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Risk Analysis, Communication, Evaluation, and Reduction at LANL

Perchlorate in Groundwater

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Perchlorate in Groundwater

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PREFACE

In 2003, Colorado State University (CSU) undertook an independent and comprehensive risk assessment for public health and the environment for chemicals and radionuclides associated with Los Alamos National Laboratory (LANL) operations. Risk Assessment Corporation (RAC) of Neeses, S.C., was selected to conduct the technical work as the primary, independent sub-contractor. The primary objective of the project will be the development of a stakeholder-based, risk-informed decision analysis framework to guide the reduction of risk. CSU is being supported by the University of California (UC) to conduct this work and to manage the project as an independent entity. CSU also will oversee the technical peer review process and convene a nationally recognized technical peer review panel to evaluate the approach and major deliverables of this project.

The purpose of this report is to assemble available information on perchlorate contamination in groundwater as background information for the RAC project. Current and past operations at LANL have employed perchlorate in two forms, perchlorate salts (of various forms but primarily magnesium, sodium, potassium and some ammonium) and perchloric acid ($HClO_4$). Monitoring for perchlorates at the LANL facility has revealed a legacy of contamination by this chemical in shallow, intermediate, and deep groundwater underlying the laboratory. Perchlorate was detected in 10 of the 14 samples collected from water-supply well Otowi-1 (O-1) in the regional groundwater aquifer in 2000 at an average concentration of 2.48 μg/L.

The potential effects of the perchlorate concentrations detected in Otowi-1 are uncertain. Guidance from the U.S. Environmental Protection Agency in 1999 indicated a provisional acceptable range for perchlorate in drinking water of 4 to 18 mg/L (EPA 1999), however, the drinking water limit continues to be the subject of EPA review. More recently (EPA, 2002a) the EPA derived a reference dose value which, when applied to a 70-kg person consuming 2 L of water per day, would result in a Drinking Water Equivalent Level (DWEL) of 1 μg/L (1 ppb) as a drinking water standard. A subsequent peer review for EPA questioned some of the assumptions that resulted in this reference dose. The EPA is reviewing the reference dose in light of the peer review comments and has also requested a study by the National Academy of Sciences. A final MCL is unlikely to be proposed by EPA before 2004. The final MCL could differ from 1 μg/L because these reviews may alter the reference dose and the MCL considers factors other than toxicity. The New Mexico Environmental Department (NMED) is proposing to add perchlorate to its list of toxic pollutants for groundwater and surface water this year (NMED, 2002).

Human health risks associated with perchlorate will need to be evaluated by the RAC team. The purpose of this paper is to provide general background information on perchlorate issues with respect to groundwater for use by the RAC team and LANL. The paper is intended to provide an overview of the national issue, biogeochemistry, toxicity, analytical methodologies, perchlorate issues at Los Alamos, and potential treatment approaches.

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GLOSSARY

ARA – Applied Research Associates
AWWARF – American Water Works Association Research Foundation
BGS – below ground surface
CAS – Chemical Abstract Service
CSU – Colorado State University
DoD – Department of Defense
DoE – Department of Energy
DWEL – drinking water equivalent level
EPA – Environmental Protection Agency
FBR – fluidized bed reactor
g/cm^3 – gram per cubic centimeter
g/L – gram per liter
GAC – granular activated carbon
GWRTAC – Groundwater Remediation Technology Analysis Center
HE – high explosives
HMX – octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
IC – ion chromatography
IPSC – Interagency Perchlorate Steering Committee
ISEP – ion separation process
ITRC – Interstate Technology and Regulatory Council
kg – kilograms
LANL – Los Alamos National Laboratory
LC/MS/MS – liquid chromatography and tandem mass spectrometry technique
MCL – maximum contaminant level
MCLG – maximum contaminant level goal
MDL – method detection limit
mg/L – milligrams per liter
mg/kg/day – milligrams per kg body weight per day
MMR – Massachusetts Military Reservation
NASA – National Aeronautics and Space Administration
NMED – New Mexico Environmental Department
NOM – natural organic matter
NPDES – National Pollutant Discharge Elimination System
NRC – Nuclear Regulatory Commission
NSF – National Science Foundation
O – Otowi
PCE – perchloroethylene
PPB – parts per billion
PRB – permeable reactive barrier
PRM – perchlorate-reducing microbes
RAC – Risk Assessment Corporation
RDX – hexahydro-1,3,5-trinitro-1,3,5-trizine
RfD – reference dose
RLWTF – Radioactive Liquid Waste Treatment Facility

RO – reverse osmosis
SCWO – supercritical water oxidation
SDWA – Safe Drinking Water Act
TA – Technical Area
TCA – trichloroethene
TCE – trichloroethylene
TDS – total dissolved solids
TNT – trinitrotoluene
UCMR – Unregulated Contaminant Monitoring Rule
μg/L – micrograms per liter
US – United States
USGS – U.S. Geological Survey
VOCs – volatile organic compounds
TSH – thyroid-stimulating hormone

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1.0 Perchlorate Overview

In 1997 perchlorate, an unregulated compound associated with many military applications, was found to be threatening the water supplies of 12 million people in the western United States (U.S. Environmental Protection Agency (EPA) 1999). The concern was triggered when elevated levels of perchlorate were discovered in California drinking-water supplies as a result of new analytical capabilities. With evidence indicating perchlorate may cause child developmental problems and thyroid cancer, water suppliers took many drinking-water wells out of service as a precautionary measure. When the perchlorate issue first became a concern in 1997, it was compounded by the fact that there were no proven treatment technologies for removal of perchlorate from public drinking-water supplies.

The high-profile publicity surrounding perchlorate in the western states coupled with the lack of proven treatment technology prompted congressional funding to study the problem further. At present, perchlorate contamination in groundwater is being addressed in 20 states (Roote 2001; Logan 2001). A large body of information is available on the treatability of perchlorate in groundwater with many technologies capable of removing perchlorate to detection limits. Nevertheless, this chemical continues to present significant challenges to field investigations and remediation specialists. This is largely due to the anion's persistence, high solubility, and limited propensity to adsorb, which enable it to move with groundwater and create large contaminant plumes. There is currently no federal primary drinking-water regulation for perchlorate. As detection limits decline and the debate over the safe limit for perchlorate continues, public water suppliers and treatment engineers are faced with many challenges. These concerns fuel research efforts to better understand the human and ecological effects, refine analytical methods, and fully develop efficient, cost-effective strategies for removing perchlorate from groundwater. This paper provides an overview of current information with respect to perchlorate chemistry, analytical methods, regulatory issues, and treatment approaches as they relate to the groundwater issues at Los Alamos National Laboratory (LANL).

2.0 Perchlorate in Groundwater at Los Alamos

Environmental releases of treated and untreated effluents have occurred at a variety of locations as a result of activities at LANL dating back to the Manhattan Project (LANL 2002a). According to a Perchlorate Issues Update prepared by LANL (LANL 2003a), perchlorate first surfaced as an issue in 1999 when EPA required drinking water monitoring under the Unregulated Contaminant Monitoring Rule (UCMR). Perchlorate continues to be used in current laboratory operations requiring treatment and monitoring of wastewaters at the facility in accordance with the National Pollutant Discharge Elimination System (NPDES). Extensive efforts have taken place at the lab to manage the use, handling, treatment and ultimate disposal of perchlorate at numerous technical areas within the facility (TA-3, TA-9, TA-35, TA-43, TA-46, TA-48, TA-50, TA-53, TA-55, and TA-59).

The detection of perchlorate in shallow, intermediate and deep groundwaters underlying the Lab has prompted extensive monitoring of this compound as part of Environmental Surveillance activities at Los Alamos (LANL 2002a). Current and past handling of perchlorate-containing materials, the discharge of unregulated waste effluents, and vapor-phase releases of perchlorate are described in Los Alamos National Laboratory Perchlorate Issues Update (LANL 2003a). LANL has pulled together a team of experts from across the Laboratory to gather background information. The following is a brief synopsis of LANL's current understanding of the distribution of perchlorate at the LANL facility and surrounding area adapted from LANL (2003a). This information is relevant to addressing human health issues associated with perchlorate in groundwater, drinking water supply wells, surface water, and springs.

Pajarito Canyon, Water Canyon, and Cañon de Valle High Explosive (HE) Corridor: Since the early 1940s, wastewater and contaminated stormwater generated within the HE corridor have been discharged into these canyons through a number of outfalls. Historically, the effluent was not treated to remove perchlorate. In 1997 nineteen HE outfalls were eliminated. Recent effluent samples at the High Explosives Waste Water Treatment Facility (HEWTF) show a range of perchlorate concentrations from 4 to 58 μg/L (LANL (2003a). LANL (2003a) reports that soils from firing and rockets have been contaminated from burning and past experiments. Stormwater that comes in contact with this soil may pose another source of perchlorate and mechanism for transport.

Mortandad Canyon: Perchlorates in treated effluents from actinide research were discharged into Mortandad canyon for a period of approximately 40 years. In 2002, ion exchange treatment was added at the Radioactive Liquid Waste Treatment Facility (RLWTF) at TA-50 to remove perchlorates. In 2000 and 2001, the annual average concentration of perchlorate in the RLWTF effluent was 254 μg/L and 169 μg/L, respectively. Perchlorate levels ranging from 140 μg/L (perched groundwater) to 400 μg/L (unsaturated water extracted from core sample) have been detected in samples of groundwater from the perched intermediate zone. Perchlorate was detected in alluvial groundwater at concentrations up to 280 μg/L in 2000.

Acid Canyon (tributary of Pueblo Canyon): Acid Canyon was the original disposal site for liquid wastes generated by research on nuclear materials for the World War II Manhattan Atomic Bomb Project at TA-1. Wastewater from actinide research at TA-1 was discharged untreated from 1943 to 1951 and was discharged after treatment at TA-45 from 1951 to 1964. The effluents likely contained perchlorate at concentrations similar to TA-50. Perchlorates at concentrations of about 2 to 4 ug/l have been detected in water supply well Otowi-1 (O-1) in Pueblo Canyon.

DP Canyon: Effluent from actinide research (the plutonium processing facility at TA-21) was released from 1952 to 1986. The effluents likely contained perchlorate at concentrations similar to TA-50. Perchlorate concentrations of 200 to 1000 ppb have been detected in core samples extracted during the drilling of well LADP-4 downgradient from TA-21 according to LANL (2003). The report is ambiguous as to whether these

samples were of water extracted from the core (i.e., concentration in μg/L) or of the soil core itself (i.e., concentration in μg/kg).

Pajarito Canyon: Numerous accidental waste spills and intentional releases of waste materials occurred at TA-35 in the 1950s and 1960s. In 2003, high explosives wastewater, from the Anchor East Site (TA-9), has been recently analyzed and found to have perchlorate concentrations of over 500 μg/L.

Ten Site Canyon (tributary to Mortandad Canyon): Partially treated wastewater from the Ten Site Wastewater Treatment Plant (TA-35) was released as a result of spills and operational problems encountered from 1951 to 1963.

Rio Grande Springs: Perchlorate has been detected at concentrations near or below method detection limits in water samples collected from springs along the Rio Grande (lowest reported of 1.29 ug/L at Spring 5 to highest reported of 6.62 ug/l at Spring 4B by LANL 2002a). LANL (2003a) has raised questions regarding the certainty of the analytical methodology employed in the analysis of these samples. The New Mexico Environment Department insists that the samples are valid and that perchlorate is indeed found in these springs (McQuillan et al., 2003).

3.0 Perchlorate as a National Issue

Soon after the development of an analytical method for the detection of perchlorate in aqueous samples in April 1997, the substance was detected in a variety of environmental settings. In military applications perchlorate compounds are used in solid fuels for rockets and missiles, military and commercial munitions, explosives, blasting agents, and nuclear reactors. The use of perchlorate is widespread in industry; perchlorate is used as an additive in lubricating oils, leather finishing, dyeing, electroplating, aluminum refining, rubber manufacture, fertilizer, and the production of paints and enamels (EPA 1999). Perchlorate is rarely found naturally with one natural source identified in Chile (as a component in potassium nitrate). The U.S. Geological Survey (USGS) and the Air Force Research Laboratory have identified potassium perchlorate in samples of sylvite in New Mexico (Harvey 1998 as cited by Urbansky 2001). The EPA has identified perchlorate users and manufacturers in 44 states and environmental releases (of unspecified magnitude and character) in 20 states. Logan (2001) estimates that in 1999 perchlorate contaminated the water supplies of nearly 15 million American people, mostly in California and Nevada. Maher (2002) reports that tests of over 4000 drinking-water sources in California detected perchlorate in 255 wells, of which 49 showed concentrations above 18 μg/L. In New Mexico, two public drinking water supplies are reported to contain concentrations of perchlorate: Clovis at 5 μg/L and Deming at 16 μg/L (LANL 2003a). More contaminated areas may be identified with additional environmental testing. A map showing the distribution of identified perchlorate release sites in the United States is shown in Figure 1.

Concerns over the presence of perchlorate in drinking-water supplies touched off a nationwide effort in 1998 to facilitate and coordinate the retrieval of accurate information

concerning perchlorate. Attention was devoted to the following technical issues: perchlorate occurrence, health effects, analytical detection, ecological impacts, waste stream handling, and treatability. The Interagency Perchlorate Steering Committee (IPSC), chaired by the EPA and Department of Defense (DoD), was formed to bring together government representatives as well as affected state, tribal, and local governments to create information-transfer links for interagency and intergovernmental activities addressing the perchlorate issues. The IPSC has representatives from more than 20 different government agencies (IPSC 1998).

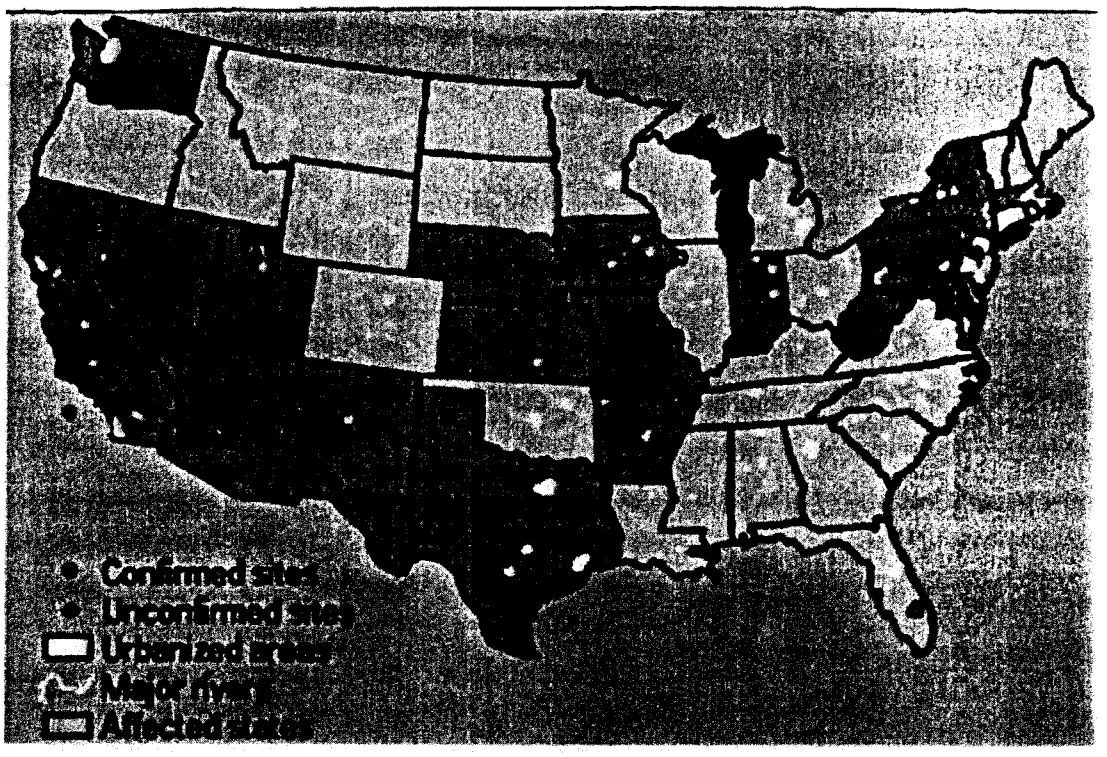

Figure 1. Perchlorate Releases in the United States (Source: Logan 2001; EPA 1999).

Numerous treatability studies have been conducted since 1997 on both waste streams and groundwater containing perchlorate. In waste streams, perchlorate concentrations are usually elevated—500 to 10,000 mg/L or more. In contrast, in groundwater or surface water, perchlorate concentrations tend to be low—between 5 μg/L and 500 mg/L (Roote 2001). While several technologies have been demonstrated to be useful for treatment of waste streams, the low concentrations in groundwater and surface water have posed particular challenges for a number of standard treatment technologies. Technologies to treat low levels of perchlorate are further discussed below.

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4.0 Perchlorate Biogeochemistry

Perchlorate is the nonvolatile, anionic component of solid salts of ammonium, sodium, or potassium perchlorate. The perchlorate anion's high solubility in water coupled with its limited propensity to adsorb to most soil surfaces leads to high mobility in aqueous environments. Perchlorate can persist in the environment for many decades under typical groundwater conditions because of its resistance to reactions with other available constituents in the subsurface. The chemical properties of perchlorate set it apart from the other halogenated chemicals such as trichloroethene (TCA), trichloroethylene (TCE), and perchloroethylene (PCE) that are commonly a problem in groundwater.

Dilution and precipitation are considered to be the two most important processes influencing the fate and transport of perchlorate in natural aqueous environments (ITRC 2002). Sorption is not expected to be a significant factor in attenuating perchlorate since both soil particles and perchlorate are negatively charged. The accepted mechanism for perchlorate adsorption to soil particles is through outer-sphere complexes, where the ions engage in simple electrostatic bonds (Vanderwaals) and serve to balance electric charge on the surface (Sparks 1995; Sposito 1994). These adsorption processes are often influenced by pH, soil mineralogy, organic content, ionic strength, and competing ions (Urbansky and Schock 1999; Urbansky 2002). The chemical properties of perchlorate compounds are summarized in Table 1 (reproduced from ITRC 2002). The ionic salts of perchlorate are extremely soluble in water. Salts of perchlorate have different solubility in water, with potassium perchlorate being the least soluble.

Flowers and Hunt (2000) explain that, depending on site release history, perchlorate can be distributed in the subsurface as a source area of undiluted perchlorate-contaminated brine, along with a plume of more dilute perchlorate-contaminated groundwater. Perchlorate ions are very dense, so concentrated solutions tend to sink in slow-moving liquids (Parr 2002). This phenomenon should be considered during characterization and remediation of contaminated aquifers. ITRC (2002) noted that in high enough concentrations, perchlorate will precipitate out of solution, but the salts formed will re-dissolve readily.

Perchlorate is thermodynamically a strong oxidizing agent, with chlorine in the +7 oxidation state. However, it is unreactive toward most abiotic reducing agents in cold and dilute environments (Tofan et al. 2000). In contrast, a body of research has evolved that demonstrates that perchlorate is vulnerable to biotically induced reactions (Coates et al. 1999; Hatzinger et al. 2000). Specifically, perchlorate can be used as an electron acceptor in biologically mediated reactions under reducing conditions and be reduced to chlorate and, ultimately, chloride. The most common natural degradation pathway for perchlorate is respiratory microbial reduction. For this to occur oxygen and nitrate must be depleted and an appropriate electron donor must be present. As such, if reducing conditions exist or can be created in a perchlorate-contaminated aquifer, biotransformation of perchlorate into its less-toxic reaction products may occur. This phenomenon holds promise as a means to remove perchlorate from contaminated aquifers using in-situ bioremedial approaches.

Site characterization is crucial to the evaluation of remediation alternatives for perchlorate-contaminated groundwaters. Settings such as river and stream valleys, fractured rock, and karst strata offer many challenges to identifying effective economical remediation alternatives. Fate and transport modeling should be developed according to site-specific field conditions. The National Science Foundation has sponsored a Swiss/U.S. team to develop models to describe solute interactions and transport of perchlorate in subsurface environments (Selim 1988). A Porous Media Flow Code Development program has been conducted at LANL to support modeling of the transport of dissolved materials in the subsurface on and near the LANL facility (LANL 2003 b).

Table 1. Chemical Properties of Perchlorate Compounds (ITRC 2002)

Properties	**Ammonium Perchlorate (NH_4ClO_4)**	**Potassium Perchlorate ($KClO_4$)**	**Sodium Perchlorate ($NaClO_4$)**	**Perchloric Acid ($ClHO_4$)**
CAS No.	7790-98-9	7778-74-7	7601-89-0	7601-90-3
Molecular Weight	117.49	138.55	122.44	100.47
Color/Form	White orthorhombic crystal	Colorless orthorhombic crystal or white crystalline powder	White orthorhombic crystal	Colorless oily liquid
Taste/Odor	Odorless	Slightly salty taste	Odorless	Odorless
Density/Specific Gravity	1.95 g/cm^3	2.53 g/cm^3	2.52 g/cm^3	1.67 g/cm^3
Solubility	200 g/L @ 25°C	15 g/L @ 25°C	2096 g/L @ 25°C	Miscible in cold water
Sorption Capacity	Very low	Very low	Very low	Very low
Volatility	Nonvolatile	Nonvolatile	Nonvolatile	Volatile
Octanol/Water Partition Coefficient (log KOW)	-5.84	-7.18	-7.18	-4.63
Vapor Density (Air=1)	No information	4.8	No information	3.5
Note: no vapor pressure or evaporation rate information is available for these compounds.				

5.0 Perchlorate Toxicity

Concern over perchlorate stems from its potentially toxic effects. Fifty years ago, Standbury and Wyngaarden (1952) and Wyngaarden et al. (1952) reported the inhibitory effect of perchlorate upon the accumulation and retention of iodide by the human thyroid gland. The perchlorate ion is of similar ionic size to iodide. Because of this similarity, perchlorate

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competitively inhibits the active transport of iodide into the thyroid gland and also stimulates the discharge of unorganified iodide from the thyroid (Wolff 1998; Stanbury and Wyngaarden 1952).

This discovery had immediate therapeutic application, and potassium perchlorate began to be used to treat thyrotoxicosis, including Graves' disease. More recently, perchlorate has been used (alone or in combination with other anti-thyroid drugs) to treat amiodarone-induced throtoxicosis, a condition in which an underlying thyroid abnormality is unmasked when the iodine-containing drug amiodarone is given to control cardiac arrhythmia (Dollarhide 2002). Although perchlorate has been used in clinical treatment for some time, very few data suitable for risk assessment purposes were available until recently. Many studies have examined the effects of perchlorate in Graves' patients but few have studied the effects in normal humans.

The toxicity of perchlorate at low, nontherapeutic dose levels has become an area of intense research in the past 5 years. Perchlorate is known to exert its effect not by reacting with organs or cells, but by impeding normal cellular processes. Cells in the thyroid gland (as well as the salivary and gastric glands) possess an iodide pump that brings iodide ions into the cell for subsequent generation of iodinated hormones necessary for normal body function. The pump discriminates among anions on the basis of size. Perchlorate interferes with this process by competing for uptake and blocking the uptake of iodide, resulting in decreased thyroid hormone (T4). As a result of decreased T4 production, the pituitary gland releases more thyroid-stimulating hormone (TSH), causing the thyroid to grow.

In adults, the thyroid helps to regulate metabolism. In children, the thyroid plays a major role in proper development in addition to regulating metabolism. Impairment of thyroid function in expectant mothers may impact the development of the fetus and newborn and result in effects including changes in behavior, delayed development, and decreased learning capability. Changes in thyroid hormone levels may also result in thyroid gland tumors.

In 1997, an independent peer review panel was convened (funded by the U.S. Department of Defense and the Perchlorate Study Group, which is a coalition of aerospace, defense, chemical, and other industries that use or manufacture perchlorate) that evaluated the suitability of the perchlorate database for developing a reference dose (RfD) for chronic environmental exposure by the oral route. Overall, the panel concluded that the database for perchlorate was insufficient to support the development of an RfD (Dollarhide 2002). The studies that were conducted in normal humans did not look at long-term exposure to perchlorate. Long-term studies in animals clearly show thyroid toxicity at high doses, but generally these studies did not examine targets other than the thyroid. In summary, the perchlorate database defined the mechanisms by which perchlorate acts on the thyroid but provided little information on the dose-response of perchlorate or the likely effects in normal humans after chronic exposures to low doses. Questions left unanswered by the existing data included the shape of the dose-response curve in humans, the effects of perchlorate after long-term exposure, and the possibility of effects in organs or systems other than the thyroid.

The independent panel recommended that additional studies of perchlorate be conducted. As a result of this recommendation, a second panel of risk assessors, perchlorate experts, and thyroid experts was convened to develop a prioritized list of toxicological studies to be conducted under current U.S. EPA guidelines. Since that time, a battery of studies have been conducted and either published or submitted to regulatory agencies in order to support risk assessment activities for perchlorate. Available animal studies include developmental neurotoxicity, 90-day rat toxicity, rabbit developmental toxicity, rat developmental toxicity, rat two-generation reproductive toxicity, developmental brain morphometry in rats, developmental motor activity in rats, mutagenicity/genotoxicity, and a variety of predictive immunotoxicity assays in both mice and rats all conducted under current U.S. EPA guidelines. In addition, the kinetics of perchlorate has been studied in male rats, pregnant and lactating rats, and fetal rats. Several human studies have been published as well, including occupational studies, epidemiology studies in neonates and school age children, and clinical studies in adults (Dollarhide 2002). Under contract to the U.S. Department of Defense and the Perchlorate Study Group, Toxicology Excellence for Risk Assessment (TERA) has used these data to develop a proposed reference dose of 0.002 mg/kg/day, based on a critical effect of decreased serum T4 levels (Dollarhide 2002).

At approximately the same time that TERA was conducting its analysis of the new data, the EPA completed its draft toxicity assessment for perchlorate (EPA 2002a). Both noncancer and cancer health effects were considered to derive a single oral risk benchmark based on precursor effects for both neurodevelopmental and thyroid neoplasia. Both of these are historically established effects of perturbations of the hypothalamic-pituitary-thyroid feedback system. The draft assessment concluded that the potential human health risks of perchlorate exposure include interference with iodide uptake and disruption of normal thyroid function, impacts to the developing nervous system in the fetus and newborn, and tumor formation. A draft oral reference dose of 0.00003 mg/kg/day for the perchlorate ion was provided in this document. This value should be adjusted by a factor of 0.72 for any salt of perchlorate. This reference dose value results in a derived drinking water equivalent level (DWEL) of 1 μg/L (1 ppb) (assuming a body weight of 70 kg and an ingestion rate of 2 L of water per day).

EPA conducted an independent peer review of their draft toxicity assessment for perchlorate (EPA 2002b). The published report on this peer review questioned several elements of the assessment, including how human health data had been used and the application of uncertainty factors in developing the draft oral reference dose. EPA is currently addressing issues raised by peer reviewers before finalizing the toxicity assessment. Additionally, EPA requested in March 2003 that the data and findings be submitted to the National Academy of Sciences for review. This review is expected to take several months.

6.0 Regulation of Perchlorate in Groundwater

Perchlorate was placed on EPA's Safe Drinking Water Act Contaminant Candidate List in 1998 (EPA 1998). In 1999 EPA required monitoring of drinking water for perchlorate under the Unregulated Contaminant Monitoring Rule (UCMR). Under UCMR all large public water supplies and a representative sample of small public water supplies are required to monitor

perchlorate over the next two years (EPA 2003a). The U.S. Geological Survey is monitoring for perchlorate in surface waters. As of this date no federal primary drinking-water standard for perchlorate has been set.

The EPA named perchlorate a contaminant of concern after studies linked the chemical to thyroid disorders and other potential health problems. The health impact of perchlorate at low doses remains unresolved. Since 1992, the EPA has recommended a series of safe drinking-water levels of perchlorate ranging from 4 to as high as 31.5 µg/L (EPA 1999, 2003c) based on their evolving understanding of perchlorate toxicity. As noted above, the EPA is currently in the process of developing appropriate drinking-water and clean-up standards for perchlorate (U.S. EPA 2002a). EPA's most recent draft toxicological review of perchlorate (EPA, 2002a) provides an interim RfD of 0.00003 mg/kg/day for the perchlorate ion. This value should be reduced by a factor of 0.72 for any salt of perchlorate. This reference dose value results in a derived DWEL of 1 µg/L (1 ppb). This 2002 study has undergone peer review (EPA 2002b) and questions raised by peer reviewers regarding interpretation of data are still being evaluated by EPA.

In the interim before the EPA establishes a final RfD and sets a regulatory limit for perchlorate in drinking water, several states have set temporary or interim standards (see Table 2). As shown, a number of states have chosen limits close to the current analytical detection limit of perchlorate as discussed in Section 7 below. The uncertainty associated with safe levels of perchlorate contributes to the challenges faced by engineers and scientists at a number of sites.

Table 2. Standards and Guidance Concentration Levels Currently Set for Perchlorate (ITRC 2002)

State/Agency	Drinking Water (µg/L)	In-situ Remediation Level (µg/L)
Arizona	31	14
California		4
Massachusetts	1.5	
New Mexico		1 (?)
New York	5	
Nevada	18	18
Texas	22	4
USEPA Draft Toxicological Assessment	1	
EPA Region 1		1.5
EPA Region 9	4	

7.0 Analytical Methods for Perchlorate

Extensive monitoring for perchlorate began in the late 1990s as a result of the Unregulated Contaminant Monitoring Rule (UCMR). Perchlorate was found in public water supplied to 12 million people in the western United States (EPA 1999). EPA Method 314, employing ion chromatography (IC), is the accepted protocol for analysis of perchlorate in contaminated groundwater. This method has a detection limit of 4 μg/L in natural waters (LANL 2003a). Detections of perchlorate in water supplies at levels below this detection limit have challenged water suppliers and remediation engineers addressing perchlorate issues. Furthermore, uncertainty regarding the safe level and the ultimate discharge limit (1 to 18 μg/L) has created a demand for the ability to accurately and reliably measure levels of perchlorate less than 1 μg/L. .

7.1 Monitoring Programs at LANL

The monitoring program for perchlorate at Los Alamos was prompted by the discovery of this contaminant in California drinking water supply wells. The Los Alamos monitoring program includes a variety of environmental samples including groundwater, surface water, water supply wells, as well as monitoring wells included in the Hydrogeologic Work Plan (LANL, 1998). In 2000, the presence of perchlorate in water supply well Otowi-1 (O-1) was discovered at a concentration of 3.5 μg/L. Monitoring since 2000 has confirmed the presence of perchlorate in O-1 at concentrations ranging between 2 and 4 μg/L. As a result of these detections, a monthly monitoring schedule was established for O-1 along with PM-1, PM-2, PM-3, PM-4, and PM-5, while a semiannual monitoring schedule is used for the remaining six water supply wells (LANL 2003a).

LANL (2002a, 2003a) reported many difficulties in reliably measuring perchlorate in groundwater at concentrations below 4 μg/L. Analytical problems were attributed to the clean-up steps required in Method 314 to lessen the occurrence or interference from other ions. Variability in the performance of these clean-up steps between laboratories in many cases accounts for a background signal above zero and "false positives" in the range of 1 to 4 μg/L. The limits of the approved EPA Method 314 prompted LANL to investigate new methods for analyzing perchlorate at levels below 1 μg/L (see 7.3 for description).

7.2 Monitoring Programs at Other Sites

Investigators at other perchlorate-contaminated sites have encountered similar issues in monitoring for perchlorate. Detection limits for perchlorate below 4 μg/L are being achieved as part of a massive study and clean-up effort underway for the last several years at the Massachusetts Military Reservation (MMR) on Cape Cod. MMR is a 21,000-acre facility located in the coastal towns of Bourne, Falmouth, Mashpee, and Sandwich in Barnstable County, Massachusetts. Contamination of soil and groundwater exists over large areas of the site as a result of explosives training and demolition-disposal activities.

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Because of increasing concerns about potential adverse health effects of perchlorate in drinking water and the possibility that munitions containing perchlorate had been used at MMR, the EPA directed the National Guard to begin sampling for perchlorate in groundwater in the year 2000 (AMEC 2002). EPA Method 314 is being used to analyze for perchlorate in groundwater samples. At the time the perchlorate-monitoring program for groundwater was being developed at MMR, most commercial laboratories using Method 314 could achieve a Method Detection Limit (MDL) for perchlorate in water of 4 µg/L. The MMR-specific Action Level of 1.5 µg/L prompted the need for the contract lab to lower the MDL. Subsequent studies were performed that allowed for reductions in the MDL for perchlorate in groundwater. Table 3 shows the different MDLs used at MMR and corresponding dates these MDLs were employed.

Table 3. Chronology of Method Detection Limits (MDLs) for Perchlorate in Groundwater at MMR

Method	MDL (µg/L)	Date
Method 314	1.5	8/00 – 9/01
Method 314	0.85	10/01 – 11/01
Method 314	0.35	11/01 – 7/02
Method 314	0.35 to 0.43	7/02 – present

7.3 New Developments in Perchlorate Analysis

LANL is in the process of developing a new low-level analytical technique for perchlorate called liquid chromatography/mass spectrometry/mass spectrometry (LC/MS/MS). This method is under development and has not been approved by EPA for perchlorate analysis. The two MS steps serve as a confirmation for the presence and level of perchlorate. LANL (2003a) indicates the proposed Method Detection Limit is 0.05 µg/L and the Reporting Limit is 0.15 µg/L. The method works well across a range of natural water chemistry, but problems with the internal standard have been encountered. Steps have been taken by LANL to resolve this difficulty and a performance evaluation of the LC/MS/MS method is planned before it is employed for low-level perchlorate analysis at the site. The performance evaluation should be completed in the summer of 2003. EPA's Office of Water is reviewing the method.

Applied Research Associates (ARA 2000) has also developed a new field method for measuring perchlorate. The method involves ion pair pre-concentration with a colorimetric assay on the pre-concentrate (Thorn 2003). The field method has been used in prescreening of samples prior to confirmation analysis. The ARA method has been employed in field and lab testing of groundwater remediation equipment for real-time assessment of system performance. This field method is being employed at MMR and is reported to achieve a MDL of less than 1 µg/L.

8.0 Treatment Approaches for Perchlorate in Groundwater

Perchlorate contamination in groundwater is being addressed at numerous sites throughout the United States (Roote 2001; Logan 2001). Site investigators, site remediation engineers, and municipalities have encountered many challenges in defining contaminated areas, mitigating uncontrolled releases, and ensuring safe drinking water is supplied to the public. The best approach to managing perchlorate in groundwater is site specific as each site has a unique location, history, and hydrogeologic setting. Human health and ecological concerns are also site dependent. Concerns relating to human health are typically managed through source control, source remediation, groundwater remediation, wellhead treatment and in some cases point of use treatment. A large body of information is available on the treatability of perchlorate in groundwater with many technologies capable of removing perchlorate to detection limits. Nevertheless, this chemical continues to present significant challenges to field investigators and remediation specialists.

A number of treatment technologies have been demonstrated to be useful for treatment of perchlorate in waste streams. However, to date, technologies for the removal of low levels of perchlorate (in the single parts per billion) from groundwater are largely unproven. Great strides are being made to develop reliable, cost-effective technologies to address cases where perchlorate contamination threatens the integrity of public water supplies. Because of perchlorate's unique physical and chemical properties, its removal from groundwater cannot be achieved using conventional water-treatment technologies such as air stripping, filtering, and sedimentation. Furthermore, the ion is only weakly removed by activated carbon (ITRC 2002).

The optimum treatment technology for a particular perchlorate contamination site may depend on several factors, including perchlorate concentration, the presence and concentration of co-contaminants, other water-quality parameters (including pH, alkalinity, natural organic matter (NOM), total dissolved solids (TDS), metals, etc.) and geochemical parameters (nitrate, sulfate, chloride, dissolved oxygen, redox potential, etc). The presence of perchlorate-reducing microbes (PRM) and substances inhibitory to PRM activity will influence perchlorate treatment technology effectiveness. For in-situ treatment of perchlorate contamination, variables related to the site and hydrogeologic setting, such as depth, distribution of contaminants, soil permeability, and groundwater flow velocity are also important factors to consider.

Perchlorate treatment technologies may be classified into two categories: removal technologies and destruction technologies (ITRC 2002). Removal technologies include membrane filtration (reverse osmosis and nanofiltration), ion exchange, electrodialysis, and tailored carbon. Destruction technologies include chemical reduction, thermal oxidation, and biological treatment. Removal technologies all require subsequent processing of perchlorate residuals. The National Research Council reported that natural attenuation of perchlorate has a low likelihood of success given the current level of understanding (NRC 2000). An engineered approach is therefore needed to manage the contaminant.

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The following sections provide an overview of technologies specific to perchlorate treatment and do not address the treatment of groundwater that includes a mixture of contaminants. It should be noted, however, that perchlorate often is found in groundwater with a variety of co-contaminants. At sites where contamination has resulted from production or testing of weapons devices (solid propulsion, explosive devices, or pyrotechnic), typical co-contaminants will include volatile organic compounds (VOC), halogenated solvents, and explosive compounds such as trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-trizine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). The most common co-contaminates at these sites are nitrate and sulfate. The presence of these and other compounds in contaminated groundwater will influence the choice of appropriate treatment technologies. At Los Alamos, perchlorate is present in groundwater in combination with a variety of radionuclides as well as nitrate.

The Groundwater Remediation Technology Analysis Center (GWRTAC) published a technology status report for perchlorate treatment technologies (Roote 2001). The report describes perchlorate removal technologies that have been investigated or deployed full-scale. The database includes information on 65 perchlorate treatment technology projects. Table 1 of the GWRTAC report contains a summary of pertinent information on these studies. Of the 65 studies in the database, 47% are laboratory, 40% are pilot, and 11% are full-scale. Approximately 53% of the studies have been completed. The applicability of a treatment technology for a particular application depends on wastewater quality requirements, the volume of water to be treated, contaminant concentration, presence of co-contaminants, and site-specific, hydrology and geochemical conditions.

8.1 Perchlorate Removal Technologies

As mentioned above, a number of technologies have been evaluated for removal of perchlorate from groundwater, including membrane filtration, ion exchange, and tailored carbon. These treatment techniques all involve subsequent processing of perchlorate treatment residues. The following sections describe the treatment technologies in greater detail.

8.1.1 Membrane Filtration

Nanofiltration and reverse osmosis (RO) are forms of filtration employing a membrane to preferentially remove chemicals from solution. Nanofiltration and RO will effect sufficient removal of perchlorate but cost information is largely lacking (Urbansky 1998). The Metropolitan Water District of Southern California indicates that nanofiltration can reduce perchlorate concentrations from 18 μg/L to less than 4 μg/L in a contaminated surface water supply. Membrane filtration technologies will require subsequent disposal of more concentrated side streams. The potential for fouling of membranes in municipal treatment systems have raised questions on the practicality of employing this technology for water supplies . RO treated water would likely need to be remineralized to prevent degradation of the distribution system and render the water palatable. These technologies are likely best suited for point of use.

8.1.2 Ion Exchange

Ion exchange is a physical-chemical process by which ions are transferred from the liquid phase to the solid phase. Ions held by electrostatic forces to charged functional groups on the surface of the solid are exchanged for ions of similar charge in a solution in contact with the solid (Mihelcic 1999). Ion exchange treatment depends upon a selected exchange resin to remove anions or cations from a contaminated liquid. When the ion-exchange capacity of the resin is exhausted, the column is regenerated producing a concentrated waste stream in need of further treatment or disposal. It should be noted that non-regenerable resins also have been developed for removal of perchlorate. After the capacity of the resin is reached, the non-regenerable resins are removed for off-site disposal. A benefit of using non-regenerable resins is that the treatment-vessel configuration is essentially the same as for widely-used granular activated carbon (GAC) treatment, thus reducing design and materials costs. Non-regenerable resins may find application for temporary treatment applications or emergency situations. Many studies have been directed toward the use of ion exchange technology for the removal of perchlorate from water. Of the removal technologies, ion exchange is the only technology that has been employed full-scale for drinking-water applications involving perchlorate. A challenge with ion exchange is to identify ion-exchange resins that selectively remove perchlorate when other anions (notably chloride, sulfate, and bicarbonate) are present at higher concentrations.

Calgon Carbon Corporation has developed a counter-current ion separation process (ISEP process) that selectively removes low concentrations of perchlorate from groundwater (Venkatesh et al. 2000). The combined process has been demonstrated in California's Big Dalton site and is able to reduce perchlorate concentrations in groundwater from 76 μg/L to below detectable levels (4 μg/L) at a flow rate of 2,500 gallons-per-minute (gpm). Furthermore, the firm has developed a catalytic process that destroys the perchlorate in the concentrated brine produced by the separation process. The California system is operating , and Calgon has reportedly received a permit from the State of California to release the treated water to municipal water distributors for human consumption (Calgon 2000).

Another company, Applied Research Associates, Inc., has coupled an ion exchange process for perchlorate removal from groundwater with a hydrothermal/thermal treatment process to destroy the concentrated perchlorate in the brine (Roote 2001).

Finally, Oak Ridge National Laboratory and the University of Tennessee have developed a "bifunctional" anion exchange resin/tetrachloroferrate regeneration process that has been tested at the field-scale level (Gu et al. 2000, 2001). The process is reportedly highly selective for perchlorate and does not require groundwater pretreatment to remove dissolved organic matter or competing anions (such as chloride, sulfate, bicarbonate, or nitrate). The regeneration process is cost effective while generating minimal secondary wastes.

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8.1.3 Electrodialysis

The technology employs the application of direct current potential across an ion permeable and selective membrane. This process separates the ionic species from the aqueous solution, which requires the disposal of a more concentrated solution (containing the removed ionic species) (Hernon et al. 1994). No demonstration projects for removal of perchlorate were found.

8.1.4 Tailored Granular Activated Carbon

Adsorption is a natural process in which molecules of a liquid or gas are attracted to and then held on the surface of a solid. Adsorption treatment technologies take advantage of this natural process to remove undesired chemicals. The adsorbent most commonly used in treatment is granular activated carbon (GAC).

In GAC treatment, water to be treated comes in contact with the carbon by flowing through one or more packed bed absorbers. A packed bed absorber is simply a column packed with GAC. Organic pollutants in the water are attracted to and held on the surface of the carbon. Compounds are removed from water but are not destroyed. Once the micropore surfaces of the adsorbent (GAC) are saturated with organics, the adsorptive capacity of the GAC is exhausted and the concentration of constituents in the effluent increases. This process is referred to as breakthrough. Once breakthrough occurs, the carbon must be removed and replaced with either fresh or regenerated carbon. The single most critical operating parameter for activated carbon adsorption processes is the time it takes for breakthrough to occur. Activated carbon can be somewhat compound-specific. In other words, GAC does not remove all organic compounds equally well. GAC works best for low-solubility, high molecular weight, non-polar branched compounds. The effectiveness of liquid phase carbon adsorption and the loading that is possible (mass of constituents adsorbed/mass of carbon) is determined through adsorption isotherms.

GAC technology has been widely applied for the removal of many organic compounds from contaminated groundwater. In the typical application, approximately 10,000 bed volumes can be processed through an absorber before breakthrough occurs. In full-scale plants, carbon replacement is infrequent and often takes months or years (Cannon 2002), resulting in an economical treatment alternative.

Currently, there is limited experience in the application of GAC for the removal of perchlorate from groundwater. Research conducted at Pennsylvania State University (Cannon and Chongzheng 2000) has shown that conventional activated carbon does have a limited ability to remove perchlorate from water. However, breakthrough is expected to occur at only 1,000 bed volumes of processed water. For long-term treatment applications, conventional carbon is expected to be expensive because carbon would need to be replaced after only weeks of service. Nonetheless, conventional carbon has been used to treat perchlorate-contaminated water generated from pump testing and other site-investigation-related activities.

Research is underway at Pennsylvania State University under the direction of Dr. Fred S. Cannon to explore ways to enhance the ability of GAC to remove low levels of perchlorate from groundwater. Research is being conducted under a grant from American Water Works Association Research Foundation (AWWARF) and the DOE. The enhancement involves preloading conventional bituminous activated carbon with NSF-approved organic cationic polymer to produce a "tailored carbon." Tailored carbon was able to treat 30,000 bed volumes of groundwater contaminated with very low levels of perchlorate. Tailored carbon appears to offer an economical alternative to conventional carbon for the treatment of perchlorate. However, as of this date, there have been no field-scale demonstrations of this technology.

8.2 Perchlorate Destruction Technologies

Ultimate destruction technologies for perchlorate include chemical reduction, thermal oxidation, and biological treatment. Biological treatment can be performed ex-situ (above ground) or in-situ (below ground).

8.2.1 Chemical Reduction

Perchlorate is stable relative to many common reducing agents necessitating the evaluation of more exotic agents such as titanium, vanadium, molybdenum, and ruthenium. Although the less common agents are more promising, they are too unstable or toxic to be considered practical for groundwater treatment (Urbansky 1998). In addition, catalysts that might enhance the rate of perchlorate reduction have not been identified. Chemical reduction thus does not appear to be a viable technology at present.

8.2.2 Thermal Oxidation

Supercritical water oxidation (SCWO) has been shown to destroy perchlorate in aqueous streams. A bench-scale demonstration of SCWO was carried out at a facility in Utah. While the technology is capable of destroying perchlorate, the high temperature and operating pressure renders this technology cost-prohibitive for drinking-water applications.

8.2.3 Biological Treatment

Biological treatment processes have received the most research attention for perchlorate treatment. Both ex-situ and in-situ approaches have been developed and tested with promising results. Because of the oxidized nature of the perchlorate ion, the basic biological approach involves the creation of anaerobic (no oxygen) conditions in the contaminated water by adding a readily biodegradable substrate (such as acetate, brewer's yeast extract, molasses, or compost extract) and isolating the water from the atmosphere (to prevent oxygenation). Addition of the substrate typically induces indigenous microbes to extract electrons from the substrate and deliver them to the perchlorate, thereby inducing biotransformation of the perchlorate parent ion into daughter ions (chlorate and then chloride) (Catts 1997; Logan 2001; Roote 2001; ITRC 2002).

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It is generally accepted that microbial reduction of perchlorate proceeds according to the following chemical reaction:

$$ClO_4^- \rightarrow ClO_3^- \rightarrow ClO_2^- \rightarrow ClO^- \rightarrow Cl^- + O_2 \quad (1)$$

The biological process completely destroys the perchlorate molecule. The products of the biochemical reaction are chloride ions and oxygen. Perchlorate is not transferred from one medium to another and thus with ex-situ biological treatment there is no need for media treatment and disposal. Excess biosolids from bacterial growth are removed from ex-situ systems on a continuous basis and are nonhazardous.

A carbon or hydrogen electron donor is normally necessary to drive reaction (1). Most perchlorate-respiring microorganisms are capable of functioning under a variety of environmental conditions and use oxygen, nitrate, and chlorate, but not sulfate, as the terminal electron acceptor (Logan 2001). Incidentally, any other electron acceptors that might be present in the groundwater (e.g., nitrate) are often also biotransformed.

Applications of the anaerobic approach to treat perchlorate-contaminated groundwater have produced promising results as well. Two types of bioreactors, fluidized and fixed bed, have been used. The fluidized bed reactor (FBR) is a fixed-film reactor column that fosters the growth of microorganisms on a hydraulically fluidized bed of media (activated carbon). The fluidized bed media provides a large surface area on which a film of microorganisms can grow and produce a large inventory of biomass in a small reactor volume. The result of this biological growth is a system capable of high performance for target contaminants in a relatively small and economical reactor volume. The main system disadvantage is the cost of pumping to maintain a high recycle rate. The FBR perchlorate destructive system is capable of reducing perchlorate to less than 4 µg/L at ambient water temperatures. In a fixed-bed bioreactor, the biofilm support media (sand or plastic) does not move during water treatment. Biomass buildup on the packing requires that the system be periodically backwashed to prevent clogging.

The initial biological perchlorate treatment method was developed by the U.S. Air Force Research Laboratory, Materials Manufacturing Directorate over eight years ago to treat high-level (i.e., 1,000 to 10,00 mg/L) perchlorate concentrations in wastewater from a rocket-manufacturing facility in Utah. Due to the demonstrated success of the process in treatability tests, a production-scale, continuously stirred bioreactor system began operation at the facility in 1997.

Research efforts have been directed toward adapting the biological approach to low-level perchlorate concentrations in groundwater. Pilot-scale tests of an anaerobic fluidized bed bioreactor were conducted at the Aerojet Superfund Site near Sacramento, California, in 1996. Those tests demonstrated that the bioreactor system could reduce perchlorate concentrations in groundwater from over 5,000 µg/L to the low hundreds of micrograms per liter (Hatzinger et al. 2000).

Pilot-scale tests also have been conducted at one of the San Gabriel Valley Superfund Sites in southern California where perchlorate concentrations of 150 μg/L have been encountered in groundwater (U.S. EPA 1999). Results from those tests indicated that the bioreactor could reduce perchlorate to nondetectable levels (presumably 4 μg/L).

Treatability tests of anaerobic-fluidized or fixed-bed bioreactors have been conducted on low-level perchlorate concentrations in groundwater by the companies Applied Research Associates, Inc., EnSafe, and Envirogen and by researchers at Pennsylvania State University and Southern Illinois University. In virtually every case, promising results have been reported or anticipated (ARA 2000; Winningham et al. 1999; Waste Treatment Technology News 2001; Logan 2001; SERDP 2000; ESTCP 2000).

8.2.4 In-Situ Treatment of Perchlorate

In-situ bioremediation of groundwater has the potential to eliminate the need for above-ground treatment. Anoxic conditions can be established by either creating permeable reactive biobarriers containing high concentrations of organic matter or by injecting substrates into the ground. A complete description of in situ bioremediation of perchlorate is beyond the scope of this document. A description of the methodology to evaluate the viability of this technology can be found in ITRC (2002).

Perchlorate-reducing bacteria have been isolated from diverse environments with more than 30 different strains identified (ITRC 2002). An electron donor is necessary in order to reduce perchlorate to chloride and oxygen. The electron donor serves as the food source for the bacteria. Incomplete oxidation of the electron donor can pose problems in public water-supply aquifers. Residual substrate can stimulate bacteria growth in water-distribution systems and contribute to the formation of disinfection byproducts (Logan 2001). A variety of electron donors have been reported as suitable amendments to anaerobic environments to encourage perchlorate degradation. Naturally occurring substrates include compost, cottonseed, mulch, chips, vegetable oil, and kenaf (a high-fiber plant from the hibiscus family). Synthetic substrates include fructose, sucrose, acetate, lactate, ethanol, and citrate. Laboratory studies have shown a variety of responses to amendments depending on site conditions.

Finally, in-situ anaerobic biological treatment has been developed and field-tested at a number of sites. The most common approach involves the installation of a permeable bioreactive barrier for the biological destruction of perchlorate migrating in groundwater. The permeable barrier is constructed out of compost or other high-organic, permeable material. As the contaminated groundwater migrates through the barrier, biological processes reportedly reduce the perchlorate to nondetectable levels.

Full-scale, multi-barrier technology is currently being employed to treat alluvial groundwater in Mortandad Canyon at the LANL. The barrier consists of four different layers of materials arranged as a permeable reactive barrier (PRB) (Strietelmeier et al. 2001). Perchlorate is among the contaminants targeted for treatment. Perchlorate is biologically reduced within the LANL

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multi-barrier to innocuous chloride ions. The multi-barrier uses two layers that provide biological activity sufficient to reduce perchlorate to non-detectable levels. Both of these layers are made from inexpensive waste materials (hydroxyapatite obtained as fishbone and pecan shell waste as a carbon-based support material). Both materials are capable of supporting the growth of a microbial biofilm that is highly effective at reducing both nitrate, the primary contaminant targeted in this groundwater, and perchlorate to non-detectable levels as the groundwater flows through the barrier. Both materials also serve other purposes in the system, primarily radionuclide and metal removal. The system has been installed downstream from the discharge point for the LANL Radioactive Liquid Waste Treatment Facility. The barrier is expected to perform the groundwater cleanup function for 10 years or more, and will be sampled periodically throughout this period for characterization of the groundwater and to document performance. The materials also will be sampled periodically to assess their persistence and to analyze changes in material structure and composition, and in microbial population composition with time.

8.3 Estimated Treatment Costs

Among the documents identified during this literature review was a document that provided information concerning a technology screening evaluation conducted by Harding Lawson Associates (HLA) for the Baldwin Park Superfund Site (California) Groundwater Operable Unit (HLA 1997 as cited by Catts 1997). Table 4 summarizes estimated costs by treatment method reproduced from Table 6-8 of the HLA draft report.

Table 4. Estimated Cost for Treatment of Perchlorate

Treatment Method	Total Capital Cost	Annual O&M Cost	Total Annual Treatment Cost		Normalized Treatment Cost
	($ Million)	($ Million)	($ Million)	($/gallon)	
Biological with GAC/FB	35	3.0	6.6	0.60	1.0
Ion Exchange	28	5.5	10.4	0.95	1.6
Liquid Phase GAC	46	16.0	20.7	1.88	3.1
Electrodialysis	84	5.0	13.6	1.06	2.1
Reverse Osmosis	65	10.0	16.6	1.52	2.5
Capacitive Deionization	131	3.0	16.6	1.52	2.5

Adapted from Catts (1997):
- Total annual treatment cost determined by adding annual operation and maintenance (O&M) cost and total capital cost amortized over 20 years at 8%.
- All costs in 1997 dollars.
- All costs are accurate to within plus or minus 50%.
- Costs of land and related environmental requirements are not included.

Because the HLA report is somewhat dated, contains only site-specific cost estimates, and does not benefit from recent improved understanding of perchlorate treatability, the cost data provided in Table 4 should be taken only as general indicators. As shown above, biological

treatment and ion exchange technologies are the most economical of the technologies evaluated in this analysis.

9.0 Summary

Perchlorate remains a widespread concern in the United States because of the:

- Potential health effects at low concentrations with a safe limit still under debate
- Widespread distribution of perchlorate in the environment
- Presence of perchlorate in drinking-water supplies
- Lack of fully developed treatment technology for low levels
- Effects perchlorate may have on ecosystems.

Biological treatment and ion exchange are among the technologies being used for remediation of groundwater and treatment of drinking water contaminated by perchlorate. Several other promising technologies, including tailored granular activated carbon (GAC) and in-situ bioremediation, also are being developed.

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