of a treatment train that guarantees removal of residual organisms.

10.3.2.4 Thermal Treatment

Public stakeholders are generally comfortable with thermal desorption when it is used to remove hazardous substances such as perchlorate from soil, but communities may oppose the thermal destruction of contaminants. The combustion of chlorine-containing compounds may generate low levels of toxic products of incomplete combustion, such as dioxins. Because of this concern, emissions may be contained and tested. If they contain unacceptable levels of hazardous substances, they are returned to the treatment system for additional processing (Crowe and Schade 2002).

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Appendix A

Case Studies

AEROJET CASE STUDY

Aerojet Site Background

In the early 1950s Aerojet-General Corporation (Aerojet) came to eastern Sacramento County to establish a site to develop, manufacture and test rocket propulsion systems. The site chosen consisted of over 12,500 acres of formerly dredged land in a remote area approximately 16 miles east of downtown Sacramento (Figure A-1). The gold-dredging activities by the Natomas Company left the site in a condition that at the time was considered unsuitable for most types of development.[1] (See end notes on p. A-20.)

The dredging removed soils and rock up to 100 feet bgs over a majority of the Aerojet site, leaving large cobble piles in nearly parallel rows with little soil or vegetation. The cobble piles are separated by fine-grained slickens ponds that represent the settling area of the wash water from the dredging. Buffalo Creek represents the primary drainage feature across the site, draining approximately 40% of the site. A majority of the property has no discernable drainage and rainfall infiltrates within the cobble piles.[2] Buffalo Creek, together with Alder Creek along the northern edge of the Aerojet site, direct storm water runoff to the American River (Figure A-2).

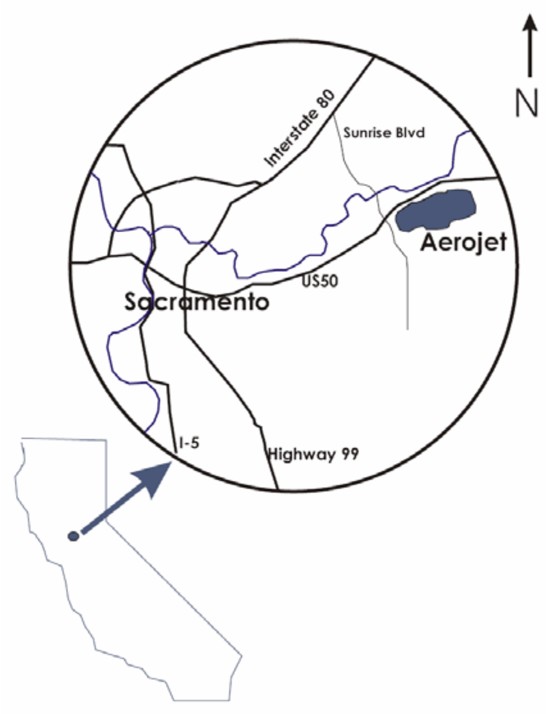


Figure A-1. Aerojet site location.

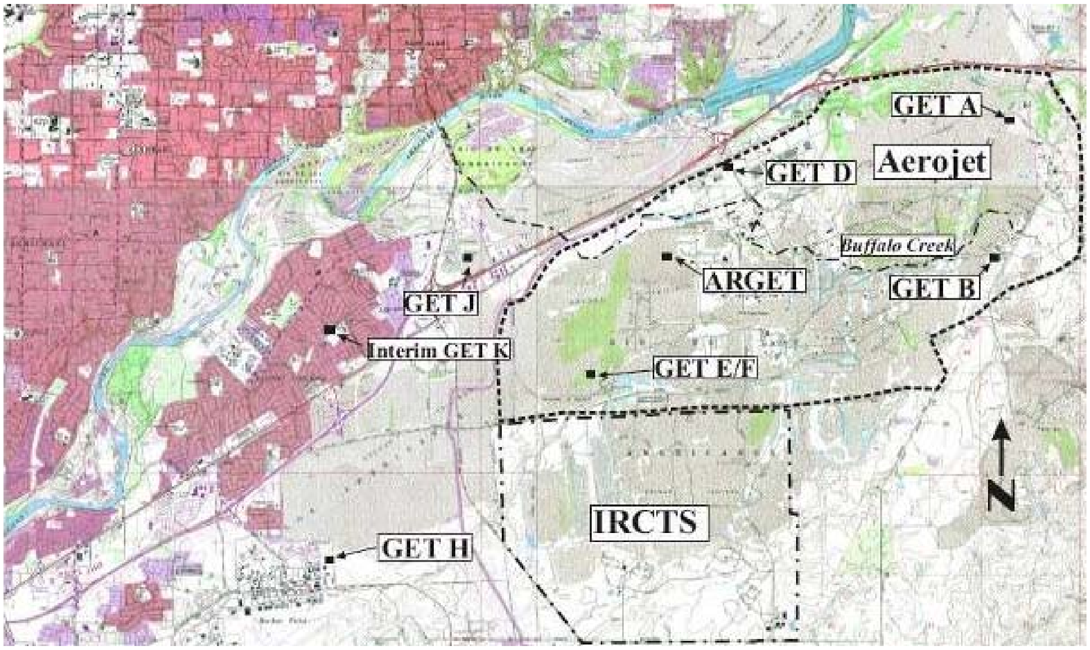


Figure A-2. Aerojet site map.

Groundwater is found at less than 10 feet bgs at the eastern edge of the Aerojet site. Traveling west across the site, the depth to groundwater increases to more than 100 feet by the time the western edge of the Aerojet site is reached. With the large amount of infiltration on the Aerojet property and the occurrence of bedrock at shallow depths to the east, groundwater flow is radial at the site. At the east side of Aerojet there is flow to the north and south. The flows gradually shift westerly so that at the west side at the Aerojet site the flow is to the west-southwest.

The groundwater in the vicinity of the Aerojet site is of excellent quality and used extensively for domestic, commercial, and industrial use. The groundwater has low concentrations of dissolved salts and metals. The fresh groundwater extends to 600–900 feet bgs surrounding Aerojet in Pliocene to Pleistocene sediments. Below that there is a layer of brackish water in Cretaceous marine sediments.[2]

The land surrounding the Aerojet site was initially open space or was used for agricultural or industrial purposes. Aerojet also leased adjacent properties for buffer purposes and for waste treatment and disposal. Over time, property to the west and north of the Aerojet site was put to residential use. In addition, 4,000 of the initial 12,500 acres was leased by the McDonnell-Douglas Corporation (MDC) to conduct rocket propulsion systems (see Figure A-2). The MDC area is known as the Inactive Rancho Cordova Test Site (IRCTS).

Aerojet conducted three general types of industrial activities: solid rocket manufacturing and testing, liquid rocket manufacturing and testing, and chemical manufacturing. The solid rocket manufacturing activities consisted of development and manufacture of solid rocket propellant (primarily ammonium perchlorate), which is loaded into rocket motor casings. Solid rocket propellant was formulated, mixed, cast, and cured. Solid rocket testing took place in isolated areas where the solid rocket motor was strapped down. The rocket motor was fired to test propellant and motor performance. As this document concerns the chemical perchlorate, liquid rocket manufacturing and testing and chemical manufacturing will not be discussed further except to point out that the pollutants released by those processes (i.e., N-nitrosodimethyamine, hydrazine, PROWL®) commingled with the pollutants produced from the solid rocket development in many instances. These commingled pollutants require the development of multiple treatment technologies to clean up the pollutants.

Solid rocket manufacturing and testing was done for the U.S. military services and space agencies. Solid rocket products developed and manufactured by Aerojet consisted primarily of jet-assisted take-off motors; tactical rockets such as Falcon, Hawk, Harpoon, Sidewinder, Maverick, Bullpup, Genie, Sparrow, AMRAAM, Tartar and Navy Standard Missle; ballistic missiles Minuteman I, II and III, Polaris, Midgetman, Peacekeeper, and space boosters; and sounding rockets.[3]

Sources of Perchlorate in Soil and Groundwater

During the solid rocket motor manufacturing processes, large amounts of solvents, primarily TCE, and copious amounts of water were used to ensure cleanliness of casings and tooling to minimize explosion and fire hazard. Washdown of the manufacturing facilities transferred ammonium perchlorate and solvents to unlined ponds and low areas surrounding the facilities.

The water and pollutants migrated readily through the dredged materials to impact soils and groundwater.

There are times when rocket propellant must be removed from the rocket motor casing. To do so the rocket motor was taken to the hog-out facility, where the propellant was removed using a water knife to avoid explosion hazards. The water containing ammonium perchlorate in both solid and dissolved forms was discharged to unlined and lined ponds. Leakage from the ponds and overflow from the hog-out facility created the largest source of perchlorate in groundwater at the Aerojet site, with concentrations exceeding 100 mg/L. Two hog-out facilities were used, one by Aerojet on the 8500-acre property and one by MDC on the IRCTS.

Perchlorate is also found at areas where waste ammonium perchlorate rocket propellant was taken to be destroyed by burning and detonation. Waste propellant was stockpiled on pads in the open burn/open detonation area on site and off site at Area 41 (Cavitt Ranch). Leaching from the stockpiled areas and incomplete destruction of the waste materials led to rainfall moving the perchlorate into the soil and groundwater at those two areas.

Another source of perchlorate in soils and groundwater is the Aerojet solid waste disposal sites. Four landfills were established to receive waste construction materials, asbestos, and general office waste. Groundwater downgradient from the landfills was found to contain perchlorate up to 26 μg/L. During characterization of the landfill waste materials, low concentrations of perchlorate up to 1 mg/kg were found throughout the waste materials. It is believed that the perchlorate in the landfill came from disposal of the cardboard boxes that were used to ship perchlorate to Aerojet.

There is also a source of perchlorate in groundwater on the IRCTS not associated with solid rocket testing and manufacturing. A now defunct company, Kinnetech, tested down-hole explosives for use in the oil industry at the Alpha/IOC-1 complex on the IRCTS, which was not used for testing solid rocket motors. Explosives containing perchlorate were placed below the water table and detonated and the results analyzed.

Two areas where it might be expected to find perchlorate in soils and groundwater are the solid rocket testing area and Magazine Area, where perchlorate and other explosive materials are stored. However, the Stage 1 Remedial Investigation conducted in the early 1990s and subsequent groundwater monitoring found no indication that perchlorate is in the soils or groundwater beneath the solid rocket testing area or the Magazine Area. At the solid rocket test area it is believed that the ignition of the small rocket motors completely consumed the perchlorate—the residual perchlorate was of such small quantities that it could not be measured, or the residual perchlorate was carried away by the wind to be deposited downwind. At the Magazine Area it is not surprising that perchlorate has not been found in the soils. Being explosive, perchlorate is handled and stored very carefully. Containerized perchlorate is stored in bunkers in the Magazine Area waiting processing into solid rocket propellant. Opening of the containers does not occur until the containers are in the processing area.

Groundwater Contamination

The practices described above caused pollution of the groundwater with perchlorate and solvents at many locations on the Aerojet and IRCTS sites. In 1979, the California Central Valley Regional Water Quality Control Board (Regional Water Board) issued Cleanup and Abatement Orders to Aerojet due to the disposal practices and the finding of TCE in off-site private water supply wells. At the time, perchlorate was not believed to be a contaminant of concern at the concentrations being detected (around 1000 µg/L) but was used as an indicator of waste and waste migration.

The investigation into the sources of contamination and groundwater pollution led to Aerojet being placed on the Superfund list in 1982 and the development by Aerojet of interim groundwater extraction and treatment systems (GETs). Designed to minimize the flux of VOCs off site, the GETs were installed 1982–1985 in Sectors A, B, D, E, and F on the Aerojet property (see Figure A-2). The systems used air stripping to remove VOCs and solar ponds to remove NDMA, where needed. The treated water from GETs D, E, and F was recharged back to the groundwater via groundwater recharge wells downgradient from the extraction system. Those GETs also intercepted perchlorate, and the perchlorate was recharged back to the groundwater as it was not removed by the treatment systems. Thus, the plume of perchlorate was allowed to continue its migration off site. The recharge water contained up to 8000 µg/L perchlorate at GETs E and F.

In December 1995, EPA confirmed its provisional reference dose of perchlorate, which when translated into a drinking water value, produced a range of 4–18 µg/L. Monitoring of groundwater conducted at the property boundary by Aerojet at the time showed concentrations of perchlorate at up to 8000 µg/L at the property boundary. The practical quantitation level (PQL) was 400 µg/L. The Regional Water Board asked Aerojet to collect samples from downgradient water supply wells and analyze the samples for perchlorate. All samples came back with no reportable concentrations of perchlorate. However, when pressed, Aerojet stated that several water supply wells had detectable concentrations of perchlorate estimated to be in the 100–200 µg/L range. Aerojet was issued a Cleanup and Abatement Order in October 1996 requiring the development and application of treatment technologies to remove perchlorate from the GETs effluent. Aerojet's development of the fluidized-bed reactor in response to this order is discussed below in the perchlorate treatment section.

The initial detections of perchlorate led to the closing of two public water supply wells. Through efforts by the Regional Water Board's contract laboratory and soon after the California Department of Toxic Substances Control's Hazardous Materials Laboratory, the PQL for perchlorate was initially lowered to 32 µg/L and then to 4 µg/L in the first part of 1997. The lowered PQL revealed that an additional seven additional water supply wells had detections of perchlorate >4 µg/L. Wells were turned off, new wells and pipelines were constructed to bring water supplies to the areas where wells were closed. Figure A-3 depicts the perchlorate plume.

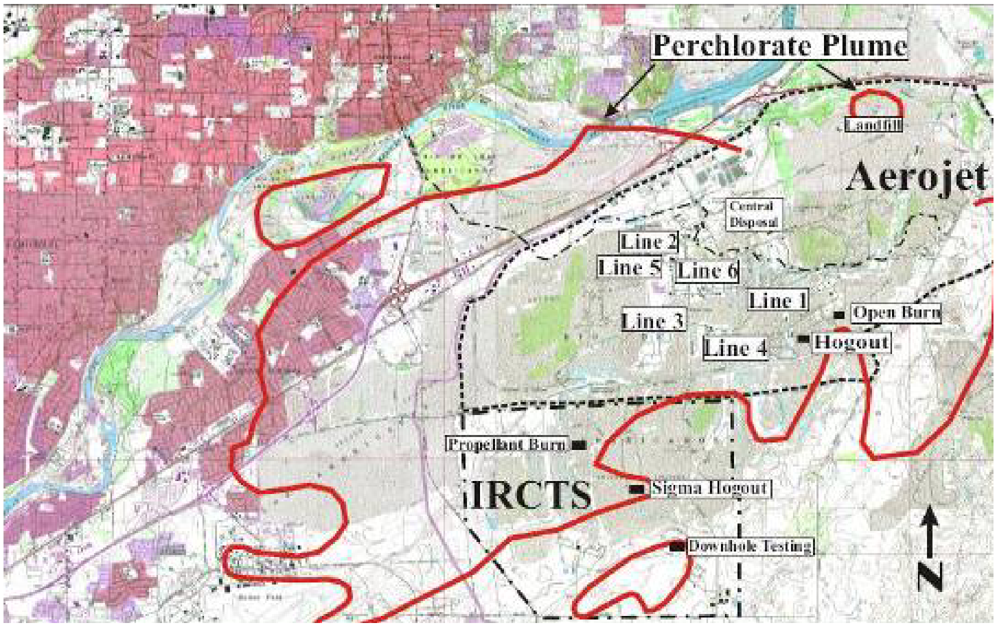


Figure A-3. Aerojet perchlorate plume.

Subsequently, Aerojet was directed to develop a Remedial Investigation/Feasibility Study (RI/FS) for the plume of pollutants, including perchlorate, which had migrated past the property boundary to the west where the impacted water supply wells are located. The area was designated the Western Groundwater Operable Unit (WGOU) (see Figure A-4). Aerojet completed the RI/FS for the WGOU in 2000, with EPA issuing a ROD in 2001. The remedy specified in the ROD included groundwater P&T at the leading edge of the plume and the property boundary and long- and short-term alternative water supply plans to replace water supplies taken out of service in the future due to the pollution. Cleanup values specified include perchlorate at 4 µg/L, the lower end of the risk range at the time of the ROD. Aerojet is in the process of implementation of the remedy and conducting treatability studies to look at alternative ways of addressing the perchlorate pollution in situ and ex situ, as discussed further below. At the same time, MDC and Aerojet were required to address the off-site migration of perchlorate emanating from the IRCTS.

Treatment of Extracted Groundwater

Initial Studies on Perchlorate Reduction

In December 1995, under request by the Regional Water Board, Aerojet provided information on results of bench-scale and pilot studies performed to determine methods to treat wastewater containing perchlorate. Aerojet had been studying the removal of perchlorate from wastewater generated from its hog-out facility and for application to the GET facilities. Aerojet worked with a consultant to evaluate the feasibility of treating perchlorate-impacted groundwater at the Aerojet site. In the initial evaluation, the consultant determined that biological and chemical reduction were potentially viable treatment processes based on their ability to treat similar oxygen-containing compounds such as nitrate.

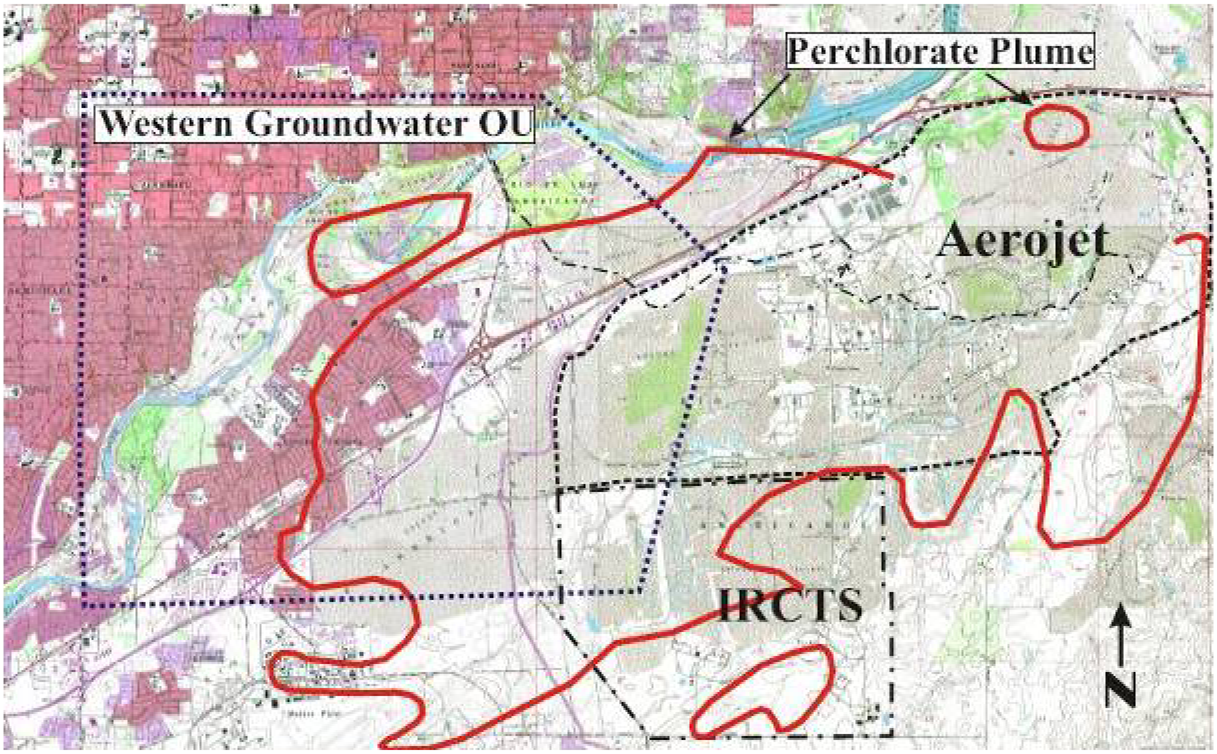


Figure A-4. Western Groundwater Operable Unit boundary.

The consultant performed laboratory treatability studies on both biological and chemical reduction of perchlorate. Biological reduction was evaluated for both a carbon/fluidized bed reactor (FBR) and a standard fixed-film (FF) using plastic media support. Water from the effluent of GET F was amended with an organic substrate, ethanol or acetate, and nutrients (nitrogen and phosphorous) prior to being fed into the FBR and FF treatment systems. The feed source to supply the biological mass was the return activated sludge from the City of Grand Rapids Wastewater Treatment Plant. Flow rates of 370 mL/min and 98 mL/min were run through the FBR and FF treatment systems, respectively. Ethanol was chosen as the carbon source due the potential cost-effectiveness compared to the use of acetate. Influent concentrations of perchlorate were 7000–9000 µg/L.[4]

The results of the treatability studies showed that both the FBR and FF systems were capable of reducing perchlorate. The data showed that perchlorate reduction occurred under anaerobic conditions and slightly lowered the pH from 7.6 to 6.8. Under optimum operating conditions the loading rates of perchlorate to the treatment systems were 0.11 g perchlorate L^{-1} day^{-1} for the FF system and 0.7 g perchlorate L^{-1} day^{-1} for the FBR system using the same ethanol feed concentration of 17.5 mg/L. The testing also showed that the FBR system appeared to be more resilient and recovered more quickly from system upsets than did the FF system.[4]

In addition to biological reduction, jar tests were used to determine the viability of chemical reduction of perchlorate. The reducing agents sodium sulfite, sodium bisulfite, and sodium thiosulfate were added at concentrations of 10–1000 g/L. The conclusions from the test were that even at the highest dosages of reducing agents, chemical reduction was ineffective in reducing perchlorate under normal conditions.[4]

Pilot-Testing Biological Reduction

In 1996, based on the results of the laboratory-testing showing that there was a potential effective treatment for the removal of perchlorate, the Regional Water Board directed Aerojet to perform an on-site pilot study. Aerojet initially developed an on-site demonstration of the GAC/FBR at the GET F facility. A GAC/FBR capable of handling 30 gpm was supplied with water from the air stripper at GET F. The reactor was 20 inches in diameter and 15 feet tall. The carbon source for the testing was ethanol, and nitrogen and phosphorous were also added to ensure sufficient nutrients were available for bacteria growth. A dual-media filter was added to the pilot system to handle the waste biosolids and a frac tank to handle the backwash water from the filters. Return activated sludge from the Sacramento Regional Wastewater Treatment Facility was added to the FBR as the source of bacteria.[5]

Aerojet supplied the results of the pilot testing in February 1997. Those results showed that the GAC/FBR pilot system achieved good removal of perchlorate with effluent concentrations of perchlorate below the PQL at the time of 400 μg/L at a hydraulic loading rate of 15 gpm and influent concentrations of 6000–8500 μg/L perchlorate (50 pounds of perchlorate per day per 1000 ft^3 of bed volume). Ethanol feed rates were high initially at 80 mg/L and gradually reduced until there was no residual ethanol or detectable concentrations of perchlorate. Besides occasional problems with equipment such as level sensors and the ethanol feed system, several conditions arose that required adjustments to the system. At one point during steady-state conditions, there was rapid fluidized bed growth associated with the buildup of biological material. This caused carryover of the GAC into the fluidized bed recycle system and plugging of the recycle line. This problem was rectified by controlling the fluidized bed height by periodically recirculating a portion of the top of the bed through a pump that sheared off the biomass from the granular carbon, allowing the carbon to settle to the bottom and the lighter biomass to wash from the system. Later it was found that the bed height control pump tended to grind the carbon into fine particles that allowed the carbon to be washed away with the biomass. GAC was periodically added to the system to rectify this problem. A different bed height control system would be necessary on the full-scale system.[6]

The pilot study showed several factors affecting performance of the FBR treatment system:

- Sufficient ethanol is required to accomplish the reduction of perchlorate. The study determined that approximately 3.6 parts of ethanol are required for each part of perchlorate.
- Dissolved oxygen concentrations affect perchlorate removal. When concentrations of dissolved oxygen exceeded 0.1–0.2 mg/L, the removal of perchlorate diminished.
- An important factor in the removal of perchlorate is the organic loading rate. High organic loading rates caused a rapid fluidized bed growth that resulted in bed height control problems, which could be potentially overcome with a modified bed height control system.

Implementation of an FBR System at GET E/F

Based on the positive results of the bench-scale and pilot studies, Aerojet was directed in 1996 to develop an Engineering Evaluation/Cost Analysis (EE/CA) for adding perchlorate treatment to the GET E and GET F facilities. Aerojet initially proposed a treatment system at GET F that was later modified to a single treatment system combining GET E and GET F (GET E/F). The GET F system would be sized to handle 1500 gpm of combined flow, using FBRs with GAC as the support media for removal of perchlorate, UV light with hydrogen peroxide to remove NDMA and most of the VOCs, and air stripping to remove the remainder of the VOCs. The treated water would continue to be recharged to the groundwater to maintain the hydraulic barrier to help control contaminant plume migration.

The initial proposed full-scale treatment system for perchlorate at GET E/F consisted of an FBR system to remove perchlorate at concentrations of 7–10 mg/L, followed by filtration for removal of waste biomass and disinfection for pathogen removal prior to recharge into groundwater. Disinfection was designed to remove pathogens associated with the activated sludge used to provide the bacteria for biological reduction. Phosphorous and nitrogen would be added, as groundwater source does not generally contain sufficient concentrations of these nutrients for maintenance of a viable biomass. As the treated water would be sent to the UV/peroxide treatment system for removal of NDMA and VOCs, the water leaving the FBRs would pass through a filter screening system to remove of residual waste biomass. The filter system consists of continuous-backwash sand filters, backwashed with final effluent from the FBR system with the backwash discharged to a holding tank to settle out the biomass, which is then trucked to the sanitary sewer. The effluent from the filtering process would then be disinfected using a UV disinfection process to remove *E. coli* that were found to be present during the initial start-up phases of the pilot study. To eliminate the need for the disinfection system, Aerojet used biomass from a wastewater system at a jam manufacturer to provide the initial biomass for the system. See Figure A-5 for a schematic of the treatment system.

During the design process an evaluation was made on whether the use of silica sand media in place of GAC was preferred, whether methanol should be used as the organic substrate instead of denatured ethanol, and whether to place the air-stripping process behind the perchlorate FBRs. Through short-term pilot studies it was determined that GAC would be used as the media to support bio-growth as it appeared to provide a faster start-up, better performance, and quicker recovery under process upset conditions and a lower perchlorate concentration in the effluent. These differences were believed to be due to the fact that GAC had a rougher surface and could support a greater biomass concentration. The pilot studies also showed that methanol-fed FBRs were slower to start up and did not provide as good of performance as the ethanol-fed FBRs, and therefore ethanol was maintained as the organic substrate. It was decided to place the air strippers behind the FBRs so that there would be a lower dissolved oxygen concentration entering the FBRs, thereby reducing the ethanol and nutrient needs. In addition, switching the order of treatment processes would reduce the biomass production and subsequent disposal costs and potentially allow for increased flow rates through the FBRs that would accommodate future increased flows to the plant.[8]

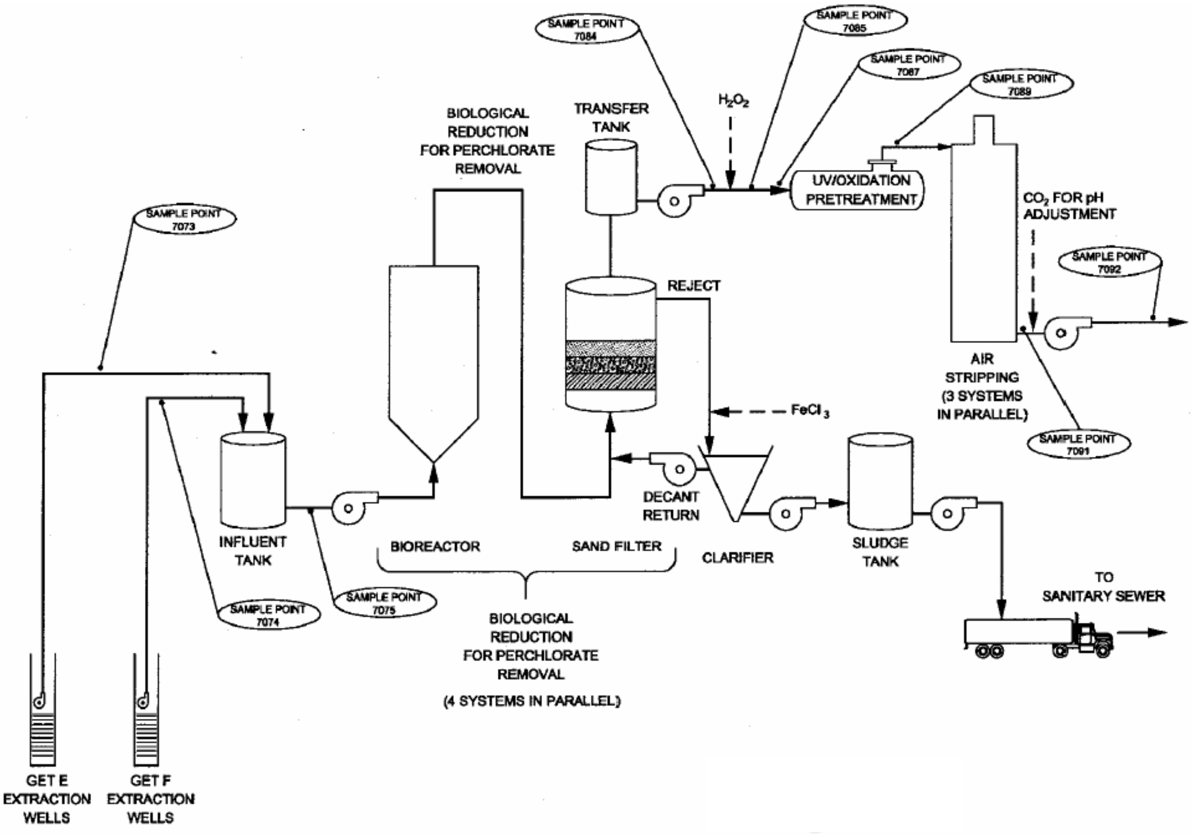


Figure A-5. Schematic of the GET E/F treatment system.

During 1997 and 1998, Aerojet designed and built the GET E/F treatment system. The design was modified to include GET E and the hydraulic capacity increased to 3600 gpm, with four FBRs each able to process 900 gpm. Sufficient space and infrastructure was provided to allow the GET E/F treatment system to be expanded to 7200 gpm if needed. Each of the FBRs is 14 feet in diameter and 21 feet tall and filled with 40,000 pounds of GAC. The recycle rate is 900 gpm with a forward flow rate of 900 gpm, giving a total flow rate through each FBR of 1800 gpm. The FBRs are operated in an upflow mode, fluidizing the GAC and providing a large surface area for attachment of the biomass. Final effluent from the plant is passed through bag filters to remove any residual solids prior to recharge to groundwater. The plant commenced operation in December 1998, processing only the flow from the GET F extraction wells and using only two FBRs 1 and 2.[9]

During early operation of the GET E/F facility, Aerojet had difficulty in controlling the bed height on FBR 1. Both FBRs 1 and 2 were seeded with the same initial biomass and approximately the same volume. The only difference was that FBR 1 received most of the biosolids that had settled to the bottom of the seed tank. Even with the difficulty in controlling bed height, nondetectable concentrations of perchlorate were in the effluent from the FBRs (PQL of 4 µg/L). Aerojet had the biomass of the two reactors studied, and the conclusion was that a population of filamentous bacteria, *Thiothrix ramosa*, a sulfur bacterium, had developed primarily in the bottom of the FBR where the reduced sulfur from the bioreactor recycle was mixing with dissolved oxygen from the influent groundwater. The bed height limiters at the top of the FBRs were not able to shear the filamentous bacteria from the GAC. The growth of the bed height increased uncontrolled.[9]

Aerojet commissioned evaluations for the development and implementation of possible control strategies for the bed height. Two control strategies were developed and tested. The first was to minimize influent dissolved oxygen concentrations, as most filamentous bacteria grow under aerobic conditions and use dissolved oxygen as an electron receptor. The second was to minimize the reduced sulfur concentration, as it combines with the dissolved oxygen in the bottom of the reactors creating an environment that favors filamentous bacteria. The studies showed that reducing the dissolved oxygen concentration lowered the filamentous bacteria growth and the resulting bed height. The studies also showed that the concentrations of filamentous bacteria were much greater in FBR 1 than in FBR 2. Based on that information Aerojet killed the bacteria population in FBR 1 and reseeded it using biomass from FBR 2, at the same time seeding FBRs 3 and 4 to allow the flow from the GET E extraction wells to be added to the treatment facility. The results of this modification were that the bed height in all four FBRs rose to approximately 12–14.5 and stabilized, negating the need to make changes in attempt to reduce dissolved oxygen or reduced sulfur. In addition, the bed-height reducers were modified to allow removal of biomass from the bottom of the reactor instead of only from the top, thereby improving the systems ability to maintain bed height.[9]

Over subsequent years, the GET E/F facility was modified to remove the nutrient addition system, as it was shown that there were sufficient concentrations of micronutrients to achieve sufficient biomass growth. In addition, with the issuance of the ROD for the WGOU and subsequent enforcement documents, GET E/F was modified to allow the discharge of the effluent to surface waters under an NPDES permit that would allow the water to be taken out downstream of the discharge for reuse within the groundwater basin.

The remedy under the ROD increased the flow to be treated at the GET E/F facility. Aerojet performed a pilot test on one FBR that showed that each FBR could process up to 1500 gpm and still meet the effluent limitation of 4 μg/L. Some piping and additional VOC and NDMA treatment capacity changes were made to bring the rated capacity of the GET E/F plant to 6000 gpm. Also, a clarifier was added to enhance settling of biomass in the backwash tank and reduce the concentrations of suspended solids to meet effluent limitations in the NPDES permit. To date, the GET E/F facility is in substantial compliance with the effluent limitation of 4 μg/L.

IX Treatment of Perchlorate at GET Systems

More recently, Aerojet has also employed IX resin treatment systems at several GET facilities for the removal of perchlorate from extracted groundwater. IX systems have been constructed on site at GETs B and D and off site at GETs H, J, and K. At GETs B and D perchlorate concentrations in the influent were relatively low at 150–250 μg/L. Flow at the facilities is currently 1500 gpm at GET B and 1000 gpm at GET D. Given the relatively low concentrations and low flow rates at these two GETs and the evaluation in forthcoming operable unit feasibility studies of the GETs, Aerojet determined that it was more cost-effective to use IX instead of the FBR technology, which has a relatively high capital cost. The off-site GET systems had much lower concentrations of perchlorate but higher flows than GETs B and D. Not only did the reduced capital cost for IX come into the decision on the off-site GETs, but the O&M costs (primarily replacing spent resin) was comparative to the FBR technology. In addition, the off-site treatment systems are located in communities adjacent to residences and commercial facilities, making the FBRs less attractive given the need to store ethanol and the potential for the generation of nuisance odors.

Aerojet has used the following IX resins to treat perchlorate-impacted water:

- US Filter A-284
- US Filter K-9708
- Rohm & Haas A-530E
- Rohm & Haas PWA-2

Each resin has different perchlorate adsorption capacities, with A-284 having the lowest and PWA-2 the highest capacities. Aerojet has found that fine (<5 micron) particulate matter in the influent water could cause IX plugging problems. Depending on the extent of this problem, Aerojet selects the IX media based on time for breakthrough of perchlorate. For example, if Aerojet is experiencing plugging quickly, A-284 is selected because the perchlorate adsorption capacity is low, resulting in the shortest run time before breakthrough. If the PWA-2 were used at a system with high fine particulate matter, a portion of the PWA-2 would be wasted as the resin would need to be changed due to clogging instead of due to resin saturation with perchlorate. Aerojet tries to match the run time to the estimated time that clogging will occur. The clogging can be a problem even with bag filters on the influent. This is particularly true with the IX units at GET B.

The other concern with IX is disposal of the spent resin. Since Aerojet is a Superfund site, Aerojet must dispose of its material at CERCLA-approved facilities. Due to future liability concerns associated with the leachability of perchlorate, Aerojet has decided to either dispose all perchlorate-impacted waste material in a Class I landfill or incinerate the waste. Aerojet prefers to incinerate the waste; however, only a limited number of incineration facilities that are CERCLA-approved.

Biodegradation of Perchlorate in Groundwater

Starting in 1998, Aerojet conducted several treatability studies looking at in situ bioremediation of perchlorate in groundwater using various extraction and electron donor delivery schemes and electron donors. Usually, these treatability studies attempted to address the biodegradation of TCE at the same time, since in nearly all cases where there is perchlorate in the groundwater, there is also TCE.

The first study was a laboratory study designed to assess whether the indigenous microorganisms could be stimulated to anaerobically biodegrade perchlorate to chloride and water and whether perchlorate and TCE could be biodegraded jointly. The study showed that the indigenous microorganisms could rapidly biodegrade perchlorate in microcosms amended with a variety of carbon substrates/electron donors, including ethanol, molasses, and liquefied food waste. No lag or acclimation period was observed before onset of the degradation activity, with calculated half-lives of 1.2–1.8 days. The second part of the study demonstrated that molasses and liquefied food waste could biodegrade perchlorate to less than the Action Level (at the time 18 µg/L). However, TCE was not degraded as well as perchlorate. The best results for TCE occurred with the addition of food waste and bioaugmentation with the natural dehalogenating microbial inoculum referred to as KB-1.[11]

In February 2000 Aerojet used the positive results of the laboratory study to propose a field demonstration pilot test of in situ bioremediation of perchlorate and TCE in groundwater. The objectives of the pilot study were to (1) confirm the performance of enhanced in situ bioremediation of perchlorate-impacted groundwater on a field scale through electron donor addition, (2) evaluate TCE dechlorination through electron donor, (3) evaluate TCE dechlorination through bioaugmentation with KB-1, (4) identify and optimize design and operational factors that influence the performance of field-scale bioremediation systems, and (5) assess the ability and costs for full-scale use of the system. The pilot test took place at Area 20, where groundwater is 30–40 feet bgs and contains approximately 15 mg/L perchlorate and 2 mg/L TCE. The pilot test consisted of a closed-loop system where groundwater was extracted, amended with electron donors and KB-1, and recharged 65 feet upgradient back to the same aquifer via a second well. Figure A-6 shows the system layout and cross-section.[12]

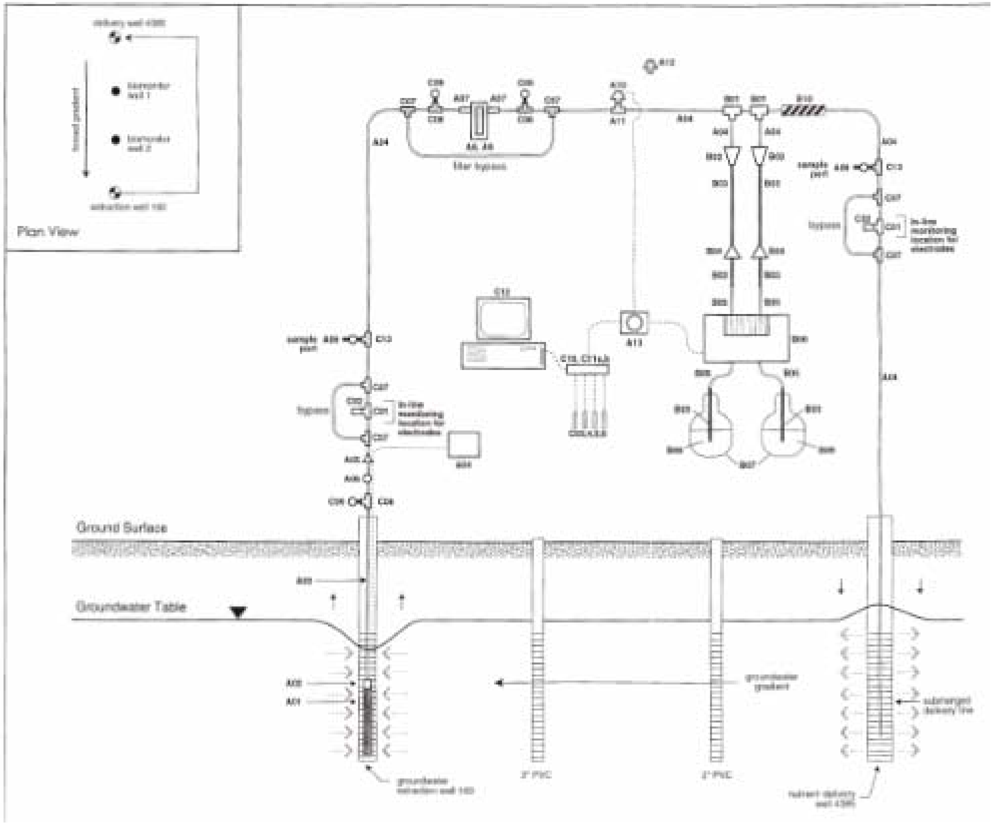


Figure A-6. IRCTS pilot study layout.

The pilot test last for 280 days from mid-July 2000 until mid-April 2001. The extraction well operated at 5 gpm during the test. The initial electron donor was calcium magnesium acetate

(CMA), which was followed by sodium acetate and subsequently sodium lactate. CMA was used due to its relative cost, availability, and accepted use as a commercial product, and sodium acetate was used when CMA was not available. Initial concentrations of CMA and/or sodium acetate were 50 mg/L on a time-weighted average in four pulses per day. Concentrations of acetate in the extraction well were nondetect, showing that the acetate was being consumed over the 65-foot distance. Acetate was being effective in reducing perchlorate but not effective on reducing TCE, so at day 64 the there was a switch to sodium lactate as the electron donor.[13]

Initial ORP and dissolved oxygen concentrations were 153–162 mV and 4.0–4.8 mg/L, respectively. During the acetate addition phase the ORP dropped to around –50 mV with significant perchlorate reduction (13 to 0.43 mg/L in the first 15 feet during the first 7 days of the test, and to 0.004 mg/L 35 feet away from the extraction well by day 63). The switch to sodium lactate caused the ORP to be reduced to –100 mV. Similar reductions in perchlorate occurred; however, the dechlorination of TCE was slow with TCE dechlorination half-life within the treatment area of up to 335 days. Therefore, bioaugmentation with KB-1 was initiated on day 157. Positive results were immediate, and the concentrations of TCE were reduced to <5 µg/L within 35 days, resulting in an estimated half-life of 6 days.[13]

Nitrate concentrations declined during the test from 5.5 mg/L to less than 1 mg/L. Sulfate concentrations, initially around 11 mg/L, remained stable during the acetate portion of the pilot test, indicating that perchlorate bioremediation can occur without stimulating sulfate reduction. Sulfate reduction was not wanted, as it would increase the demand for electron donor, develop more strongly reducing redox potential that could result in mobilization of metals, and sulfide reduction causes the production of sulfides that would cause the water to have an unpleasant odor. The addition of lactate promoted sulfate reduction, as shown by the concentrations of sulfate dropping to <0.5 mg/L. Other changes in groundwater quality that occurred during the test were the increase in concentrations of dissolved iron and manganese above their respective secondary drinking water standards of 300 µg/L and 50 µg/L.[13]

The conclusions of the test were that adding acetate or lactate could readily biodegrade perchlorate in situ to <4 µg/L without a significant acclimation period. Acetate was preferred since it did not promote strongly reducing or anaerobic conditions, did not stimulate sulfate reduction, and had little impact on secondary drinking water parameters. In addition, TCE could be dechlorinated in situ through the addition of lactate and KB-1, however, not without the mobilization of iron and manganese. One system maintenance issue of concern was the clogging by biomass of the well screen and delivery lines. Initial swabbing and redevelopment of the well screen and reducing the frequency of electron donor helped control the microbial biofouling.

Aerojet followed on the success of the Area 20 with several more in situ pilot tests on the Aerojet main site and the IRCTS. Those projects were designed to look at different well configurations to create biological reduction zones in the aquifer, look at a variety of electron donors, and evaluate mechanisms to reduce the impacts on secondary water quality parameters. A summary of those projects follows.

- *Pilot Test of In Situ Bioremediation to Treat Perchlorate in GET D Recharge Water.* In 2001 Aerojet conducted a test on a recharge well in the GET D, whose effluent contained perchlorate at concentrations near 200 µg/L. The goal was to add an electron donor to the effluent prior to recharging the water into the aquifer and establish a biological reduction zone in which the perchlorate would be reduced. If successful, Aerojet would not need to construct an aboveground treatment facility to remove perchlorate at GET D. The test utilized acetate and ethanol as the electron donor, and it was shown that in situ biodegradation of perchlorate occurred within 25–75 feet of the recharge wells. Perchlorate was reduced to <4 µg/L and the half-life was estimated at 4–5 hours. Iron and manganese were mobilized, but sulfate reduction did not occur. The study did not last long enough to determine if/when the iron/manganese concentrations were reduced to concentrations that were not a concern. Biofouling of the recharge well was controlled with chlorine dioxide addition that prevented growth of the biomass within or immediately adjacent to the well. Figure A-7 shows the layout of the system.[14]

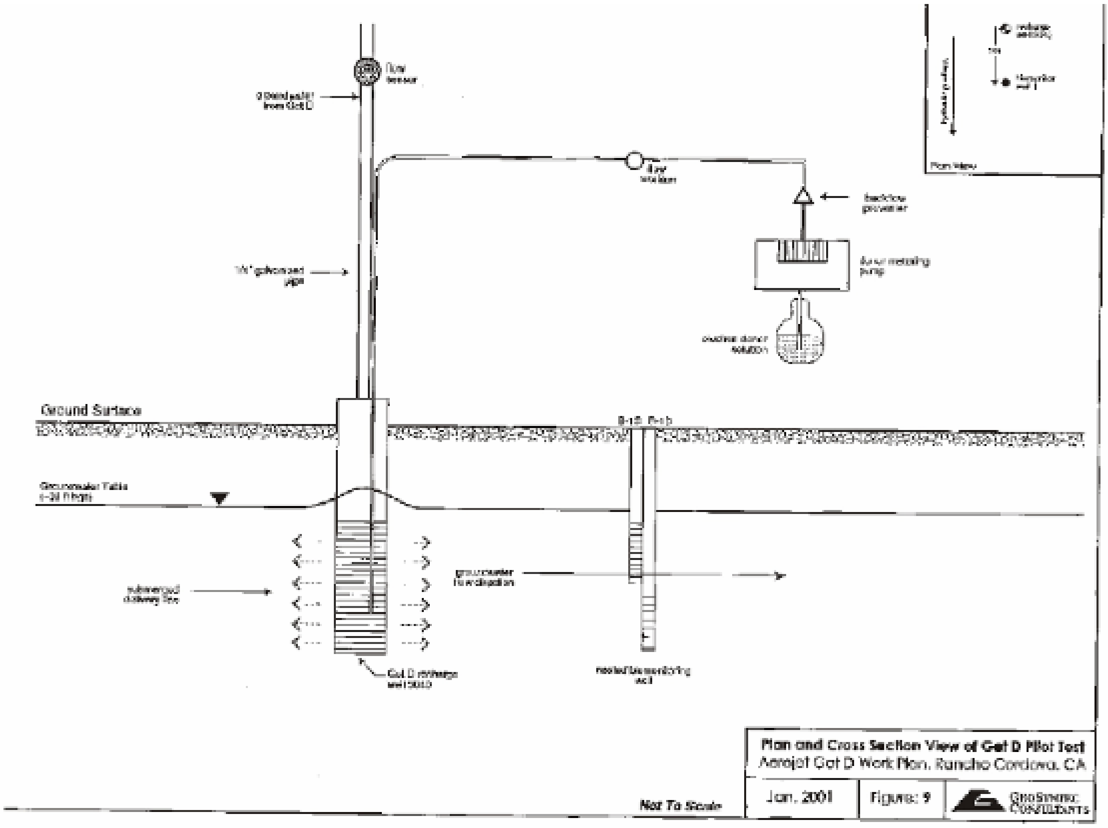


Figure A-7. GET D pilot study layout.

- *Pilot Test for In Situ Bioremediation of Perchlorate and Trichloroethene in Groundwater Using and Active Biobarrier.* Also during 2001, SERDP and Aerojet conducted a pilot test at the Area 20 site discussed above. The goal of the project was to demonstrate that an active biobarrier approach would work for plume migration control and treat perchlorate and TCE. The pilot system used two extraction wells 400 feet apart with a recharge well in the middle, all aligned perpendicular to the direction of groundwater flow. In this manner, groundwater would be captured across the plume and bioremediation cell established also across the plume (Figure A-8). Groundwater was extracted at 10 gpm from each extraction well, amended with ethanol, and recharged through the recharge well. Chlorine dioxide was used to control biofouling. The results of the 72-day pilot test showed that perchlorate degradation was initiated without a significant acclimation period with concentrations decreasing from >8000 µg/L to <4 µg/L within 35 feet of the recharge well, resulting in estimated half-lives of 0.5–1.8 days. TCE dechlorination also occurred with concentrations falling to <5 µg/L within 35 feet of the well. However, complete dechlorination of TCE to ethene occurred in only the portion of the test area that had been previously augmented with KB-1 during the Area 20 pilot test described above. Outside that portion of the test area, dechlorination stalled at 1,2-dichloroethene.[15]

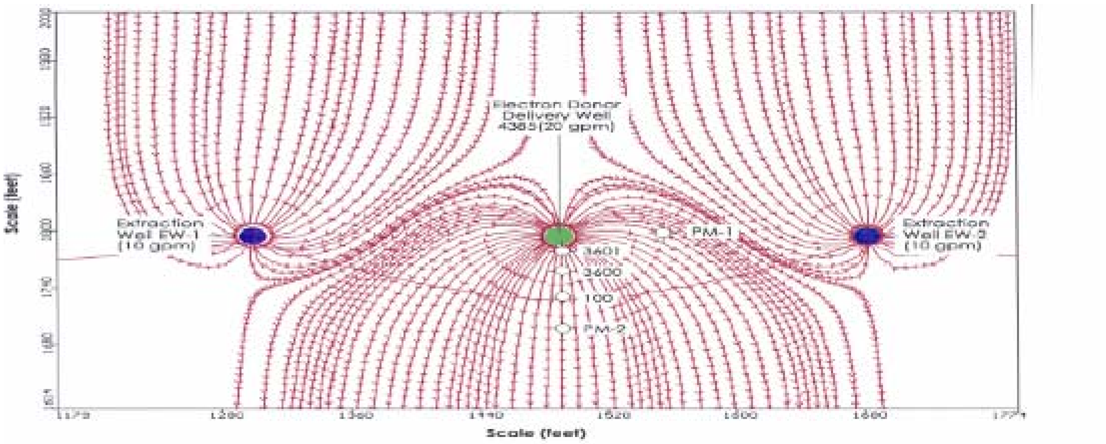


Figure A-8. Area 20 biobarrier pilot study layout.

- *Phase II Pilot Test of In Situ Bioremediation to Treat Perchlorate in GET D Recharge Water.* This pilot test was conducted by Aerojet in 2002 to ascertain whether perchlorate concentrations in the recharge water could be reduced from 225 µg/L to <4 µg/L without inducing concurrent manganese reduction and causing dissolved manganese concentrations to exceed the secondary drinking water standard of 50 µg/L. The pilot test confirmed that electron donor optimization can reduce and potentially mitigate mobilization of manganese. However, it was concluded that it would be difficult to completely prevent manganese oxide dissolution during perchlorate bioremediation with large projects.[16]

- *Pilot Test of In Situ Bioremediation of Perchlorate and Trichloroethene in Groundwater, IRCTS.* This pilot project conducted by Aerojet and Boeing on the IRCTS was very similar to the active biobarrier test described above. Extraction and recharge well configuration was the same; however, there was approximately 500 feet between the extraction wells and the recharge wells. Ethanol was used as the substrate, and KB-1 was added to promote the dechlorination of TCE. The active portion of the test has been completed, and the results confirmed the results of the previous pilot tests with effective remediation of perchlorate and TCE. Mobilization of manganese did occur within the biologically active cell. Currently monitoring is ongoing to determine whether the dissolved manganese concentrations return to background downgradient from the pilot test area.[17]

- *Small-Scale Radial Pilot Test Downgradient of the Former GET F Sprayfield.* In 2004 Aerojet conducted a pilot test to determine whether a biologically active zone could be created in situ by injecting a slow-release electron donor (oleate) through a recharge/extraction well. Potassium oleate in water was injected at 50 gpm for one day to create a biologically active zone around the well. Following injection, the system was allowed to acclimate for four weeks. It was believed that the potassium oleate would react with the exchangeable calcium and magnesium of the clay minerals in the aquifer and precipitate calcium and magnesium oleates, thereby reducing the mobility of the oleate. Groundwater was then extracted at the well at 4 gpm, pulling the perchlorate at concentrations up to 6700 µg/L in the aquifer through the biologically active zone. During the acclimation phase the ORP dropped to –200 mV in the remediation zone. Extracted groundwater contained <4 µg/L during the first 9 days of extraction but then steadily increased to 500 µg/L by the 19th day. The conclusions of the study were that a number of operational features and uncertainties would limit the applicability of the technology.[18]

- *In Situ Bioremediation of Perchlorate Using Horizontal- Flow Treatment Wells.* This project, performed as part of a grant awarded by ESTCP, was similar to the other pilot projects already conducted except that the process used two wells to extract and recharge, creating a biologically active zone perpendicular to the flow of groundwater between the two wells (Figure A-9).

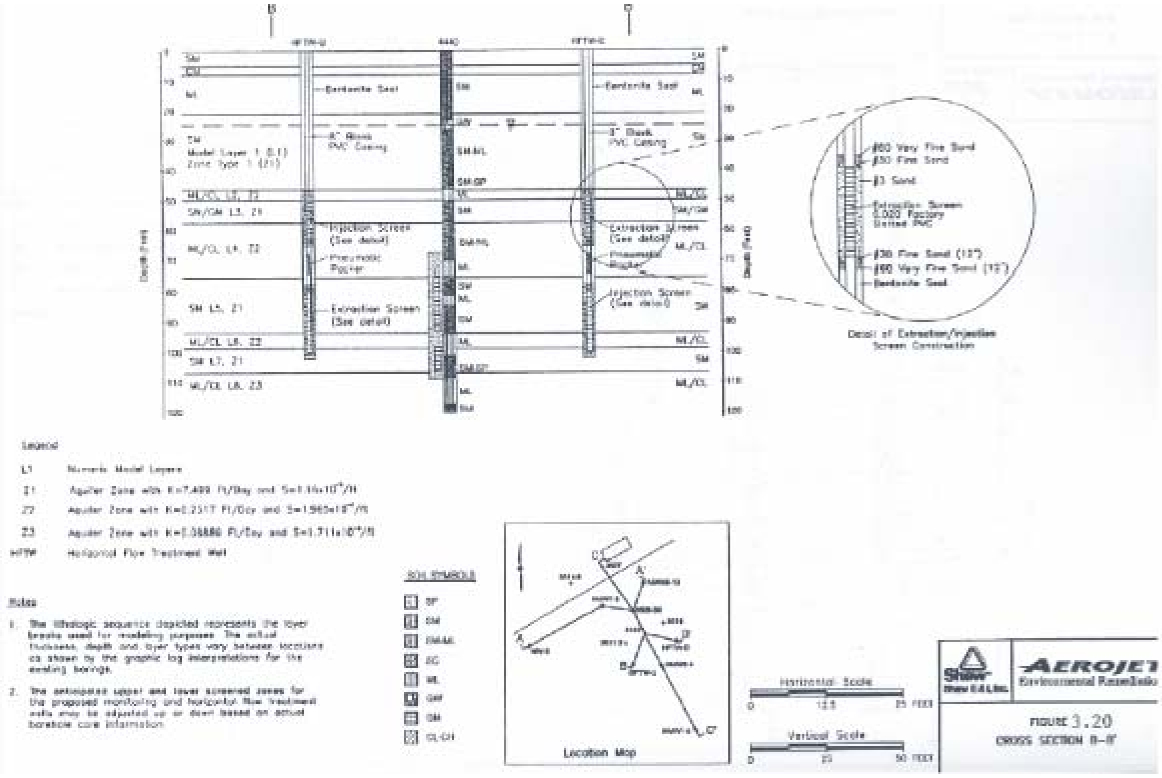


Figure A-9. Horizontal well pilot study layout.

- *In Situ Bioremediation of Groundwater at GET B.* The pilot test conducted at GET B was designed to determine whether adding electron donor upgradient of the GET B extraction wells would cause perchlorate to be degraded prior to the extraction wells and negate the need for installation of aboveground treatment at the GET B system. Corn syrup was the electron donor of choice. More than 172,140 pounds of corn syrup was applied over the 270-

day test. Due to mechanical problems and the reduced ability to pump the corn syrup during cold weather, the dosing was not equally distributed to each recharge well. Reductions in perchlorate from approximately 170 µg/L to 75 µg/L were noticed in monitor wells closest to the recharge wells. However, the reductions were not consistent throughout the aquifers.[19] Figure A-10 shows the layout of the system.

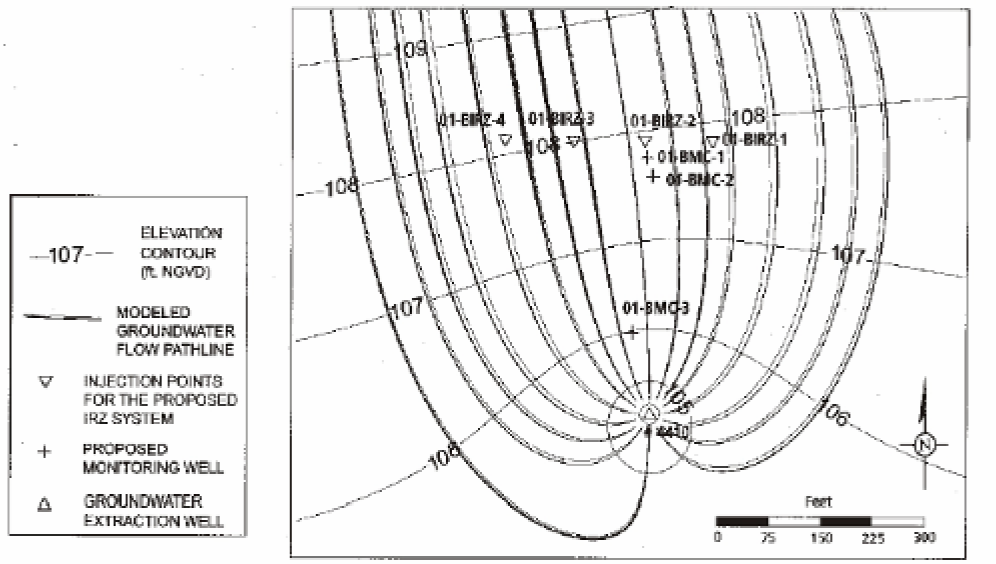


Figure A-10. GET B in situ pilot study layout.

- *Pilot Test: Perchlorate Source Site Bioremediation at the Former Propellant Hog-Out Facility (Sites 50F and 51F).* Aerojet commenced a pilot test at the former propellant hog-out facility to determine the feasibility of biodegrading perchlorate in both the 30-foot vadose zone and shallow groundwater. A radial biobarrier using potassium oleate was to be constructed, as described above for the small-scale project on the IRCTS at the downgradient edge of the hog-out facility (Figure A-11). The well would then be pumped to contain water flowing beneath the hog-out facility and then recharged via the former impoundments flushing the perchlorate from the soils to the groundwater. The perchlorate would then be pulled to the extraction well through the biologically active zone and the perchlorate degraded. It turned out that there was not an indigenous population of perchlorate-degrading bacteria beneath the hog-out facility. It is believed that the high concentrations of ammonia in the ammonium-perchlorate propellant killed off the bacteria. The system has been modified to operate in batch mode with groundwater extracted at 1 gpm into a tank where bacteria and carbon source are added. Once the perchlorate is degraded, it is discharged to the former pond for infiltration. Due to lack of attachment areas in the tank, the biomass is not large and perchlorate degradation is relatively slow. As of January 2007, Aerojet was evaluating modifications that will allow the pilot test to be operated on a continuous basis rather than batch mode.[20]

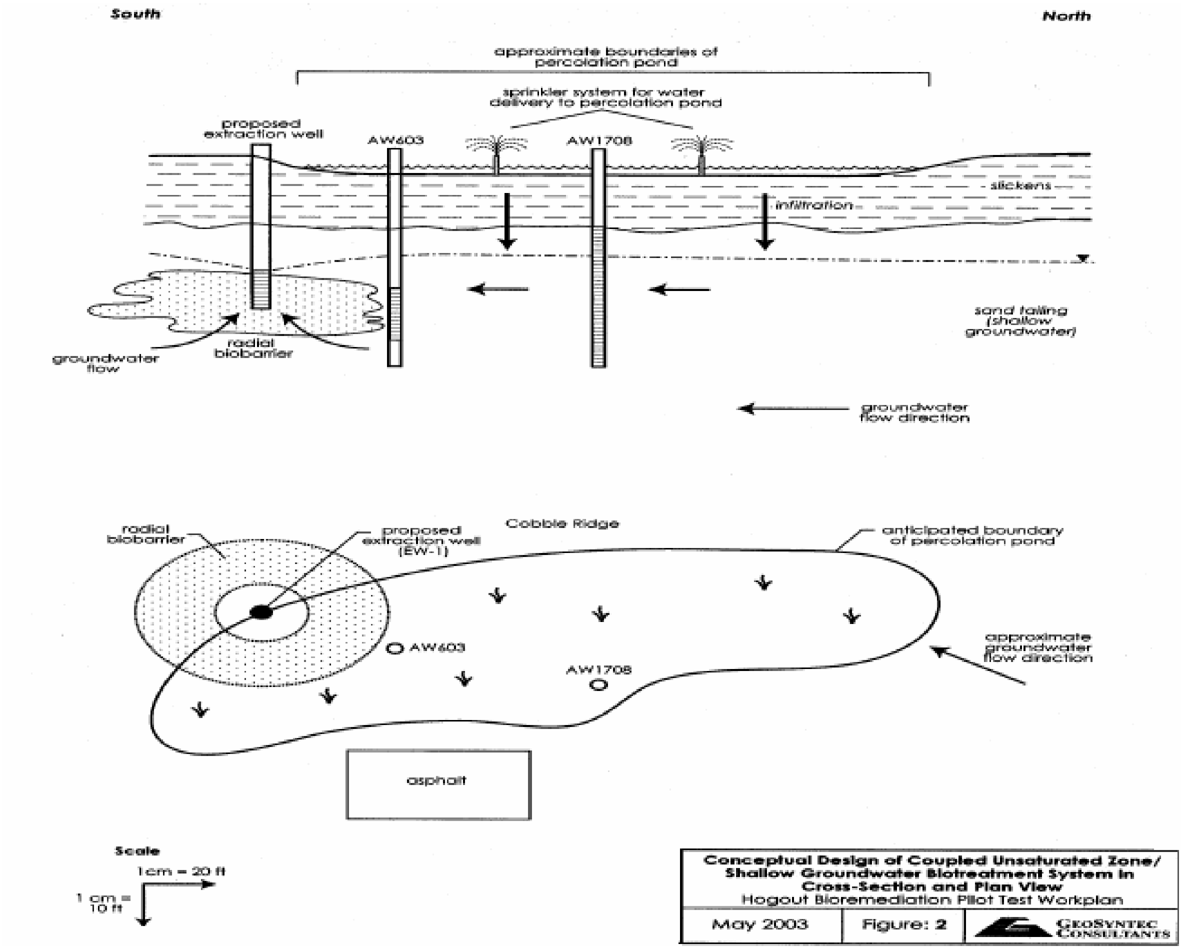


Figure A-11. Hog-out pilot study layout.

- *Pilot Test: In Situ Remediation of Perchlorate and TCE Using a Dual Permeable Reactive Barrier (Area 40, Sites 36B and 37B).* In December 2006 Aerojet constructed two permeable reactive barriers (PRBs) in parallel downgradient from Sites 36B and 37B in Area 40 and perpendicular to the direction of groundwater flow. Area 40 is one of the few areas where bedrock is at a relatively shallow depth (<30 feet) below the ground surface. The first PRB uses ZVI to stimulate the reduction of TCE. The downgradient PRB has molasses injected and circulated through the barrier using a series of injection and extraction wells. Initial concentrations of TCE and perchlorate upgradient of the PRBs exceeded 30,000 µg/L and 23,000 µg/L, respectively. Samples collected in the first month following installation showed that perchlorate decreased by at least an order of magnitude through the each of the PRBs. TCE reduction through the first PRB was three orders of magnitude.

Biodegradation of Perchlorate in Soils

While investigating, evaluating, and implementing treatment methods for removing perchlorate from extracted groundwater, Aerojet was also evaluating methods for removing perchlorate from soil, particularly by biodegradation that was shown to be viable in water treatment. Area 41, or Cavitt Ranch, was a piece of property impacted by perchlorate that was of particular concern in that Aerojet did not own it. This property was remote from the Aerojet site and used for disposal and destruction of spent solvents and solid rocket propellant. Soils at Cavitt Ranch were no more than 3 feet thick overlying fractured bedrock. TCE and perchlorate were present in both soils and groundwater at high concentrations. Isolated areas of metals above remedial goals were also found in spots where laboratory wastes were taken for destruction.

Aerojet's first attempt at potential remediation strategies for remediation of perchlorate in soils at Cavitt Ranch occurred in late 1997 when it commissioned Dr. Robert Borch to look at the potential for heap leaching of soils to remove the perchlorate. His column studies showed that leaching of perchlorate was very efficient even when the infiltration proceeded more slowly than anticipated. The heap leaching process produced a brine that would still require treatment or another disposal alternative.[21]

In early 1999 Aerojet contracted with a consultant to perform bench-scale biotreatability tests on perchlorate-impacted soils from Cavitt Ranch. The tests included both composting and anaerobic slurry treatment of the soils. In the composting study, the soils were bulked with manure, alfalfa, and sawdust with moisture added to make the piles approximately 50% moisture. A second treatment added liquid food waste to the bulking mixture. The bench-scale composting of soils found that 30 mg/kg of perchlorate in soil was reduced to <2 mg/kg within several weeks, producing rapid perchlorate half-lives of 3–4 days. Use of the liquid food waste did not appear to change the outcome, as the native soils had sufficient bacteria of the appropriate kind to provide for perchlorate reduction. The anaerobic slurry was made using saturated soils and a variety of electron donors—ethanol, manure, food waste, vinegar, and molasses. Perchlorate biodegradation in the anaerobic slurry occurred after an acclimation period of up to 40 days, after which it proceeded rapidly, regardless of which electron donor was used, even at initial concentrations of up to 10,000 mg/L perchlorate.[22]

Following the successful bench-scale testing described above, Aerojet proposed a pilot test that looked at composting perchlorate-impacted soils at Cavitt Ranch. Two soil compost piles were constructed, one on bare ground with suction lysimeters placed to evaluate potential leaching of perchlorate during the composting trial, and one on plastic liner with a simple leachate collection system. Two to three cubic yards of perchlorate-impacted soils were used for each pile. Initial perchlorate concentrations were 200–500 mg/kg. Soils were amended in such a manner that the piles consisted of approximately 35% soil, 25% manure, 20% sawdust or wood chips, and 20% alfalfa. Clean water was added to maintain a moisture content of 35%–45% by volume. Temperature and moisture conditions were monitored within the piles. Perchlorate destruction was rapid, as the concentrations of perchlorate during the 30-day test were reduced to <0.1 mg/kg in internal soil samples and 2 mg/kg in surface samples.[23]

The successful application of bioremediation of perchlorate in compost piles led Aerojet to conduct treatability studies at sites 56B and 49B at Cavitt Ranch, wherein manure was applied to the surface over perchlorate-impacted soils. If this approach were successful it would save cost and time over constructing and monitoring compost piles. In October 1999 manure was applied at 3-4 inches (49B) and 12 inches (56B) at the two test plots. Water was applied to the test plots to maintain sufficient moisture to promote biodegradation. During the first month, surface concentrations of 1100, 4600, and 1500 mg/kg had been reduced to 15, 12, and 7.9 mg/kg, respectively, at the 56B test plot, and surface concentrations of 2000, 1800, and 470 mg/kg were reduced to 172, 98, and 1.2 mg/kg, respectively, at the 49B test plot. The lower layers (below the upper 1–2 inches) did not appear to be affected within the first month and remained dry, as no rainfall occurred during the first month.[24]

To accelerate the degradation of perchlorate at the deeper depths, Aerojet aerated the soils in a section of each of the test plots to a depth of 4–5 inches using a tine aerator. During the next seven weeks significant rainfall occurred, saturating the entire soil profile and weather bedrock with manure leachate. No differences were seen at between the tilled untilled sections. At the 56B test plot, where soils are thinner, after 18 weeks only low levels of perchlorate (maximum 16 mg/kg) remained where they had originally been up to 4600 mg/kg. At test plot 49B with the thinner manure layer and deeper soil layer, concentrations had decreased from 2000 to 62 mg/kg in the upper 2 inches and from 560 to 180 mg/kg in the deeper soils. It was estimated that during the end of the rainy season the test plots will dry out and the perchlorate will be wicked to the upward by capillary action (observed at other locations). The perchlorate will then be in the biologically active soil/manure layer where perchlorate degradation would occur until the soil became dry. Aerojet concluded that simply applying a layer of manure would be effective in remediating the perchlorate in the shallow soils at Cavitt Ranch. The study concluded that a thicker manure layer overlay is best as it provides a higher organic loading rate and increased water content for release to the underlying soil.[25]

Aerojet expanded the field application at Cavitt Ranch in April and May 2001. At 10 areas with high levels of perchlorate (50–11,000 mg/kg), soil was excavated, amended with cow manure and calcium magnesium acetate, placed back in the excavation, and covered with 6–12 inches of composted cow manure. An additional 65 bare areas (due to burning during rocket propellant destruction) with low concentrations of perchlorate were treated by a simple overlay of composted manure. One year later, the soil was resampled, and the average perchlorate concentration at the monitoring locations had declined from 452 to 1.4 mg/kg.[26]

NOTES:

1. *Remedial Investigation/Feasibility Study Statement of Work for Aerojet General Corporation*, April 11, 1984.
2. *Aerojet RI/FS Scoping Document*, July 1984.
3. *Aerojet The Creative Company*, Stuart F. Copper, 1995.
4. *Feasibility and Treatability Studies for Perchlorate-Impacted Groundwater at the Aerojet Sacramento Site*, Earth Tech, Inc., December 1995.
5. *Work Plan for the On-Site Demonstration of the GAC/Fluidized Bed Process for Treatment of Perchlorate Impacted Groundwater at the Aerojet Sacramento Site*, Earth Tech, Inc., March 1996.
6. *On-Site Pilot Scale Demonstration of the GAC/Fluidized Bed Process for Treatment of Perchlorate Impacted Groundwater at the Aerojet Sacramento Site*, Earth Tech, Inc., February 1997.
7. *Final EE/CA for the Treatability of Perchlorate-Impacted Groundwater – GET F Facility*, Aerojet and Earth Tech, Inc., July 1997.
8. *Perchlorate-Impacted Groundwater Treatment Plant, Evaluation of Potential Process Modifications*, Earth Tech, Inc., June 1998.
9. *Biofouling Control Study Report, Groundwater Extraction and Treatment Facility F, Aerojet, Harding Lawson Associates*, January 2000.
10. Personal Communication with Chris Fennessey, Aerojet General Corporation.
11. *Enhanced Biodegradation of Perchlorate and Trichloroethylene in Groundwater, Biotreatability Report*, June 1999.
12. *Workplan for a Pilot Test for Enhanced Bioremediation of Perchlorate and Trichloroethene in Groundwater at Area 20*, GeoSyntec Consultants, February 2000.

13. *Pilot Test for In Situ Bioremediation of Perchlorate and Trichloroethene in Groundwater at Area 20*, GeoSyntec Consultants, June 2001.
14. *Pilot Test for In Situ Bioremediation to Treat Perchlorate in GET D Recharge Water*, GeoSyntec Consultants, January 2002.
15. *Pilot Test for In Situ Bioremediation of Perchlorate and Trichloroethene in Groundwater Using an Active Biobarrier*, GeoSyntec Consultants, June 2002.
16. *Results of the Phase Ii Pilot Test of In Situ Bioremediation to Treat Perchlorate in GET D Recharge Water*, GeoSyntec Consultants, September 2002.
17. *Workplan for a Pilot Test of In Situ Bioremediation of Perchlorate and Trichloroethene in Groundwater, Inactive Rancho Cordova Test Site*, GeoSyntec Consultants, June 2002.
18. *Results of the Small-Scale Biobarrier Pilot Test Downgradient of the Former GET F Sprayfield*, Borch and Cox, July 2004.
19. *Final Progress Report: Pilot Study of In-Situ Reactive Zone Technology at Aerojet GET B Area, Rancho Cordova, California*, ARCADIS, September 2002.
20. *Pilot Test Work Plan: Perchlorate Source Site Bioremediation at the Former Propellant Hog Out Facility*, GeoSyntec Consultants, May 2003.
21. *Remediation of Perchlorate Contaminated Soils by Heap Leaching. Phase I – Column Leach Study*, Robert Borch, January 1998.
22. *Bioremediation of Perchlorate in Soil at Cavitt Ranch, Area 41, Laboratory Biotreatability Results*, March 1996.
23. *Remediation of Perchlorate in Surface Soils of Area 41 by Surface Application of Manure: Part 2. November 29/30 Test Plot Sampling Progress Report*, Robert S. Borch and Scott Neville, December 1999.
24. *Pilot Testing of Composting of Perchlorate-Impacted Soil at Area 41*, GeoSyntec Consultants, February 2000.
25. *Remediation of Perchlorate in Soils of Area 41 By the Application of Manure: Test Lot Sampling Results*, Robert S. Borch and Scott Neville, April 2000.
26. *Area 41 Expanded Field Trial: Bioremediation of Soils with High Perchlorate Levels by Applying Composted Manure, Final Report*, GeoSyntec Consultants, August 2002.

AMPAC CASE STUDY

The former PEPCON facility operated 1958–1988 in the southeastern portion of the Las Vegas Valley near Henderson, Nevada. Located southwest of the intersection of Gibson Road and American Pacific Drive, this facility manufactured perchlorate chemicals, including the oxidizer ammonium perchlorate, prior to being destroyed in a series of fires and explosions on May 4, 1988. American Pacific Corporation (AMPAC) is the parent corporation of the former PEPCON entity and is responsible for ongoing remediation. AMPAC is working cooperatively under the direction of the Nevada Division of Environmental Protection (NDEP) to remediate perchlorate-impacted groundwater in the vicinity of the former PEPCON plant site.

AMPAC has documented that perchlorate impacts extend vertically downward to five water-bearing zones in the immediate vicinity of the former plant site to a depth of approximately 350 feet. Site characterization work conducted 1997–2004 included completion of more than 50 nested monitoring wells, which collectively revealed, among other useful data in the wider area, that the deeper water-bearing zones do not appear to be laterally continuous for long distances. The deeper coarse-grained water-bearing units appear to pinch out (thin) into much less hydraulically conductive fine-grained silts and clays within approximately 2 miles downgradient of the former plant site. The site characterization work, however, has demonstrated that the shallow water-bearing zone is discontinuously laterally extensive to the northeast of the former plant site. Perchlorate-impacted shallow groundwater has been documented to extend downgradient of the former plant site for approximately 3 miles to locations within 1 mile of the Las Vegas Wash.

Design of a full-scale In Situ Bioremediation (ISB) Plant began in late 2004 and continued into early 2005. After a work plan was approved by NDEP in April 2005, AMPAC constructed the ISB Plant between July 2005 and the end of 2006 to capture and remediate perchlorate-impacted shallow groundwater at advantageous off-site locations. Two extraction well fields (Athens Road and Athens Pen Well Fields), comprising a total of nine extraction wells, were installed to intercept shallow groundwater migrating towards the Las Vegas Wash in areas with reasonably high hydraulic conductivity and moderately elevated perchlorate concentrations. The Athens Road Well Field additionally functions to lower the groundwater level in the vicinity of a concrete-lined flood control drainage where emergent groundwater historically impacted surface water quality. Surface waters within this drainage are discharged to an area closer to the Las Vegas Wash and result in extending perchlorate impacts to shallow groundwater to an area downgradient of the main body of the plume.

Groundwater extracted by the Athens Road and Athens Pen Well Fields is conveyed through underground pipelines to a 9000 ft^2 permanent ISB building, where the groundwater is filtered with 1-micron bag filters prior to its reinjection more than 7000 ft away. A biocide is added periodically to the filtered water to limit biological growth within the pipelines and injection wells. The filtered water is further conveyed though an 8-inch-diameter underground pipeline to a field of six injection wells. A parallel 1-inch-diameter donor line allows the electron donor to be delivered to a mixing vault, where the donor is added to and mixed with the filtered water immediately prior to reinjection. Six performance-monitoring wells are positioned throughout the area immediately downgradient of the injection wells to monitor groundwater quality and the degree of perchlorate biodegradation.

The Interim ISB System became operational in mid-June 2006 and remediated groundwater from the Athens Road extraction wells through early December 2006. This interim system was operated using aboveground, skid-mounted temporary equipment configurations. Complete degradation of perchlorate-containing groundwater was confirmed in mid July 2006.

The permanent ISB system became operational in late December 2006 following six months of operation of the Athens Road Well Field and portions of the ISB system in the above noted interim mode. System start-up, shake-down, and optimization continued through May 2007. AMPAC and NDEP expected the permanent ISB system to be fully functioning by June/July 2007. The permanent ISB system includes the following:

- a target flow rate of ~250–350 gpm with six to nine extraction wells operating achieving the target mass capture
- an average perchlorate influent concentration of ~10–12 mg/L during system start-up
- an average perchlorate mass reduction of ~40–50 pounds/day during system start-up
- use of sodium benzoate as the electron donor and chlorine dioxide as the biocide
- an on-site ion chromatograph to support the system operation and gauge the degree of nitrate, chlorate, and perchlorate reduction achieved in the performance monitoring wells, some of which are subject to interference due to preexisting contamination and dilution effects

The ISB system operates with a UIC permit issued by the NDEP allowing the use of a number of electron donors and biofouling agents to provide AMPAC with flexibility should a change in donor or biocide be needed to maintain ISB system performance.

Previous ISB bench-scale and pilot tests conducted by AMPAC and its consultants successfully reduced perchlorate to below the 18 µg/L Nevada provisional action level. A preliminary microcosm study conducted by GeoSyntec in 2001 demonstrated the presence of naturally occurring perchlorate-reducing bacteria. A pilot study conducted 2002–2003 resulted in the biodegradation of perchlorate from 600,000 µg/L to <1.5 µg/L (the laboratory Method Detection Limit for the study) in approximately 100 days. The pilot study employed a 100-foot recirculating loop system within the 160–180 foot bgs water-bearing zone. Ethanol followed by citric acid were used as electron donors during the pilot study. Subsequent column studies by AMPAC in 2004 (see below) resulted in the selection of sodium benzoate as the preferred electron donor for future use due to efficiency and handling reasons.

Key 2003 pilot test results:

- Viability of citric acid as an electron donor to naturally occurring bacteria was confirmed via observation of perchlorate biodegration in situ.
- Performance of ethanol in the in situ environment was found lacking due to apparent precipitation of solids prior to reinjection.
- Biodegradation of perchlorate-impacted groundwater with starting concentrations of ~600,000 µg/L to <2 µg/L occurred within 50 feet of the reinjection point.
- During biodegradation, minimal secondary effects on water quality were observed (e.g., no high precipitation of metals).
- Chlorine dioxide as a biocide to maintain reinjection well performance appeared promising.
- An ultrasonic tube resonator device was not successful to maintain reinjection well performance.

Key 2004 column test configuration and results:

- Soil and water samples used for the column tests were collected from water-bearing zones at locations that were very close to the eventual full-scale ISB system injection well field.
- Donors evaluated: sodium benzoate, sodium acetate, sodium formate, citric acid, and methyl soyate.
- Columns were constructed of 4-inch clear PVC pipe in 3-foot lengths.
- Approximately 2 gal of soil (from the full-scale ISB system target area) were placed in each column.
- Groundwater from the target area was pumped through the soils at approximately 20 mL/hour.
- Perchlorate degradation was observed with all donors except for methyl soyate (handling optimization work was postponed).
- Sodium benzoate was chosen as the preferred electron donor for the full-scale ISB system.

AMPAC Case Study Figures A-12 through A-18 provide views of the project and show the layout of extraction and injection areas, injection well details, and the effectiveness of the treatment process.

Figure A-12. Aerial view of treatment area looking north across Section 36 toward the Las Vegas Valley. Former location of PEPCON facility is to the south (not in picture). Las Vegas Wash is directly north of Sam Boyd Stadium and north of the reinjection area. (Courtesy of AMPAC).

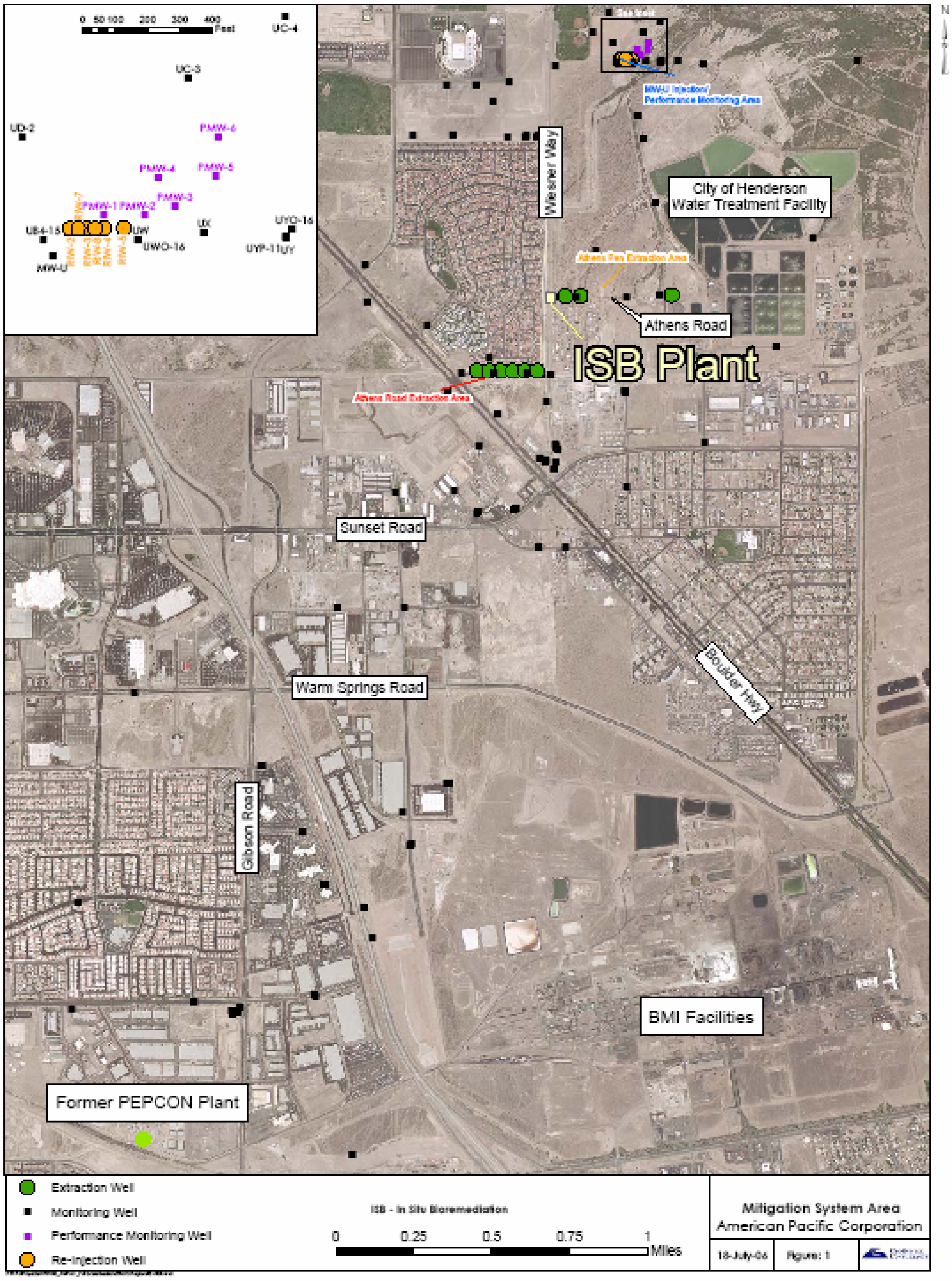


Figure A-13. Regional view of perchlorate bioremediation system.

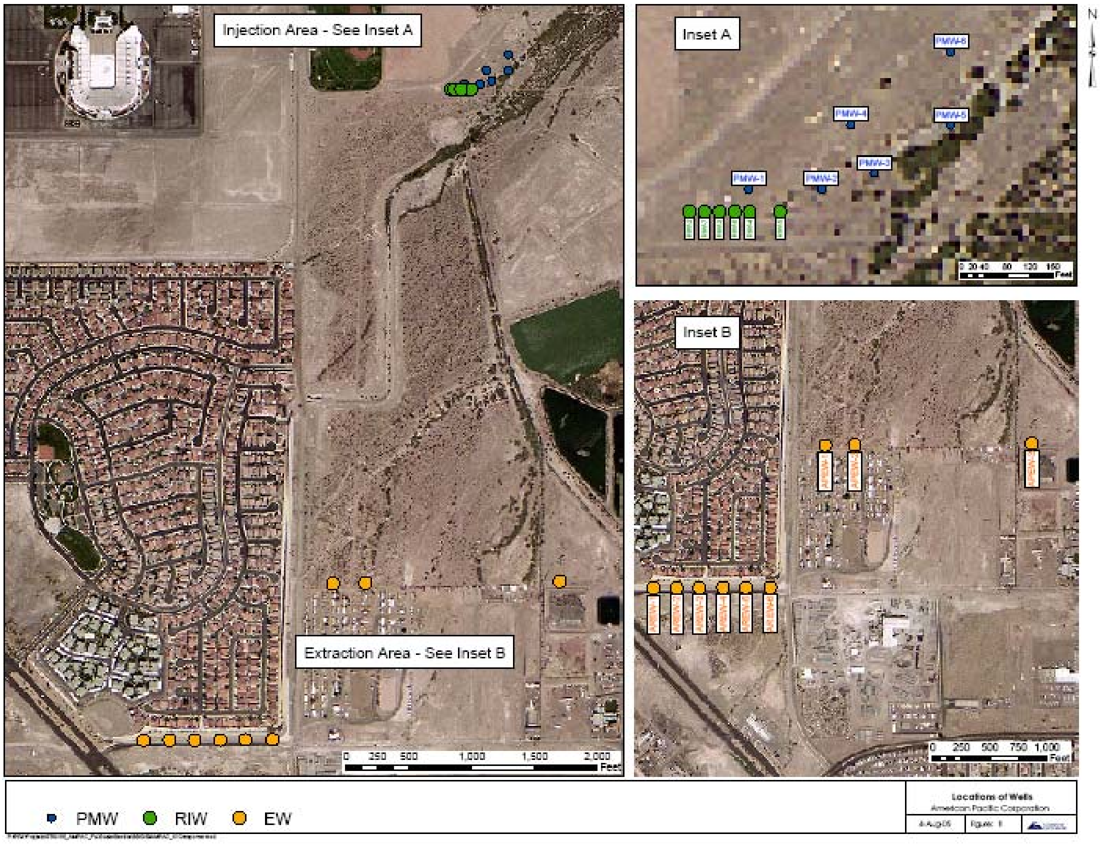


Figure A-14. Layout of extraction and injection areas. (NDEP AMPAC Case File)

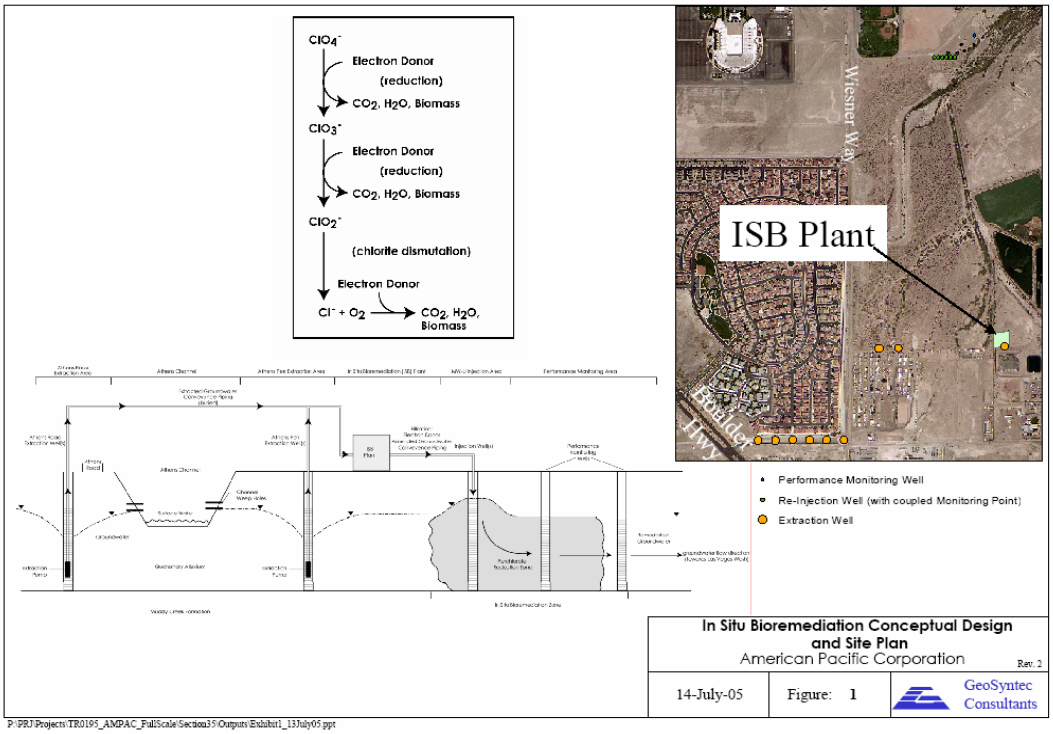
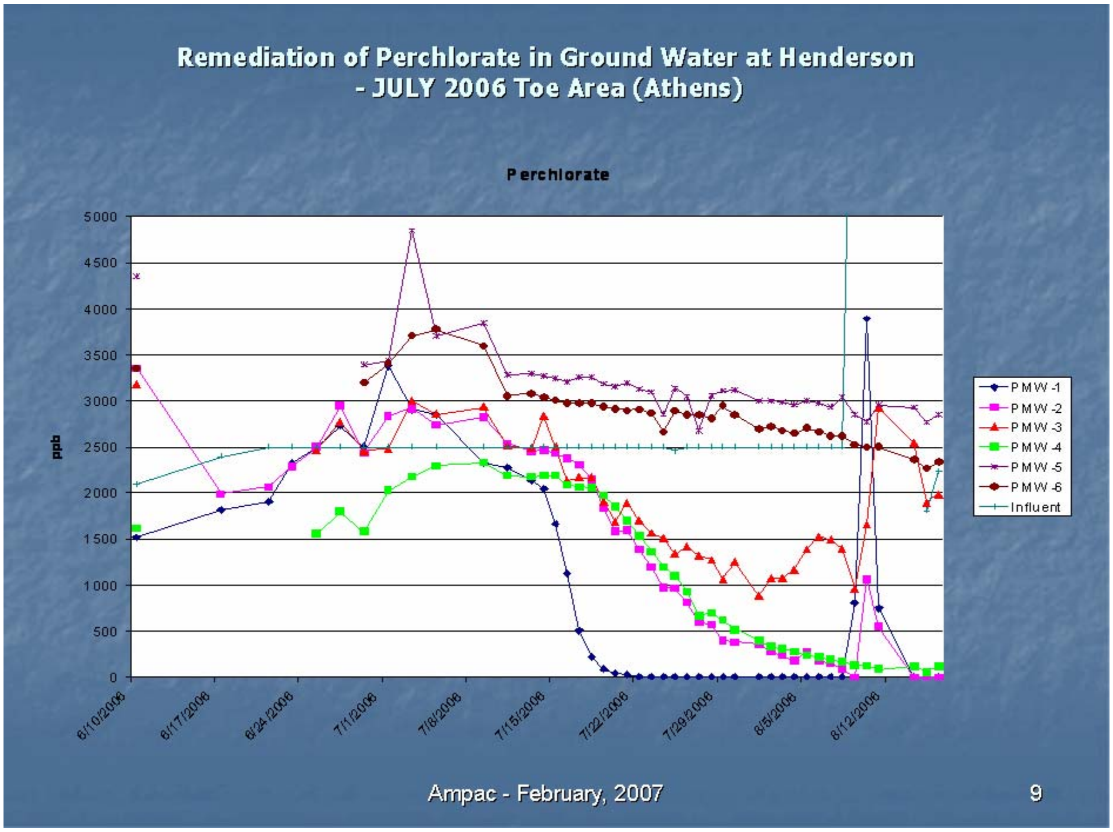


Figure A-15. Flow diagram. (NDEP AMPAC Case File)



Remediation of Perchlorate in Ground Water at Henderson - JULY 2006 Toe Area (Athens)

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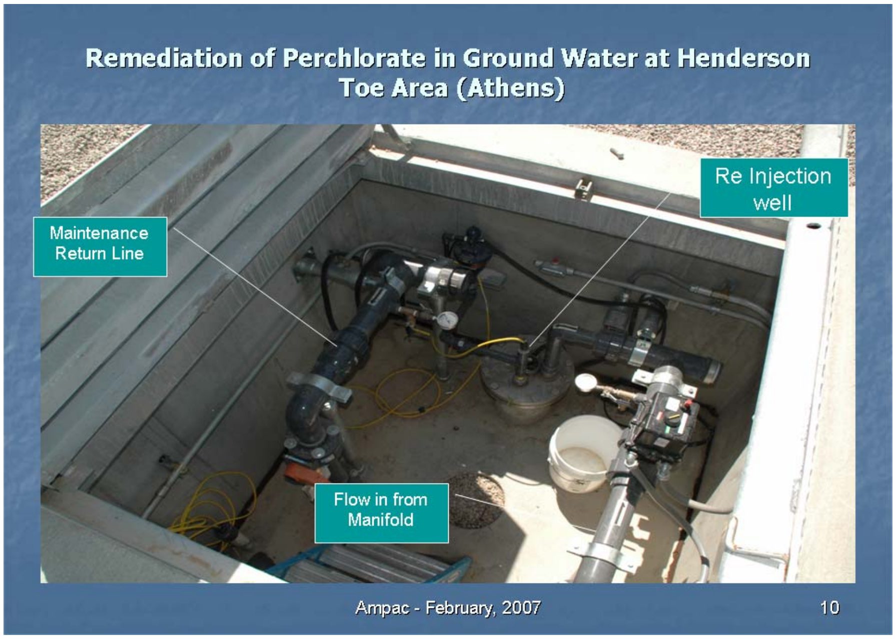
Figure A-16. Perchlorate removal in groundwater. (AMPAC 2007)



Remediation of Perchlorate in Ground Water at Henderson Toe Area (Athens)

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Figure A-17. Typical injection vault. (AMPAC 2007)

Figure A-18. Injection well vaults. (NDEP AMPAC Case File)

NAVAL WEAPONS INDUSTRIAL RESERVE PLANT—MCGREGOR CASE STUDY

Background

NWIRP McGregor was a government-owned, contractor-operated facility in McGregor, Texas, approximately 20 miles southwest of Waco. The U.S. Army Ordnance Corps originally established it in 1942 as the Bluebonnet Ordnance Plant. Over the facility's 50-year history, owners included the U.S. Army, U.S. Air Force, and the U.S. Navy's Naval Air Systems Command (NAVAIR). Industrial activities at the site included weapons and solid-fuel rocket propulsion systems manufacturing and demilitarization.

Several property owners and tenants have operated at the facility. Area M was constructed in 1944 as Bomb Loading Line 4. Before 1944, Area M was agricultural. Bomb Loading Line 4 was decommissioned in 1945 shortly after the close of World War II, and parts of Area M were leased or sold to individuals and organizations with a government buy-back clause. In 1952, the Air Force acquired much of the facility, including Area M. From 1952 to 1958 Phillips Petroleum Co. operated Area M as part of Air Force Plant No. 66 at the McGregor site. During this period, Phillips manufactured jet-assisted take-off rockets and the solid rocket propellant used in them. Astrodyne used Area M 1958–1959 for similar operations. Rocketdyne operated Area M as a manufacturing facility for solid rocket propellant and solid rockets 1959–1978. Hercules, Inc. operated Area M 1978–1995, performing operations similar to the previous tenant. Since 1996, the U.S. Navy has been working with the Texas Commission for Environmental Quality (TCEQ), EPA, and City of McGregor to complete environmental investigations and subsequent remediation activities so that NWIRP McGregor could be transferred to the City of McGregor for beneficial reuse.

Prior to facility shutdown, a multiphased RCRA Facility Investigation (RFI) was initiated in 1992 at NWIRP McGregor targeting soil, surface water, and groundwater. The RFI responded to environmental issues raised in the RCRA Facility Assessment completed by TCEQ. In the normal course of the investigations, a suite of contaminants of concern was identified. In March 1998, TCEQ notified the Navy of EPA documentation stating that NWIRP McGregor used, stored, and disposed of ammonium perchlorate, which had become an environmental groundwater issue nationally. Ammonium perchlorate was ground to meet rocket use specifications at Area F. At Area M, ammonium perchlorate was installed in rocket motors and cleaned out of rocket motors. At Area S, ammonium perchlorate was disposed by burning.

In August 1998, after reviewing all recent perchlorate sampling results, a comprehensive groundwater investigation work plan was developed to unify all site groundwater investigations and continue them off site. With increased precipitation from November 1998 to February 1999 (compared to the dry summer), groundwater monitoring wells were installed and sampled, and on- and off-site surface water sampling continued. Figure A-19 shows the potential study area.

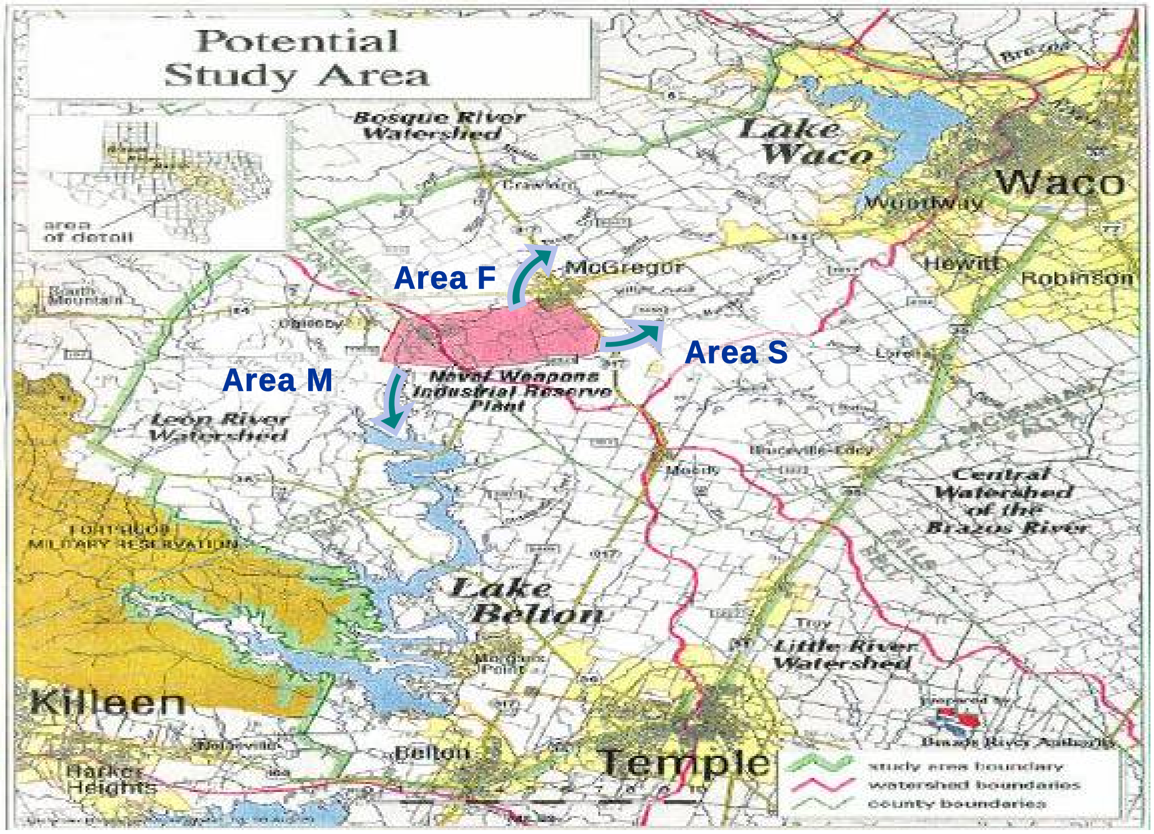

Figure A-19. Potential study areas at NWIRP McGregor.

In February 1999, TCEQ requested that interim stabilization measures (ISMs) be implemented to abate off-site migration of perchlorate from NWIRP McGregor. The Navy responded in March to the TCEQ request identifying source areas where interim corrective measures could be implemented immediately to remove, stabilize, or control perchlorate contamination. TCEQ approved the response letter. In June 1999, an ISM evaluation plan was submitted to TCEQ and EPA for review. The plan recognized that contaminated groundwater was exfiltrating to surface water at concentrations exceeding TCEQ action levels during the wet season. The groundwater subsequently contaminated the surface water (via natural springs and seeps) then flowed toward Lake Belton, a primary drinking water source in central Texas. Perchlorate concentrations up to 200 µg/L were detected in surface water approximately 1 mile downstream of the property boundary and concentrations up to 56 µg/L were detected at a location 3 miles downstream of the property boundary. There were no detected impacts to the Leon River or Lake Belton, which is nearest source of drinking water, but concern was high. On-site concentrations of perchlorate up to 91,000 µg/L were found in groundwater monitoring wells in Area M. A groundwater plume covering an area of approximately 360 acres was delineated in and around Area M. Perchlorate concentrations up to 5600 µg/L were detected in surface water samples collected from a surface water body running through Area M (Tributary M). Area M was identified as the immediate concern, with Areas F and S having lower concentrations and thus lower priority. Both TCEQ and EPA quickly approved the recommendations contained in the ISM evaluation.

Hydrology and Geology

Surface water movement and drainage across the facility are provided by tributaries of Station Creek, Harris Creek, and the South Bosque River. The area can be divided into three watersheds that correspond to these streams. All the streams within the site boundaries are intermittent. Surface water within the site and surrounding areas is used solely for agriculture, mainly as a water source for livestock. Watershed flow from Area M is through Station Creek, flow from Area F is toward Harris Creek, and Area S is towards the South Bosque River.

The U.S. Department of Agriculture’s Soil Conservation Service has mapped four soil types in and around Area M. In descending order of land area percentages, these are Crawford silty clay, Purves gravelly silty clay, Denton silty clay, and Slidell silty clay. Crawford silty clay covers most of the developed portion of Area M; Purves gravelly silty clay and Denton silty clay primarily cover the gentle slopes surrounding Area M. Slidell silty clay covers the areas along Station Creek, west of Area M, and along an unnamed tributary of Station Creek southeast of Area M. According to the Soil Conservation Service, all of these soil types occur on 1%–3% slopes, which are typical in this area.

Soil samples collected from Area M are described as dark brown, stiff silty clay with weathered limestone float. Desiccation cracks are common when the soil is dry. Based on borings completed in Area M, soil thicknesses range 0.5–6.5 feet, averaging about 2.75 feet. The base of the soil interval was generally defined as the depth of split-spoon refusal (the point at which the drill rig can no longer push a 24-inch-long, 2-inch-diameter split spoon into the ground). Soil thicknesses are approximate since refusal may not have occurred exactly at the soil/bedrock interface and may include a portion of a transitional weathered zone between the soil horizon and the underlying Main Street Limestone bedrock. Areas F and S have similar soils.

The NWIRP McGregor facility is underlain by a transgressive-regressive sequence of Cretaceous-age sedimentary rock primarily consisting of limestone and shale sequences. These rocks are covered by a thin soil regolith eroded and developed from the parent rock material. A full Cretaceous stratigraphic sequence appears to be present from the Comanchean Series through the Gulfian Series of rocks.

Based on historical and recent groundwater level measurements, shallow groundwater is generally encountered in the uppermost water-bearing zone at depths ranging from <2 feet to almost 30 feet bgs, depending on the season and well/piezometer location. Groundwater encountered in monitoring wells completed in the uppermost water-bearing zone occurs in fractures, bedding planes, joints, and minor solution features in the limestone matrix. Consequently, the upper water-bearing zone can be characterized as a heterogeneous aquifer where secondary porosity systems and topography control groundwater flow. Weathering and slight regional tectonic movements are responsible for development of these features, which are often filled in with clay. The macroporosity available in the weathered limestone can store significant quantities of water, although a network of connections between macroporosity features is not always well established.

In Situ Biological Treatment with Permeable Reactive Barriers

Area M

A series of bench-scale studies was completed to develop a biological treatment system for the site. Based on the bench-scale studies' successful results, a pilot-scale fixed-bed and fluidized bioreactors were evaluated. Both were capable of reducing perchlorate to nondetect levels.

Initially, the ISM design included a series of cutoff and collection trenches that were to be pumped to an ex situ treatment system. It was determined, based on aquifer modeling, that the ex situ fluidized-bed bioreactor was most appropriate to handle the volume of groundwater that was anticipated to occur during an extremely wet season.

Concurrent to the ex situ pilot-scale evaluation, results of new bench-scale studies indicated that an in situ biological treatment technology could also be an effective remedial tool. This finding encouraged the Navy to incorporate the concept into groundwater recovery trenches being installed for the ex situ pilot-scale study. The cost of incorporating the in situ technology into the ongoing recovery trench construction was <1% of the remediation construction cost. As a result, the in situ system was implemented as a possible stabilization measure.

The Area M in situ treatment technology effectively created a biological permeable PRB. The A-line cutoff trench runs along the southern property line. Figure A-20 provides a diagram of the trench locations. The A-line trench is 30 inches wide and up to 25 feet deep to extend through the weathered-limestone water-bearing zone. Figure A-21 shows the material used to fill the trench. The A-line trench is 1680 feet long in total, with 900 feet modified to act as an anaerobic PRB. The B-line collection trench parallels the unnamed tributary and intercepts contaminated groundwater as it migrates to the unnamed tributary. The average depth is 12–15 feet. The B-line trench is designed to be 6 feet below the bottom of the unnamed tributary. Figure A-21 shows the material used to fill the B-line trench. The B-line trench is 2950 feet long, with 1800 feet modified to act as an anaerobic PRB. The C-line collection trench is perpendicular to A-line cutoff trench and collects contaminated spring water prior to exfiltration. The average depth of the C-line trench is 12–15 feet. Figure A-21 shows the materials used to fill the trench. The C-line trench is 1425 feet long, with 975 feet modified to act as an anaerobic PRB. Influent concentrations typically ranged 3000–8000 ppb of perchlorate. The trenches were capped with a compacted clay layer to limit seeps and surface infiltration. The specific data for each of the trenches of Area M are as follows:

- A-line trench: granular activated carbon
  - 900 feet modified (1680 feet total)
- B-line trench: cotton seed and cotton seed meal
  - acetate infiltration point for additional substrate and nutrients if necessary
  - 1800 feet modified (2950 feet total)
- C-line trench: compost mixed with drainage aggregate
  - infiltration pipe: groundwater recirculation from lift station in A-line trench
  - 975 feet modified (1425 feet total)

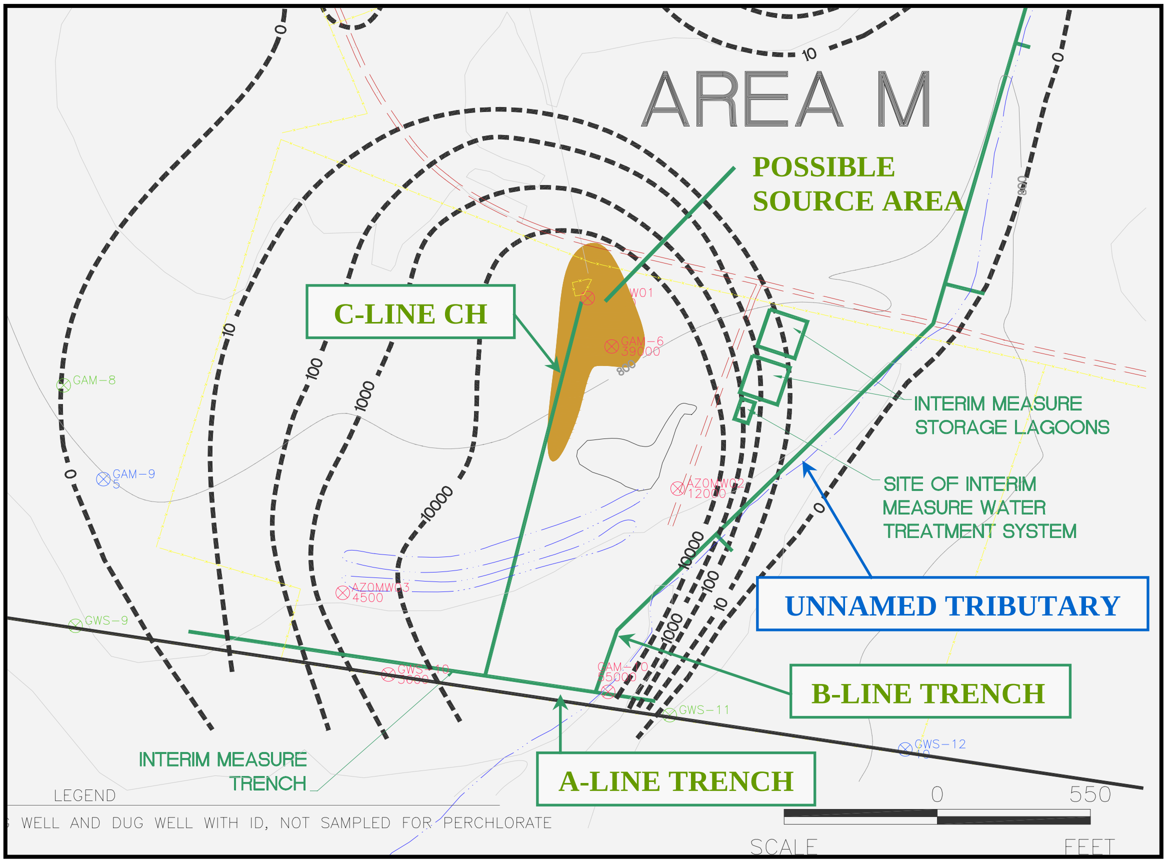

Figure A-20. Area M trenches.

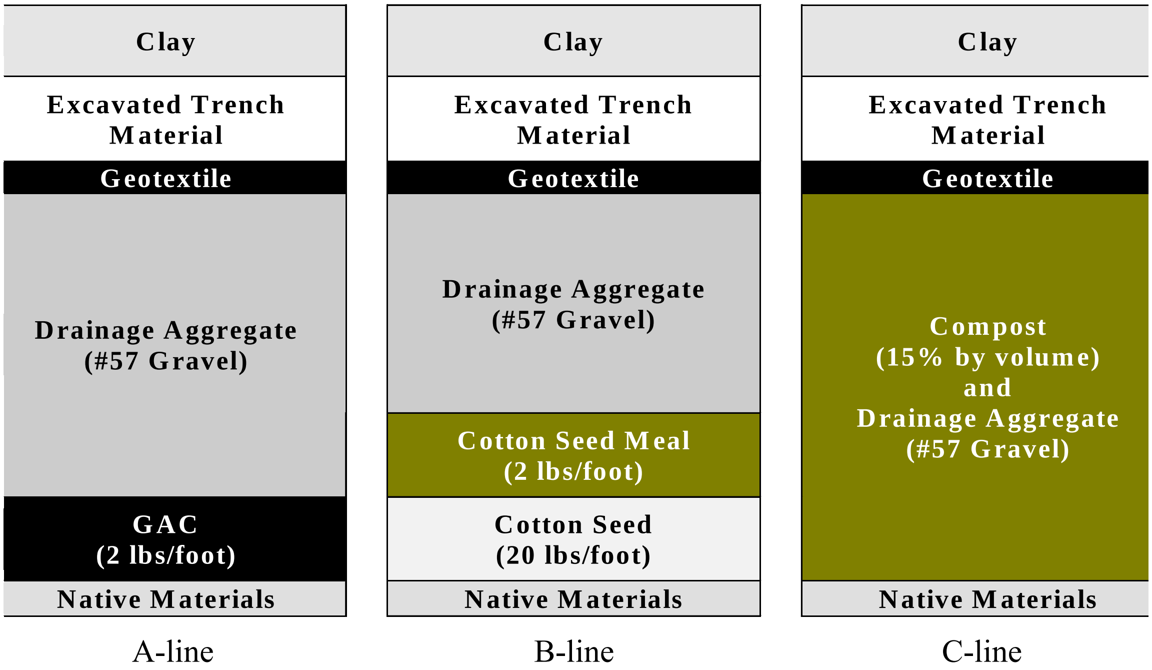

Figure A-21. Area M trench cross sections.

Results. Within three weeks of trench construction completion, perchlorate concentrations in trench groundwater decreased from 27,000 µg/L to below laboratory practical quantitation limits (usually around 4 ppb). These encouraging results lasted for approximately one year. However, increasing groundwater volume and limited carbon supply resulted in perchlorate concentration spikes. As a consequence the remediation effort returned to its original design of P&T technology through a fluidized bed bioreactor system. Figure A-22 shows the reduction in plume size over time due to this treatment system operation. The in situ pilot test proved that perchlorate and VOC groundwater could be remediated with the proper delivery system.

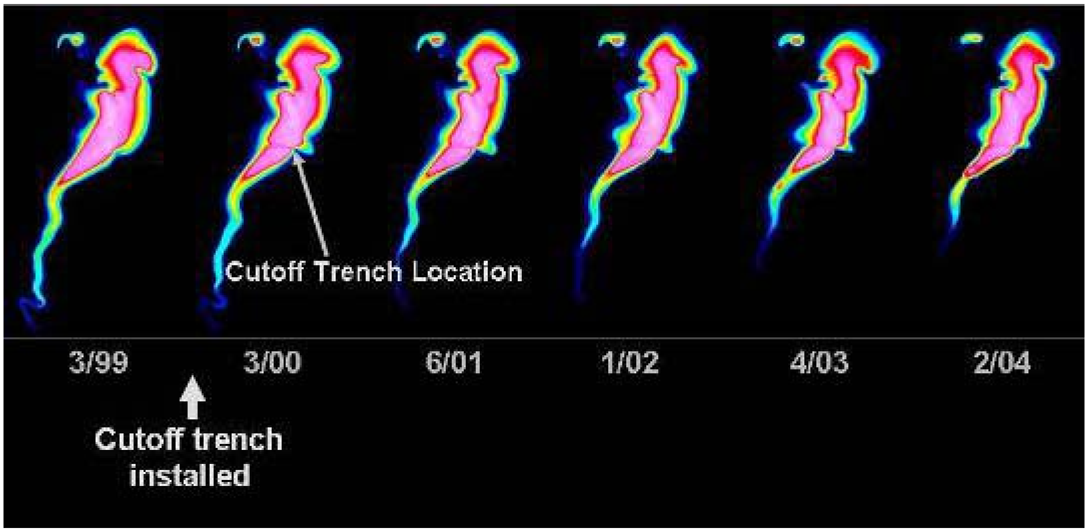

Figure A-22. Area M perchlorate plume versus time.

Area F

A series of pilot-scale, biological PRBs was designed and evaluated at Area F. These trenches were designed from the beginning to act as PRBs and thus were designed differently from the Area M cutoff trenches. The goals of the study included an assessment of the biobarrier construction issues prior to full scale implementation including: an estimation of the longevity of the biobarrier media; organic carbon reapplication and distribution; and determining the optimal biobarrier media. Table A-1 summarizes the different designs pilot-tested at Area F.

Table A-1. Area F pilot study design summary

Trench	Length (ft)	Media
1	100	Soybean oil–saturated pine wood chips and limestone aggregate
2	75	Soybean oil–saturated pine wood chips, mushroom compost, and limestone aggregate
3	75	Pine wood chips, sodium acetate, and limestone aggregate
4	75	Mushroom compost and limestone aggregate
5	75	Wood chips and limestone aggregate

Figure A-23 shows the biobarrier design for a trench. Each of the pilot PRBs was approximately 12 feet deep and 30 inches wide. The trenches were 75 feet long except for Trench 1, which was 100 feet long. They were oriented perpendicular to hydraulic gradient. Backfill material was roughly 30% organics (36 yd^3) and 70% drainage aggregate (96 yd^3 for Trench 1). Two-inch pipe with ¼-inch holes was included in the design to allow for additional electron donor addition in the future.

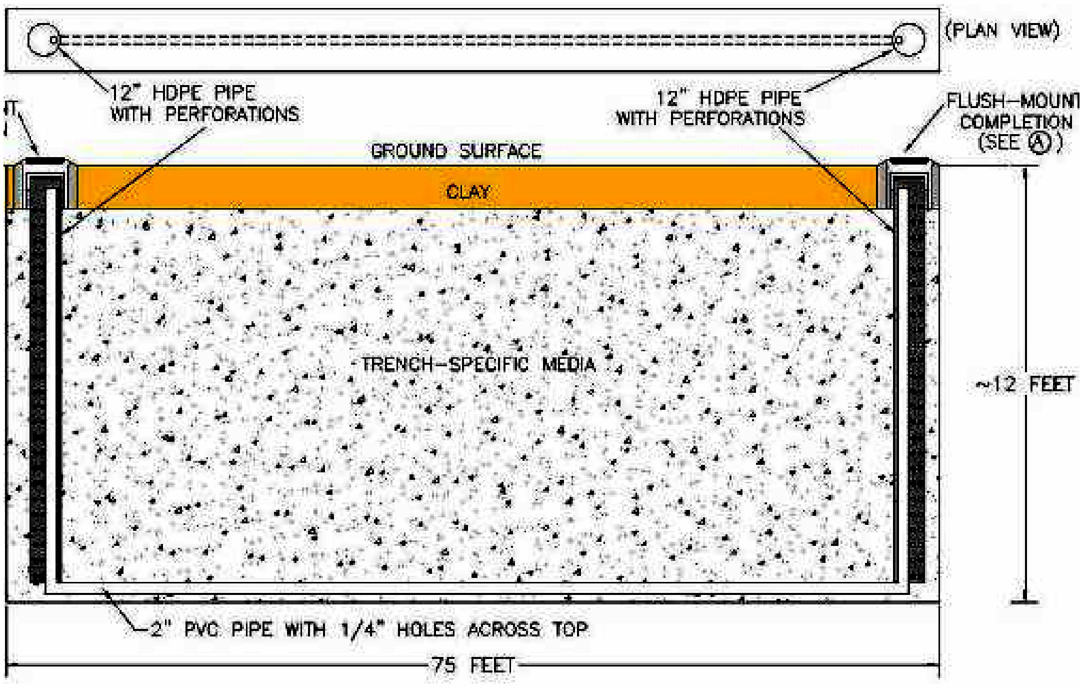

Figure A-23. Biobarrier conceptual layout and design.

Results. The results for Trench 1 will be highlighted in this case study. Within weeks of trench construction completion, perchlorate concentrations in trench groundwater decreased from >900 µg/L to below laboratory detection limits of 20 µg/L. Ongoing monitoring revealed that after 20 months of operation, downstream monitoring wells began to show elevated levels of perchlorate. TOC concentrations continued to decline in Trench 1 during this period. The depletion of the electron donor is thought to be the reason for the rebound in perchlorate concentrations. Figures A-24, -25, and -26 help to illustrate the results from Trench 1. TCE is also commingled with the plume. Figure 27 gives results for TCE concentration versus distance downgradient from the barrier over time. The longest-lasting perchlorate-reducing PRBs at Area F used the combination substrates from Trenches 1 and 2. These media were soybean oil–saturated wood chips and gravel and soybean oil–saturated wood chips, mushroom compost, and gravel. The most effective ratio of saturated wood chips with and without compost to gravel was 35:65. In these studies, nitrate was the most important electron acceptor to consider when determining the mass of electron donor to administer. From these results, it can be expected that carbon rejuvenation will be required every one or two years. Other observations from the pilot study include the importance of understanding the local hydrogeology to prevent uncontrolled seeps to the surface.

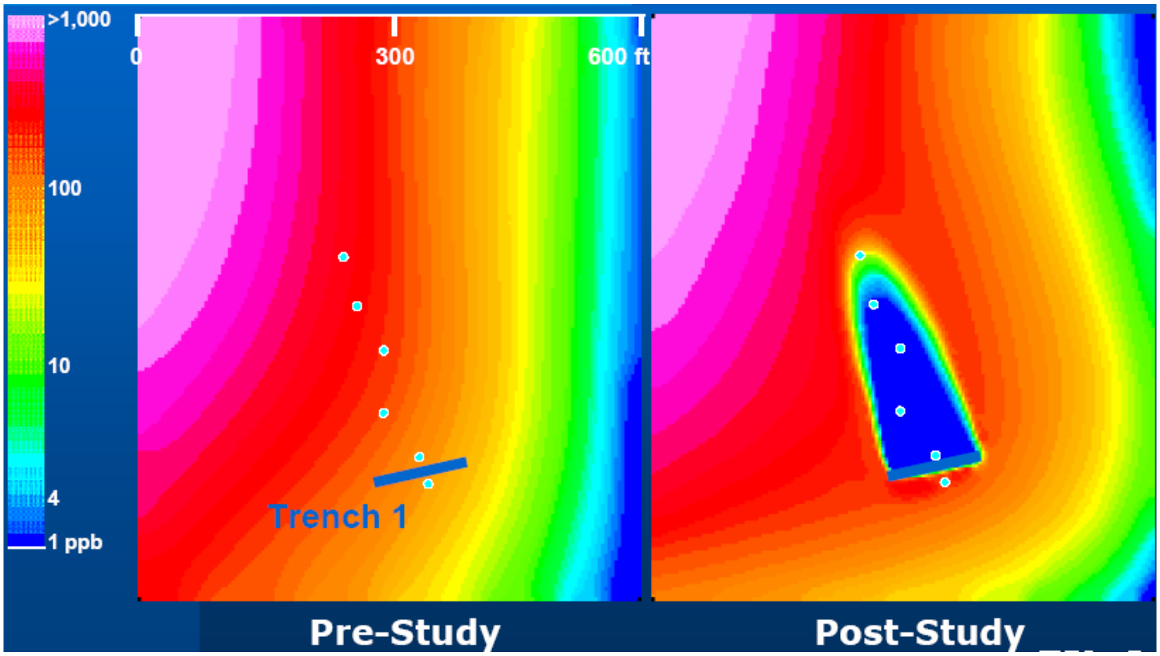

Figure A-24. Pre- and post-biobarrier impact on perchlorate plume.

When microbial communities were examined upgradient and downgradient of Trench 1, there was little similarity. The communities were primarily composed of Proteobacteria (gram negative) that are fast growing, able to use a wide range of electron donors, and quickly adaptable to a changing chemical and geochemical environment. Biomass concentrations were one order of magnitude higher in the downgradient wells (10^6 cells/mL) in comparison to upgradient wells (10^5 cells/mL).

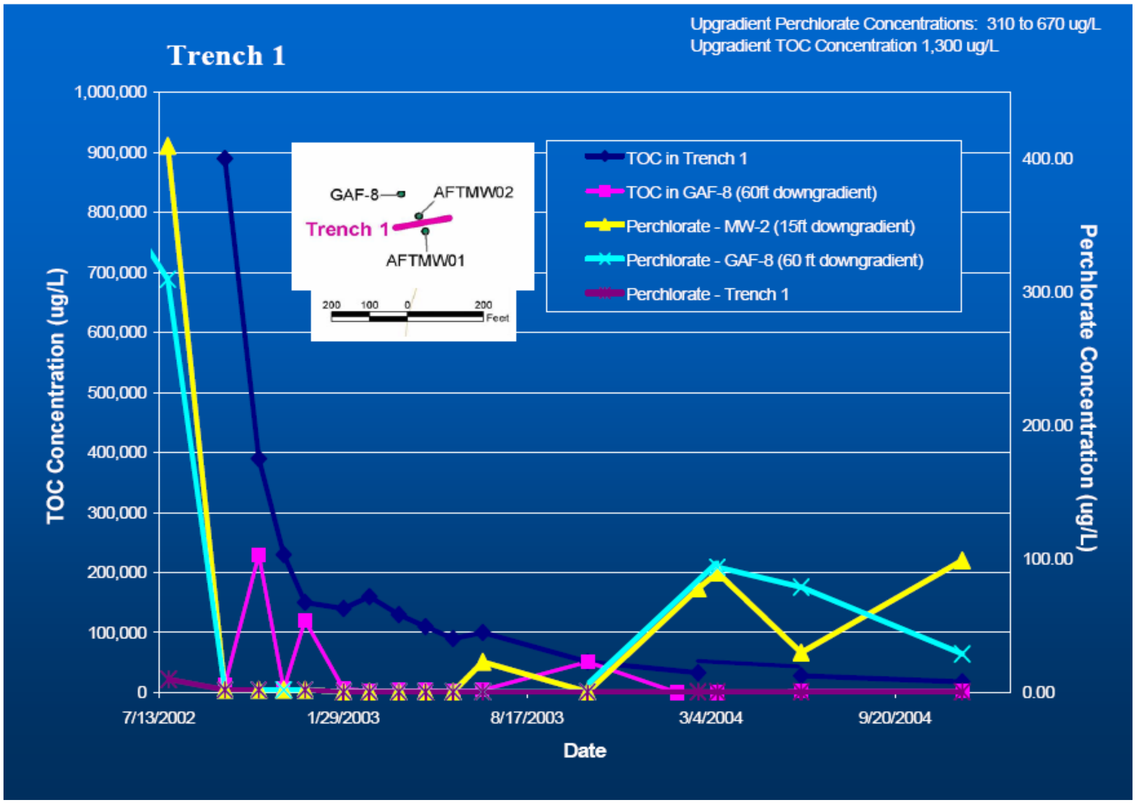

Figure A-25. Perchlorate concentration vs. time.

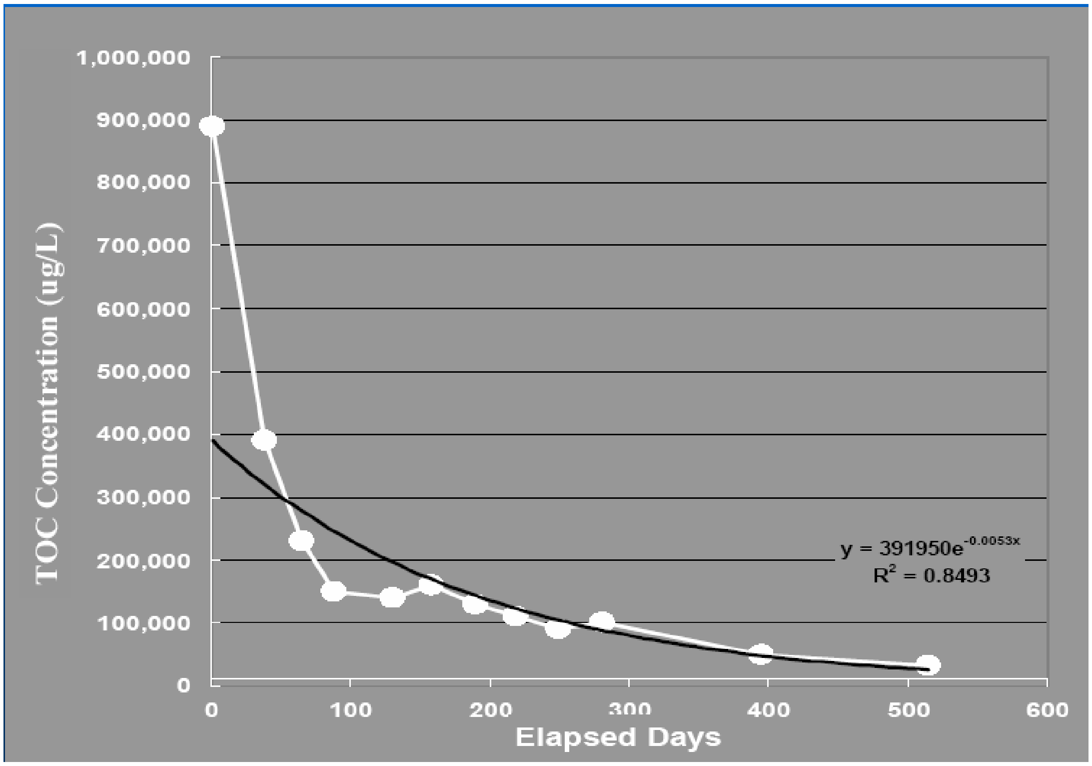

Figure A-26. TOC depletion curve.

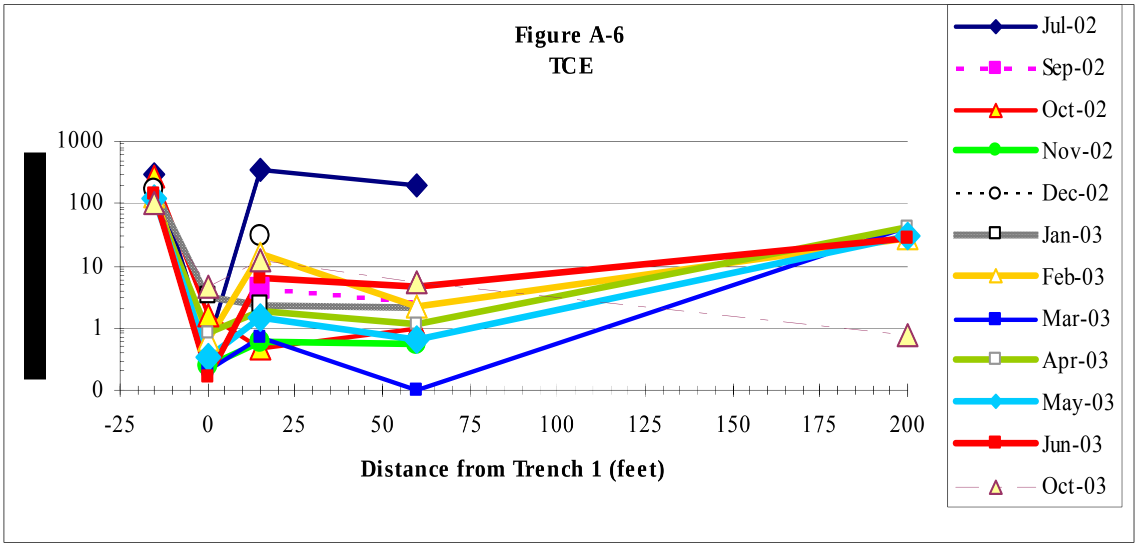

Figure A-27. TCE concentration vs. distance.

Area S

A series of full-scale biological PRBs was installed at Area S. Approximately 4800 tons of drainage aggregate, mushroom compost, and soybean oil–saturated wood chips was placed in trenches whose total length was 4000 feet. The design for each of the trenches was similar to the design shown in Figure A-23 and included subsurface piping to provide for the addition of electron donor in the future. Figures A-28 and -29 illustrate the size of the area that has been addressed with this treatment effort and the location of the trenches. Figure A-30 shows pictures of trench construction.

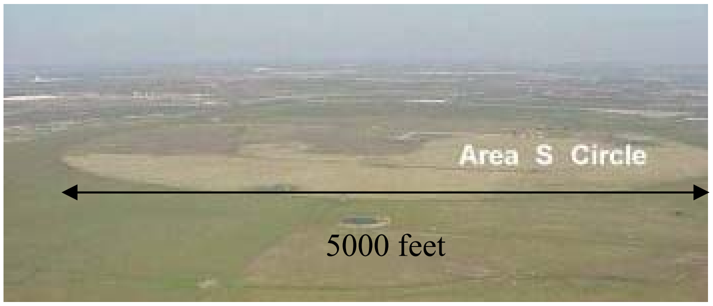

Figure A-28. Areal view of Area S.

Figure A-29. Area S trench locations to intercept perchlorate groundwater plume.

Figure A-30. Area S trench construction: the mixing area (above left), rock trencher in operation (below left), and top view of trench results (right).

Within weeks of trench construction completion, reducing conditions developed, and perchlorate concentrations in groundwater that had passed through the trenches decreased to below laboratory detection limits. Figure A-31 shows the impact that the trenches had on the groundwater plume and the reduction in the high-concentration area. With the success of these early PRBs, the Navy in 2005 installed 9000 feet of PRBs as part of the full-scale groundwater remediation plan for the facility. This is the largest application of PRBs in the world.

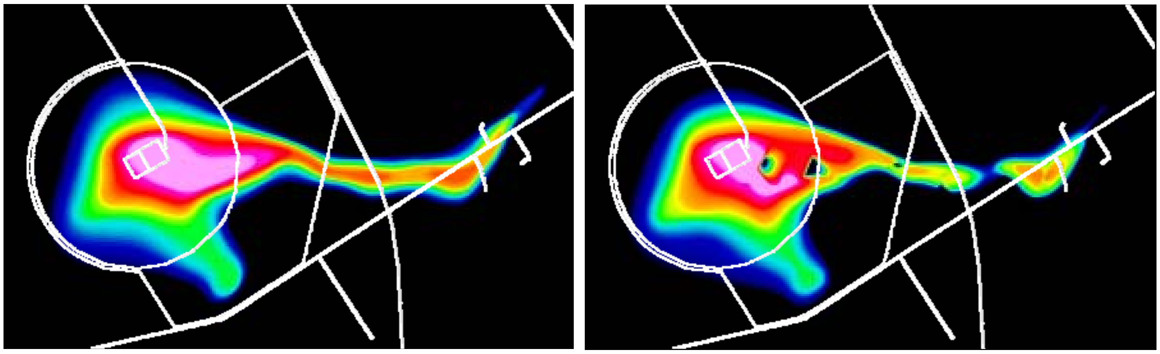

Figure A-31. Area S perchlorate plume in 1999 and in 2003 after trench implementation.

In Situ Biological Treatment of Perchlorate in Groundwater Using Bioborings

The groundwater remediation program included the installation of more than 1300 bioborings throughout the NWIRP McGregor area in locations where installation of PRB trenches was difficult. These bioborings were 12 inches in diameter and typically installed in rows. Figure A-32 is a schematic of a bioboring installation. An air rotary drill rig was used to perform the soil boring, and approximately 20 bioborings could be installed per day. Each bioboring was filled with the same organic and gravel mixture as the PRBs and sealed with cement-bentonite grout. Figure A-33 shows where some of the bioborings were installed. Figure A-34 shows a bioboring row after installation.

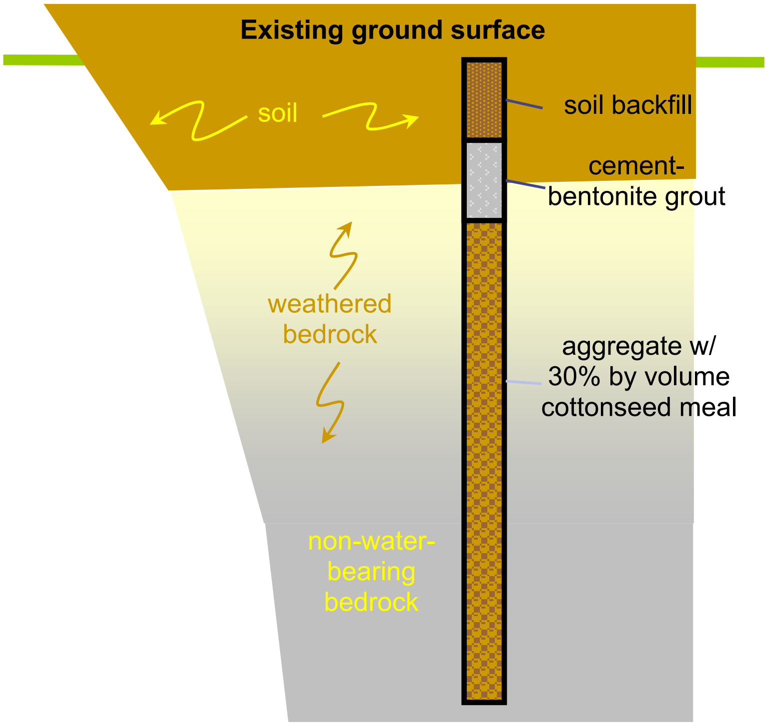

Figure A-32. Bioboring schematic.

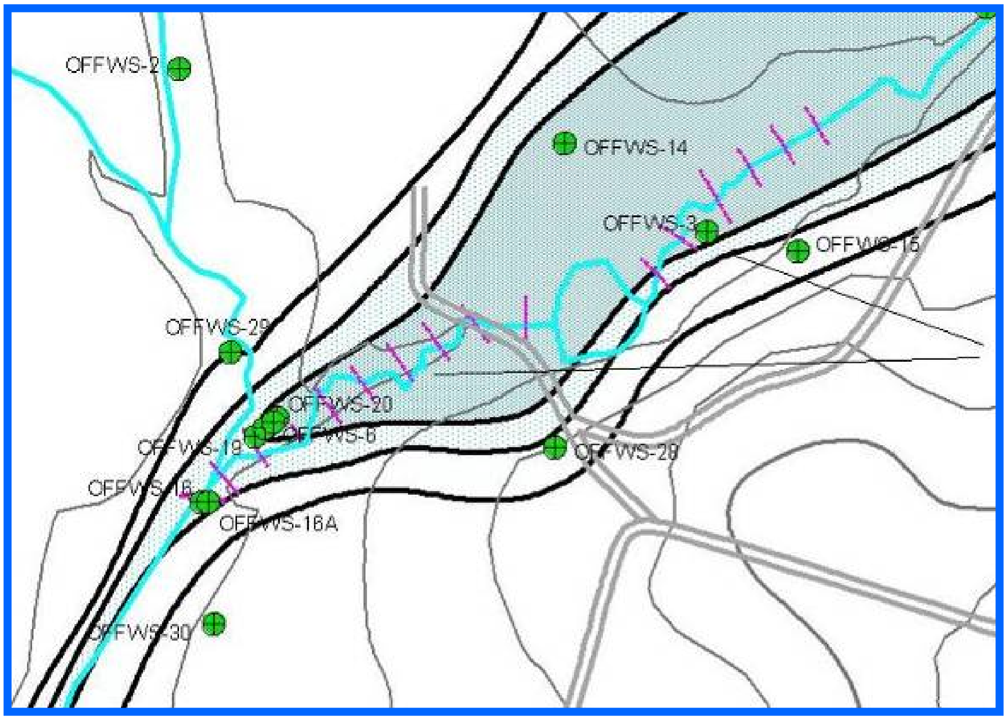

Figure A-33. Bioboring locations downgradient of Area M.

Figure A-34. Bioboring row after completion.

Results. Figure A-35 gives results of the pilot studies conducted in 2000 of bioborings that are downgradient from the cutoff trench and FBR. A general decrease in the perchlorate concentration is evident; however in this particular case, treatment is also occurring due to the treatment system at Area M. Thus, degradation is occurring but it is hard to distinguish between the upgradient effects of treatment system and the bioborings. At NWIRP McGregor, it was determined that PRBs are the best remediation technique for contaminant migration containment and treatment. Bioborings are best suited for small plume cleanup and polishing.

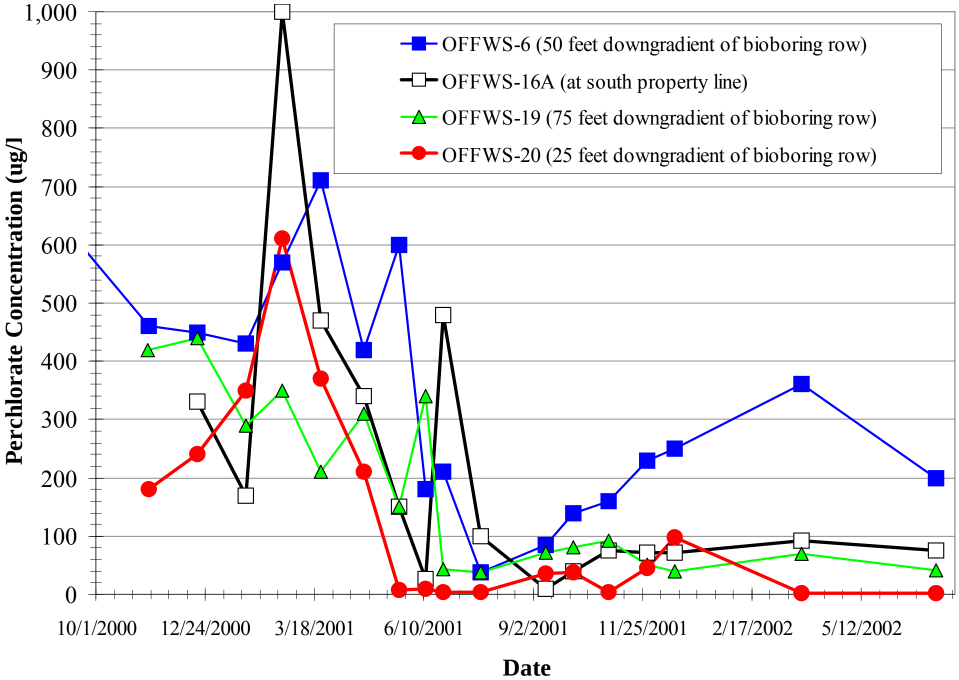

Figure A-35. Bioboring results downgradient of Area M.

Ex Situ Biological Treatment of Perchlorate in Groundwater

In November 2001, construction began on the final ex situ treatment system for Area M, a 400 gpm biological fluidized-bed reactor. The FBR was chosen over an IX unit and a packed-bed bioreactor after pilot-testing revealed that the FBR was the best technology to use based on the expected flow rates and operation costs. The FBR began operation in 2002 after receiving the necessary permits and regulatory approvals. These allowed for the discharge of treated effluent to Tributary M. Perchlorate influent levels to the FBR have averaged 2400 ppb, with a maximum of 4700 ppb. The effluent from the FBR has been <4 ppb. The system has operated at an average flow rate of 125 gpm, with a maximum of 286 gpm. The ORP has been approximately –65 mV. The collection trenches and FBR effectively minimized the off-site migration of perchlorate and VOCs. Figure A-36 shows the location of the FBR system at Area M. Figure A-37 is a picture of the installed FBR at NWIRP McGregor.

Figure A-36. FBR location at Area M.

Figure A-37. FBR installed at Area M.

The installed FBR system required intensive operator involvement because the Texas Pollutant Discharge Elimination System (TPDES) permit for the system required daily sampling for perchlorate when there was a discharge. The TPDES permit also required analysis of a grab sample if the system was being operated such that treated water was discharged in a batch mode. One of the operational goals of the trenches is to prevent seeps to Tributary M. As a result, pumping rates have to be adjusted frequently, requiring daily, manual adjustments at the FBR. ORP readings are critical to monitoring the performance of the reactor, and these had to be performed manually twice each day at the FBR. During periods of heavy rain and high groundwater levels, contaminated groundwater could up well into the treated water storage lagoons, causing significant water-management issues. In the initial operating mode, daily staffing of the treatment system was required. During the first several months of operation, approximately 72–90 operator hours per week were required to effectively operate the system and meet the TPDES permit conditions. Annual labor costs were estimated at approximately $190,000. Despite this intensive staffing, any problems arising during off hours could go undetected for up to 14 hours.

The original TPDES permit, issued in November 2002, was up for renewal at approximately the same time the Navy began to study the optimization of the system. This provided an opportunity to renegotiate sampling requirements. Several beneficial modifications were successfully negotiated based on the past operational reliability of the system and the enhancements to the system that were planned based on the optimization study. A new, phased TPDES permit was issued in July 2005. It authorized certain changes immediately and others once system optimization was completed. The most significant change was a reduction in the required outfall sampling for perchlorate from daily to weekly, once optimization activities were completed. Navy contractors completed the treatment system upgrade in September 2005. This upgrade included the following major elements:

- a control and communication system to provide remote monitoring; remote control; and continuous, uninterrupted remote alarming capability to reduce operator labor and to simplify operation
- water-management modifications to an existing treated effluent water polishing/storage unit (Soil Cell C) to increase operator flexibility and eliminate the potential for groundwater infiltration

Specific elements of the process optimization included the following:

- selection of a direct-discharge mode of operation using only Soil Cell C for effluent polishing
- rehabilitation of Soil Cell C through the clearing of vegetation, the raising of the cell bottom (to prevent contaminated groundwater infiltration), the installation of an HDPE liner, and the installation of a cascade aerator
- installation of a Human Machine Interface/Supervisory Control and Data Acquisition system with software, configuration, backup power supply, and necessary programming to allow day-to-day monitoring and process tracking to be conducted remotely
- installation of dual inline ORP probes to provide constant, real-time monitoring of FBR performance
- installation of an automated diversion valve to automatically divert water to Lagoon A in the event of a problem with the FBR
- completion of various minor piping changes to allow greater flexibility in managing untreated water during periods of heavy rainfall

Optimization of the Area M groundwater treatment system has been a success in terms of both cost savings and greater operational efficiency. Effluent sampling and operator labor have been reduced. Problems with contaminated groundwater infiltration into treated water storage lagoons have been eliminated. The optimization effort cost approximately $1,070,000. Based on savings in operator labor, laboratory analysis, and periodic maintenance of the soil cells, the payback period for the optimization effort is anticipated to be approximately 4.75 years.

Ex Situ Biological Reduction of Perchlorate in Soils

Following a successful bench-scale study, approximately 1500 yd^3 of perchlorate-contaminated site soil was transported to an on-site, engineered treatment cell lined with a 30-mil HDPE liner. Before the soil was placed into the treatment cell, it was mixed with a citric acid (to foster anaerobic conditions), nitrogen and phosphorus fertilizer (micronutrients), and soda ash (buffer) in a 40 yd^3 roll-off container in designed quantities and ratios developed during the bench-scale study. Table A-2 contains the ratio of amendments per cubic yard. Water was added to maintain at least 2 inches of water above the soil to promote and sustain anaerobic conditions. Finally, the cell was covered with a 6-mil HDPE liner. Figure A-36 shows the location of the lined soil treatment system.

Table A-2. Amendment addition rates

Amendment	Rate
Citric acid	2 pound per yd^3
Nitrogen	0.4 pound per yd^3
Phosphorus	2 pound per 100 yd^3
Soda ash	1 pound per yd^3

Initial perchlorate concentrations averaged 500,000 μg/kg and served as the design basis. The maximum perchlorate concentration was 1,800,000 μg/kg. After six months, soil was sampled at six random locations and analyzed for perchlorate. All six samples were below the practical quantitation level of 100 µg/kg. Furthermore, the perchlorate concentration in the water used to flood the cell was below its detection limit of 4 µg/L. Figure A-38 is photograph taken during the construction of the soil treatment cell.

Figure A-38. Soil treatment cell construction at Area M.

Additional soil treatment units were constructed at Area M to serve as amendment infiltration basins for source area groundwater treatment. The units also serve as anaerobic landfarms to reduce the perchlorate in soil that was brought in from other areas at NWIRP McGregor. These soil cells also have the ability to store water, and provide a polishing of the FBR discharge if necessary. Soil Cell C was modified to include a liner as part of the FBR optimization discussed in the previous section. Figure A-39 shows the liner installation at Soil Cell C.

Figure A-39. Liner installation at Soil Cell C construction at Area M.

Summary

By the summer of 2005, more than 13,000 feet of PRBs, one FBR, several soil treatment cells, and more than 1300 bioborings had been installed at NWIRP McGregor. The biological approach to remediate perchlorate is well documented and proven at this site. The total cost of the remediation efforts at NWIRP McGregor has been in excess of \$20 million. These remediation efforts, which could not have been accomplished without the partnership between the Navy, TCEQ, EPA, and the Navy’s subcontractors, have allowed the facility to continue to be transferred to the city of McGregor for beneficial reuse.

Appendix B

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Appendix C

Acronyms and Abbreviations

ACRONYMS AND ABBREVIATIONS

AFB	Air Force Base
AFCEE	U.S. Air Force Center for Environmental Excellence
AMPAC	American Pacific Corporation
ANSI	American National Standards Institute
ARAR	applicable or relevant and appropriate regulation
AWWARF	American Water Works Association Research Foundation
BOD	biochemical oxygen demand
BV	bed volume
CEQA	California Environmental Quality Act
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CFR	Code of Federal Regulations
CLWA	Castaic Lake Water Agency
CMA	calcium magnesium acetate
COD	chemical oxygen demand
CRREL	Cold Regions Research Engineering Laboratory
CSB	condensed separator bottom
CSM	conceptual site model
CSTR	continuously stirred tank reactor
CTAC	cetyltrimethyl ammonium chloride
DC	direct current
DOC	dissolved organic carbon
DOD	(U.S.) Department of Defense
DOE	(U.S.) Department of Energy
DON	Department of the Navy
DPT	direct-push technology
DTSC	(California) Department of Toxic Substances Control
ECOS	Environmental Council of the States
EE/CA	Engineering Evaluation/Cost Analysis
EPA	(U.S.) Environmental Protection Agency
ERDC	(USACE) Engineer Research and Development Center
ERIS	Environmental Research Institute of the States
ESTCP	Environmental Security Technology Certification Program
FBR	fluidized-bed reactor
FDA	(U.S.) Food and Drug Administration
FF	fixed film
GAC	granular activated carbon
GET	groundwater extraction and treatment
HDPE	high-density polyethylene
HMX	high-melting-point explosive (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)
HRC™	Hydrogen-Release Compound
HRT	hydraulic residence time
HSC	(California) Health and Safety Code
IC	ion chromatograph(y)

IC/MS	ion chromatography/mass spectrometry
IC/MS/MS	ion chromatography/tandem mass spectrometry
IRCTS	Inactive Rancho Cordova Test Site
IRMS	isotope-ratio mass spectrometry
ISB	in situ bioremediation
ISM	interim stabilization measure
ITRC	Interstate Technology & Regulatory Council
IX	ion exchange
JPL	Jet Propulsion Laboratory
KDHE	Kansas Department of Health and Environment
LANL	Los Alamos National Laboratory
LC	liquid chromatography
LC/MS	liquid chromatography/mass spectrometry
LC/MS/MS	liquid chromatography/tandem mass spectrometry
LHAAP	Longhorn Army Ammunition Plant
LLNL	Lawrence Livermore Laboratory
m/z	mass-to-charge
MassDEP	Massachusetts Department of Environmental Protection
MCL	maximum contaminant level
MDC	McDonnell-Douglas Corporation
MMR	Massachusetts Military Reservation
MNA	monitored natural attenuation
MRL	minimum reporting level
MS	mass spectrometer
MSDS	material safety data sheet
MS/MS	tandem mass spectrometry
NASA	National Aeronautics and Space Administration
NAVAIR	(U.S. Navy) Naval Air Systems Command
NAVFAC	Naval Facilities Engineering Command
NCP	National Oil and Hazardous Substances Contingency Plan
NDEP	Nevada Division of Environmental Protection
NDMA	N-nitrosodimethylamine
NPDES	National Pollutant Discharge Elimination System
NPL	National Priorities List
NRC	National Research Council
NWIRP	Naval Weapons Industrial Reserve Plant
O&M	operation and maintenance
ORNL	Oak Ridge National Laboratory
ORP	oxygen reduction potential
OSHA	Occupational Safety and Health Administration
P&T	pump and treat
PBR	packed-bed reactor
PCB	polychlorinated biphenyl
PCE	perchloroethylene (tetrachloroethene)
PCR	polymerase chain reaction
PM	particulate matter

POTW	publicly owned treatment works
ppb	parts per billion
ppm	parts per million
PQL	practical quantitation level
PRB	permeable reactive barrier
QC	quality control
RCRA	Resource Conservation and Recovery Act
RDX	Royal Demolition eXplosive (hexahydro-1,3,5-trinitro-1,3,5-trizine)
RFI	Remedial Facility Investigation
RI/FS	Remedial Investigation/Feasibility Study
RO	reverse osmosis
ROD	Record of Decision
ROI	radius of influence
RWQCB	(California) Regional Water Quality Control Board
SCWO	supercritical wet oxidation
SERDP	(DOD) Strategic Environmental Research and Development Program
SF	surface flow
SSF	subsurface flow
SVE	soil vapor extraction
SWRCB	(California) State Water Resource Control Board
TCA	trichloroanisole
TCE	trichloroethylene
TCEQ	Texas Commission for Environmental Quality
TDS	total dissolved solids
T-GAC	tailored GAC
TNT	trinitrotoluene
TOC	total organic carbon
TPDES	Texas Pollutant Discharge Elimination System
UCMR	Unregulated Contaminant Monitoring Rule
UIC	underground injection control
USACE	U.S. Army Corps of Engineers
USGS	U.S. Geological Survey
UV	ultraviolet
VOC	volatile organic compound
WGOU	Western Groundwater Operable Unit
ZVI	zero-valent iron

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