PERCHLORATE CONTAMINATION TREATMENT ALTERNATIVES

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PERCHLORATE CONTAMINATION TREATMENT ALTERNATIVES

BACKGROUND

Sources of Contamination. Perchlorate contamination problems in California are mainly the result of past unregulated discharges of ammonium perchlorate (NH_4ClO_4) from rocket fuel manufacturing plants or demilitarization of missiles. Ammonium perchlorate is primarily used as an energetics booster or oxidant in solid propellants. The ammonium ion initially present in the groundwater at contaminated sites has generally biodegraded over time. Another source of perchlorate contamination is potassium perchlorate ($KClO_4$) which is used as a solid oxidant for rocket fuel as well as for other purposes such as pyrotechnics, flares and airbag ignitors.

Chemistry. The perchlorate anion ($ClO_4\Gamma$) in its salt form is extremely soluble in both water and polar organic solvents. It is exceedingly mobile and persistent in groundwater under typical environmental conditions. Perchlorate is very slow to react and cannot be reduced with common reducing agents or be precipitated using commonly available treatment reagents (i.e., common cations).

Drinking Water Standard. There is currently no state or federal drinking water standard for perchlorate. SB 1822 (Sher), effective January 1, 2003, required that the Department of Health Services (DHS) adopt a maximum contaminant level (MCL) for perchlorate in drinking water by January 1, 2004. DHS has delayed adoption of an MCL for perchlorate until after the Office of Environmental Health Hazard Assessment (OEHHA) has set a final Preliminary Health Goal (PHG), which is expected to be issued Spring 2004. Until an MCL is in place, DHS uses a 4-microgram per liter (µg/L) advisory action level to protect consumers from adverse health effects of perchlorate. The 4 µg/L concentration corresponds to perchlorate's current detection limit.

TREATMENT TECHNOLOGIES

Most standard physical and chemical water and wastewater treatment processes are not generally applicable to remove or destroy the perchlorate ion. Available treatment alternatives that only remove the perchlorate ion require additional steps to treat or dispose of the concentrated perchlorate residual wastestream that is generated. Technologies that have been successfully used to treat perchlorate contamination have primarily involved anion exchange to remove the perchlorate ion, or biological treatment to reduce perchlorate to the chloride ion (Cl^-) and elemental oxygen (O_2). Other removal technologies such as granulated activated carbon (GAC) and membrane filtration have had limited application. Chemical reduction processes to destroy the perchlorate ion have been developed to treat the concentrated brines generated from ion exchange and membrane filtration processes but have had limited application. Additional chemical reduction processes for contaminated groundwater are being researched. Lastly, there has been some research in the area of phytoremediation which may only have limited application in the future.

Perchlorate treatment alternatives that have been implemented full-scale, demonstrated or are being researched are presented Table 1, below.   Table 1 lists the projects by technology category and provides key information regarding each specific project where available, including project description, status, throughput, effectiveness and cost. Many if not most of the full-scale projects listed are California projects.

TABLE 1
PERCHLORATE CONTAMINATION TREATMENT TECHNOLOGIES

Technology & Vendor Name	Technology Description	Scale / Status	Throughput	Projects	Treatment Effectiveness	Costs[3]
ION EXCHANGE						
Calgon ISEP® (Ion SEParator) Continuous Anion Exchange and Regeneration	System includes multiple (20 to 30) anion exchange columns mounted on a turntable attached to a rotating multi-port valve. During a 360° rotation, each resin cell is subjected to an entire cycle of adsorption, regeneration or elution, and one or two rinse steps. Regeneration is accomplished with a NaCl solution.	Full Scale - Operational	2500 gpm	La Puente Valley County Water District, CA. The Calgon ISEP® system is designed to treat 2500 gpm with 600 μg/L perchlorate and began operating in February 2000. The system uses Purolite A 850, strong base anion, acrylic, type 1 gel resin and operates 19 hours/day to control the perchlorate plume in the San Gabriel Groundwater Basin.	~ 200 μg/L to <4 μg/L	Capital = $2 million Operating Cost = $145/acre-ft.
		Full Scale - Operational	450 gpm	Kerr-McGee, Henderson, Nevada. A Calgon ISEP® PDM (perchlorate destruction module) system started up in March 2002 and operated for about six months to treat extracted groundwater from the Athens Road Well Field and the Las Vegas Wash seep area. Actual flowrates varied between 200 to 560 gpm. Maintenance problems were caused by high TDS, hardness, and sulfate. Operation was discontinued due to corrosion in the heat exchangers.	80 - 100 mg/L to < 2mg/l (D.L., ion specific electrode)	
		Pilot Scale - Completed	4.3 gpm	Baldwin Park, CA Big Dalton Well.; (Study initiated in 5/98) brine produced was 0.75% of the inflow.	18-76 μg/L to <4 μg/L.	
		Full Scale - Planned	7800 gpm	San Gabriel Valley Water Company, El Monte, CA; B6 well site; (system built, first phase of startup underway; expected operational by 2/04)	-	
		Full Scale - Planned	7800 gpm	Valley County Water District, Baldwin Park, CA; (under construction., startup 1/04)	-	
		Full Scale - Planned	4000 gpm	City of Pasadena , CA . 3500 -5000 gpm system proposed at existing wells next to JPL site; planning stage.	-	
Calgon Anion Exchange	Fixed bed non-regenerable anion exchange resin treatment	Full Scale - Operational	5000 gpm	California Domestic Water Company, Whittier, CA ; (startup 7/02)	< 14 μg/L to < 4 μg/L	$125/acre ft.
		Full Scale - Operational	5000 gpm	City of Riverside, CA, Tippecanoe Treatment Facility ; (startup 12/02)	Distribution. system. 6.4 μg/L ppb ave. in 2001 to ave. 4.6 ppb in 2002	
		Full Scale - Operational	2000 gpm	City of Riverside, CA, Gage 51-1 Treatment Facility (startup 5/03)	< 60 μg/L to < ? μg/L	
		Full Scale - Operational	2000 gpm	West San Bernadino Water District, Rialto, CA (startup 05/03)		
		Full Scale - Planned	4050 gpm	City of Monterey Park, Delta Treatment Plant, Well 12 (San Gabriel GW basin; system constructed and tested, awaiting permit, expected operational 1/04)		
		Full Scale - Planned	7800 gpm	San Gabriel Valley Water Company, El Monte, CA B5 Site (under construction., startup 4/04)		
		Full Scale - Operational	> 300 gpm	Kerr-McGee facility, Nevada. Once-through ion exchange system to treat captured surface water in the seep area has been ongoing since 11/99. Groundwater in seep area has been pumped and treated since 10/2001. The initial 4 well extraction system was expanded to nine (9) wells in 03/2003. Pumping rates varied between 300 and 600 gpm been 10/2002 and 3/2003.	System influent averages around 30 ppm. Combined with effluent from on-site IX system, effluent discharge varies from <0.5 ppm to 2 ppm, and averages 1.3 ppm perchlorate.	
		Full Scale - Planned	2000 gpm	Loma Linda, CA. Single pass ion exchange treatment; (startup planned Spring 2004)		
		Full Scale - Operational	850 gpm	Kerr McGee facility, Nevada. A single pass ion exchange system was installed to replace the Calgon ISEP system and to allow continuous treatment of the extracted groundwater from the Athens Road wells. Continuous operation since 10/2003.	System influent varies from 200 to 300 ppm perchlorate.. Combined with effluent from Wash IX system, effluent varies from <0.5 ppm to 2 ppm, and averages 1.3 ppm perchlorate.	

US Filter Anion Exchange	Fixed bed non-regenerable anion exchange resin treatment	Full Scale - Operational	1000 gpm	Aerojet, CA. Sacramento GET D facility	200 ppb to < 4ppb	
		Full Scale - Operational	2000 gpm	Aerojet, CA. Sacramento GET B facility	50 ppb to < 4ppb	
		Full Scale - Operational	800 gpm	Aerojet and Boeing (formerly McDonald Douglas), Sacramento, CA	250 ppb to < 4ppb	
		Full Scale - Operational	800 gpm	City of Morgan Hill, CA . Two wells: Nordstrom well operating; Tennant well installed. Perchlorate plume due to Olin Corp. manufacture of road flares.	<10 ppb to < 4 ppb	
		Full Scale - Operational	2000 gpm	West Valley Water Co., West San Bernadino, CA (startup 05/03)	<10 ppb to < 4 ppb	
		Full Scale - Operational	2000 gpm	City of Rialto, CA (startup 08/03)	<10 ppb to < 4 ppb	
		Full Scale - Operational	3500 gpm	City of Colton, CA (startup 08/03)	<10 ppb to < 4 ppb	
		Full Scale - Constructed	5000 gpm	Fontana Union Water Co., Fontana , CA (System being loaded with Resin as of 12/19/03; Operational by January 2004)	15 ppb to <4ppb	
		Full Scale - Operational	800 gpm	West San Martin Water Co., West San Martin, CA	17 ppb to < 4 ppb	
Ion Exchange	Originally designed for nitrate removal, anion exchange system achieves perchlorate removal.	Full Scale - Operational	10000 gpm	City of Pomona, CA		
SELECTIVE ION EXCHANGE RESINS						
SYBRON IONAC SR-7 anion exchange resin **Lawrence Livermore National Laboratory**	Commercially available regenerable nitrate selective anion exchange resin manufactured by Sybron ((SYBRON IONAC SR-7) ; resin is effective for perchlorate which has similar ion exchange properties as nitrate. In these systems, anion exchange is part of a treatment train, preceded with biological treatment to remove nitrate and followed with granular activated carbon to remove TCE.	Full Scale - Operational	1400 gpd	Lawrence Livermore National Laboratory - Building 815 SR-7 (startup July 2000; regenerant flowrate 0.25-0.5 gpm/ft3)	10 µg/L to < 4 µg/L	
		Full Scale - Operational	5000 gpd	Lawrence Livermore National Laboratory - Building 830-DISS (startup Nov. 2000; regenerant flowrate 0.25-0.5 gpm/ft3)	10 µg/L to < 4 µg/L	
		Full Scale - Operational	1000 gpd	Lawrence Livermore National Laboratory - Building 854-PRX (startup Sept. 2000; regenerant flowrate 0.25-0.5 gpm/ft3)	7.2 µg/L to < 4 µg/L	
Purolite A-520E anion exchange resin	Commercially available nitrate selective anion exchange resin manufactured by Purolite; resin is effective for perchlorate which has similar ion exchange properties as nitrate.	Lab Study		Paducah Gaseous Diffusion Plant to treat pertechnetate (TcO4-)		
		Lab Study		ORNL comparison study for bi-functional resins		
Rohm and Haas Corporation Amberlite PWA2 Perchlorate Selective Resin	Rohm and Haas has developed a proprietary perchlorate selective resin that is NSF 61 Certified for potable use. Amberlite PWA2 is a non-regenerable resin for "load and toss" applications.	Full Scale - Operational	2000 gpm	Aerojet, Sacramento, CA	50 ppb to <4 ppb	
Rohm and Haas Corporation Amberlite PWA 555 Nitrate Selective Resin	Commercially available nitrate selective anion exchange resin manufactured by Rohm and Haas; resin is effective for perchlorate which has similar ion exchange properties as nitrate.	Full Scale - Operational	1000 gpm	W. San Martin Colony and County Wells	15 ppb to <4ppb	
Oak Ridge National Laboratory (ORNL) & University of Tennessee (UT) **Purolite A-530E - Bi-Functional Resin**	ORNL and UT have developed bi-functional anion exchange resins that are highly selective for perchlorate. These resins consist of quaternary ammonium groups with large (C6) and small (C2) alkyl groups resulting in high selectivity and good exchange kinetics. The technology has been licensed to Purolite to develop a commercial version of the resin.	Lab Studies		ORNL studies demonstrating D3696 resin (a.k.a., Purolite A530e) to remove perchlorate		
		Full Scale - planned	25 gpm	Stringfellow Site, Riverside Co., CA. A full-scale 25 gpm bi-functional anion exchange resin system to treat the downgradient "toe" of the perchlorate plume (~30 µg/L) began continous operation in December 2003. The system consists of two 10 cubic feet beds in series, and can treat perchlorate to below the 4 ppb detection limit. The highly selective resin is expected to last several months before changeout is required. On-site regeneration was not an option because of location in a residential area which required a low profile and minimal operational requirements. High TDS, including sulfates (~200 mg/L) and nitrates (~70 mg/L), makes use of non-selective anion exchange resins problematic for this specific application due to frequent regeneration or changeouts, and no brine disposal options. Significant concentrations of tetrahydrafuran and MEK were detected during system startup but not in subsequent sampling. The source of these contaminants is unclear (may be from the resin system) as these compounds are not normally found in groundwater plume at this location.	30 ppb to <4ppb	
		Pilot Scale - completed	300gpm	Castaic Lake - 5 month pilot plant study (Kennedy-Jenks), 3 wells	to < 4 µg/L	

ION EXCHANGE BRINE TREATMENT						
Calgon ISEP+ TM System **Perchlorate and Nitrate Destruction Module (PNDM)**	A catalytic chemical reduction process for treating perchlorate and nitrate ions in the waste regeneration brine. A hydrogen source (ammonium) is added as a reductant, and perchlorate is reduced to chloride (ClO_4^- + $8e^-$ + $8H^+$ = > Cl^- + 4H2O). The system operates at 250º C and is relatively energy intensive.	Pilot Scale - Completed	< 2 gpm	NASA, JPL Pasadena. A seven month pilot study of ISEP+TM system prototype conducted in 1998-1999 on groundwater with 1200 µg/L perchlorate and high concentrations of nitrate and sulfate. The PNDM effectively reduced the perchlorate and nitrate present in regeneration brine waste, while greater than 96% of the sulfate was removed. The treated regenerant stream was reused (i.e., recycled) to effectively regenerate the resin. The overall process waste from the system was about 0.16% of the feed volume.	1200 µg/L to < 4 µg/L nitrates and sulfates removed to acceptably low levels.	O&M costs are estimated at about two times the cost of a comparable biological treatment unit.
Oak Ridge National Laboratory (ORNL) **Chemical Reduction of Perchlorate $FeCl_3$-HCl regenerant solutions**	Perchlorate in FeCl3-HCl regenerant solutions is degraded using ferrous iron and/or non-toxic organic reducing agents (US patent pending). While perchlorate is reduced, ferrous (Fe++) ions are oxidized to ferric (Fe+++) ions, which replenish or "regenerate" the FeCl3 - HCl solution.	Pilot Scale - Completed	1 gpm	Edwards AFB, CA, Site 285. The ORNL bi-functional resin treatment system, including a chemical regeneration process was successfully demonstrated at Edwards AFB, on groundwater with 50 µg/L perchlorate. Tests on the 1 gpm system (2 bed volumes/minute) indicated that the bi-functional resin was able to treat over 100,000 bed volumes before a breakthrough of 5 µg/l perchlorate occurred. Construction of a full-scale treatment system incorporating the bi-functional resin began in October 2002 and is expected to become operational in 2003.	50 µg/L to < 5 µg/L Destruction of perchlorate to chloride and water requires up to a one-hour residence time.	
Applied Research Associates **Integrated Thermal Treatment Process**	Perchlorate in regenerant brine is thermally decomposed at elevated temperature and pressure with the addition of reducing agents and promoters. Concentration of the brine with reverse osmosis would be necessary to make the process cost-effective. A patent application is pending.	Laboratory research		none		
BIOLOGICAL REDUCTION						
Envirogen / US Filter - Envirex fluidized bed reactors (FBR) w/ GAC media	Fluidized Bed Reactor with granular activated carbon media. Typically, ethanol is used as the electron donor.	Full Scale - Operational	5300 gpm	Aerojet, Rancho Cordova. Four fluidized bed reactors (FBR) with GAC media and ethanol feed as the food source have been in operation since 1998. The system was designed to treat 8 mg/l of perchlorate with a perchlorate loading of 44 lb/day per 1000 cubic feet of reactor volume. Total throughput design capacity of 4000 gpm, but processing 5300 gpm as of 10/03. The Aerojet System is based on pilot scale laboratory testing using a 30 gpm FBR developed by U.S. Filter and Envirogen. . The pilot scale FBR also successfully reduced high concentrations of chlorate (480 mg/L) and nitrate (20 mg/L).	Can reliably treat relatively high or low concentrations to below the 4 µg/L detection limit.	
		Full Scale - Operational	35 gpm	Longhorn Army Munitions Plant, Texas. Full-scale fluidized bed reactor with carbon media and acetic acid / nutrient additions treats 35 gpm contaminated groundwater with perchlorate concentrations up to 35 mg/l to below the 5 µg/L. Acetic acid and nutrient additions	35 µg/L to <5µg/L	
		Pilot Scale - Completed		NASA, JPL Pasadena. Pilot test completed with Fluidized Bed Reactor (FBR) using native "JPL bacteria" and ethanol as the food source.	350 - 740 µg/L to < 4 µg/L	
		Full Scale - Under Construction	900 gpm	Kerr McGee facility, Nevada. FBR system with 4 sand-media primary reactors and 4 carbon-media secondary reactors will replace the single pass ion exchange resin systems. The primary reactors biodegrade the high chlorate and nitrate concentrations to allow the secondary reactors to treat the perchlorate. Startup is planned for January 2004; Denatured alcohol will be used as the electron donor. By April 2004 the system is expected to be fully on-line treating a blended influent from the three well fields averaging 350 ppm perchlorate.	to < 20 ppb detection limit; high DL due to high concentrations of TDS and sulfate concentrations.	
Applied Research Associates, Inc.	Custom Designed Biological Treatment Systems	Full Scale - Operational	? gpm	Thiokol, Brigham City, Utah. Full-scale CSTR (continuously stirred tank reactor) biological system has operated continuously since December 1997 to treat industrial wastewater prior to discharge to sewer to treat wastestream high in salts (>2%) and nitrate. Initial pilot scale work was performed by the Air Force Research laboratory at Tyndall AFB, Florida.	> 5,000 mg/L to 4 - 400 µg/L ;	$0.35 to $1.00/ gallon

		Designed	825 gpm	Kerr- McGee, Henderson, Nevada. Based on treatability studies, ARA with Biothane Corporation designed an 825 gpm suspended-growth, CSTR biological treatment plant to treat 400 mg/L (~4000 pounds per day) of perchlorate to below 4 µg/L. (Not selected due to higher capital costs).		
Foster Wheeler/ Arcadis **Packed Bed Bioreactor**	Packed Bed Bioreactor	Pilot Scale		NASA JPL, Pasadena, CA; NASA, assisted by Naval Facilities Engineering Center, managed pilot tests conducted on several different reactors. Results as of May 2001 indicate reactors can successfully treat low concentrations of perchlorate.	< 1 mg/L to non-detect (< 1 µg/L)	
Pennsylvania State University **anaerobic packed bed reactor**	anaerobic acetate and nutrients-fed packed bed reactor with sand and plastic media; hydrogen reactors.	Pilot and Lab Scale		• Crafton-Redlands Plume, Redlands, CA.. Pennsylvania State University, funded by the American Water Works Association Research Foundation (AWWARF), is conducting anaerobic packed bed reactor pilot scale tests, one with sand and one with plastic media. Initial results show both reactors with acetate and trace nutrient additions capable of reducing concentrations of 70 µg/L perchlorate to less than 4 µg/L. Prior to the pilot scale tests, Pennsylvania State University conducted perchlorate degradation studies in laboratory scale reactors evaluating both acetate-fed, packed bed reactors and hydrogen reactors.	70 µg/L reduced to < 4 µg/L	
EcoMat **Hall reactor**	The patented Hall reactor provides an efficient circulation pattern and utilizes a floating porous media, Ecolink, which has a very high surface area to volume ratio. Ecolink is a polyurethane-based sponge that is cut into one-centimeter cubes. The dense biological growth supported with this system reported to provide high efficiencies with lower reactor volumes.	Commercial	~ 2 gpm	DOD facility, southern California. A 200 liter capacity, two-stage biological system consisting of the Hall reactor and a deaeration chamber mounted on a 4 ft. by 4ft. skid, was used treat perchlorate contaminated groundwater stored in two 20,000 gallon Baker tanks. Methanol was used as the electron donor.	350 µg/L to < 9 µg/L	$0.50/1000 gal.
Applied Research Associates, Inc **- fixed film process;** **- suspended growth CSTR process.**	Bench scale reactor was operated both as a fixed film process and as a suspended growth (continuous stirred treatment reactor (CSTR) process for their patented full-scale process on 5× and 10× reverse osmosis rejectate containing high total dissolved solids and up to 10 mg/L of perchlorate.	Bench Scale		Bench scale testing at ARA	to < 20 µg/L	
Hollow-Fiber Membrane Biofilm Reactors	Patented a hollow-fiber membrane biofilm reactor utilizes hydrogen as the electron donor to biologically degrade perchlorate. Hydrogen gas is fed to the inside of the membrane fibers, and the hydrogen diffuses through the membrane walls into the contaminated water that flows past the fibers. A biofilm on the exterior surface of hollow fiber membranes houses microbes that act as catalysts by transferring electrons from supplied hydrogen gas to an oxidized contaminant.	Pilot Scale	0.3 gpm,	Bruce E. Rittmann of Northwestern University , the technology developer, teamed with Montgomery-Watson-Harza Engineers, Inc. to conduct a pilot study in La Puenta, Calif., treating groundwater that is highly contaminated with perchlorate and nitrate. The pilot was initiated during early 2002 and continued through the year. Results have shown that the biofilm reactor can effectively treat 0.3 gpm of water, to remove both perchlorate and nitrate.		
IN SITU BIOLOGICAL TREATMENT (Groundwater)						
GeoSyntec Consultants	Groundwater is extracted, then amended with acetate (electron donor) before being re-injected at an upgradient location. Optimally system is operated and monitored to ensure a closed groundwater recirculation loop.	Pilot Scale - Completed		Aerojet, Sacramento. A pilot test was conducted to accelerate in situ bioremediation of perchlorate in a deep contaminated aquifer that is approximately 90 feet thick and extends to 100 feet below ground surface. The pilot system design was a closed groundwater recirculation loop where groundwater was extracted, then amended with acetate (electron donor) before being re-injected at an upgradient location. The system included one donor delivery well, one extraction well and two monitoring wells. Concentrations of manganese, a secondary drinking water contaminant, increased in downgradient monitor wells presumably due to the reducing environment that was created.	Perchlorate up to 12 mg/L reduced to < 4 µg/L within 15 feet of the donor delivery well in about 50 days.	

		Pilot Scale - Completed		AMPAC (formerly Pepcon) facility, Nevada. A six-month in situ biological treatment pilot project in the hot spot area of the plum was completed in 5/03. Groundwater was recirculated at rate of 10 gpm between an injection and extraction well located 100 feet apart in line with groundwater flow. The electron donor was switched from ethanol to citrate after 3 months to correct fouling problems. The groundwater has high TDS (3000 to 5000 ppm) with high concentrations of nitrates and chlorates that are preferentially biodegraded over perchlorate.	After 160 days of operation perchlorate concentrations of 500 to 800 were reduced to less than 2 ppb at the midway monitor well located 50 feet from both the injection and extraction well.	
Aerojet, Sacramento	Injection of amended water to remediate a perchlorate contaminated aquifer.	Pilot Tests - completed		Several different in situ biodegradation tests involving injection of amendments into a perchlorate-contaminated aquifer have been conducted at Aerojet including the one by GeoSyntec Consultants noted above.		
		Pilot Test - planned		Horizontal well used to inject amended water.		
		Pilot Test - planned		Amended water addition to contaminated aquifer via a percolation pond.		
Groundwater Barrier Trench with cotton seed meal and cotton seed	Groundwater collection trench constructed with composting materials, cotton seed meal and cotton seed	Full Scale - Operational		Naval Weapons Industrial Reserve Plant, McGregor, Texas. In-situ Biological Treatment of Groundwater using A 25 feet-deep groundwater collection trench constructed with composting materials, cotton seed meal and cotton seed. Results of the this pilot test along with supporting bench-scale test results indicated the capability to biodegrade perchlorate from 27,000 µg/L to below 4 µg/L.	27,000 µg/L to < 4 µg/L (not clear if bench or pilot result)	
NASA, JPL Pasadena / Arcadis **Corn syrup (electron donor) Injection**	Injection of corn syrup or other carbon source as the electron donor to promote biodegradation of perchlorate.	Full Scale - Planned		NASA, JPL Pasadena. An in situ biological treatment pilot test is planned in 2003 to evaluate use of in situ bioremediation to reduce perchlorate concentrations in the source area. A workplan is under development; Corn syrup is now being considered over molasses as the electron donor. Corn syrup does not contain significant amounts of sulfur and nitrogen like molasses. Sulfur is a concern due to potential for hydrogen sulfide formation; bacteria preferentially degrade the added nitrogen before degrading perchlorate contamination.		
Solutions IES **Permeable Barrier System w/ edible oils as the electron donor**	Biologically Active Permeable Barrier - injection of corn syrup or other carbon source as the electron donor to promote biodegradation of perchlorate.	Full Scale - Proposed		Edwards AFB. Use of slow release edible oils developed by Solutions IES in an in situ biological treatment permeable barrier system is being investigated.		
Los Alamos National Laboratory **Permeable Reactive Barrier (PRB)**	A multi-layered permeable reactive barrier; The PRB incorporates a sequence of four reactive media layers to immobilize or destroy a suite of contaminants present in alluvial groundwater, including Sr-90, Pu-238, 239, 240, Am-241, perchlorate, and nitrate. The four sequential media cells consist of gravel-sized scoria, apatite, pecan shells and cottonseed with an admixture of gravel (biobarrier), and limestone.	Full Scale - Operational		LANL, Mortandad Canyon, NM. A multi-layered PRB was installed in February 2003 to demonstrate in situ treatment of contaminants within alluvial and deeper perched groundwater; The 27 foot deep by 20 foot wide by 20 foot long PRB was designed with a 10-year lifetime and 1-day residence time within the biobarrier; Preliminary results indicate that both nitrate and perchlorate are being reduced by microbial activity in the biobarrier. After the PRB was installed, drought conditions lowered the groundwater table to below the bedrock-alluvium interface and, hence below the the bottom of the PRB. A meaningful evaluation of PRB effectiveness has thus been delayed until groundwater levels recover to normal levels.	Bench scale results: perchlorate reduced from 120 ppb to 35 ppb. Full Scale: Preliminary field data indicates non-detectable perchlorate levels (2 ppb) in wells located within the biobarrier cell; however, this is residual groundwater in bedrock underlying the alluvium; 20 ppb perchlorate was detected in the residual groundwater in the upgradient monitor well.	$900,000 to install

COMPOSTING / IN SITU TREATMENT (Contaminated Soil)						
GeoSyntec Consultants **Anaerobic Composting**	Anaerobic composting of perchlorate-contaminated soils	Pilot Demonstration	20 yards	Aerojet, Sacramento, CA. Pilot demonstration of anaerobic composting of soils from the former perchlorate burn area. Two approximately 10 cubic yard piles were treated. The degradation half life was determined to be one to two days.	Maximum detected perchlorate concentration of 4200 mg/kg. Average 23 mg/kg to about 0.1 mg/kg in seven days.	
In Situ Biological Treatment	In situ biological treatment of perchlorate contaminated soil .	Bench Scale - Completed Full Scale - Planned		Long Horn Army Ammunitions Plant, Texas. Laboratory testing indicated that soils from LHAAP containing 350 mg/kg could be treated to non-detectable levels in less than 9 days using chicken manure, cow manure, and ethanol as suitable carbon sources. Subsequent field tests at LHAAP found after ten months complete removal of perchlorate within 1-2 feet, with varied levels of reduction in the deeper layers. Upon completion of the field study, perchlorate concentrations in the wettest cells had decreased to non-detectable levels.	Perchlorate reduced to below detection limit after 10 months.	estimated: $25-50 / yard
Soil Composting	Soil Composting	Full Scale		Pueblo Army Depot, Colorado. Composting was performed to remediate soils contaminated with explosives (HMX and RDX). These soils are now known to also be contaminated with perchlorate. Analyses of treated soils are underway to assess the effectiveness of the composting process in reducing perchlorate concentrations.	Results unavailable	
Soil Bioremediation	Anaerobic composting of perchlorate soils?	Planned	1,500 cubic yards	Boeing, Santa Susana Field Laboratory, Ventura Co., CA. Approximately 1,500 cubic yards of perchlorate-contaminated soil excavated from the Happy Valley drainage channel are to be bioremediated in the Building 359 Area. The excavation activities began October 2003; The bioremediation activities will begin once Los Angeles Regional Water Quality Control Board issues Waste Discharge Requirements		
Soil Bioremediation	Anaerobic composting of perchlorate soils?	Planned	2,400 yards	Boeing (formerly McDonnell Douglas), Sacramento. Under the interim Remedial Action Plan , approved in October 2002, 3600 tons of perchlorate contaminated soil, will be treated using biodegradation stockpile methods; soil to be backfilled into the on-site excavations after it is treated/cleaned.		
Anaerobic Soil Compositing	Mixing in compost as nutrient to allow soil microbes to degrade perchlorate under anoxic conditions	Planned	?	United Technologies Corp. DTSC is reviewing a treatment proposal as part of the Post-Closure Permit Application for the Open Burn Facility. UTC manufactures propellants for the aerospace industry at their facility located southeast of San Jose, CA.		
Anaerobic Soil Compositing	Anaerobic composting of perchlorate soils	Feasibility Study		Edwards Air Force Base. Study of anaerobic composting of perchlorate soils now containerized in 55-gallon drums. The study objectives are to reduce the perchlorate concentrations in soil below the U.S. EPA Remediation Goal of 39 mg/kg, and ultimately to less than 1 mg/kg;	not known	
GRANULAR ACTIVATED CARBON (GAC)						
Granular Activated Carbon (GAC)	GAC system initially installed to treat VOC contamination for drinking water supply was later found effective to treat low concentrations of perchlorate.	Full Scale - Operational		Crafton-Redlands Plume, City of Redlands, CA. In September 2001, the Department of Health Services issued a domestic water supply permit amendment to the City of Redlands Municipal Utilities Department to operate the Texas Street GAC facility to remove perchlorate in their domestic water supply system. Penn State University is using four of the twenty-four GAC vessels at the same facility for additional studies, looking at enhancing GAC performance by preloading with iron organic complex and regenerating with reducing solution.	Influent perchlorate concentration of 60 to 138 µg/L; GAC bed regenerated every 6 weeks for perchlorate treatment versus the 8 months that was required for treatment of the VOCs.	

	A liquid phase GAC system	Full Scale - Operational	100 gpm	Edwards Site 133. GAC system (three 2000 lb. carbon canisters in series) that was constructed in May 2001 to remove VOCs is now treating 92 µg/L perchlorate as a co-contaminant; U.S. Filter has conducted bench-scale testing of modified carbon to treat perchlorate at the treatment system effluent.	Influent perchlorate concentration of 92 µg/L; September 2003 report indicates system not that effective for perchlorate.	
	Coconut Carbon to treat low levels	Full Scale Testing Planned		City of Monterey Park, Well 5		
BIOLOGICALLY ACTIVE CARBON (BAC)						
Biologically Active Carbon (BAC) **University of Illinois at Urbana-Champaign and the Metropolitan Water District of Southern California (MWDSC).**	AWWARF-funded bench and pilot scale tests indicate that biologically active carbon filtration can effectively remove low levels of nitrate and perchlorate under anaerobic conditions with the addition of an electron donor. Nitrate reduction can also enhance perchlorate reduction kinetics, making BAC filtration particularly attractive for combined nitrate-perchlorate remediation.	Pilot Scale				
MEMBRANE FILTRATION						
Reverse Osmosis (RO)	Water is forced through a semi-permeable membrane. RO has been used to treat various water sources to remove high concentrations of total dissolved salts. Although performance data is not available, RO would also be expected to effectively remove perchlorate ions. Unselective removal of dissolved ions results in a more corrosive, lower pH effluent. Degradation of the membrane in treating perchlorate may be a concern.	No Applications		none		
Nanofiltration	A partially permeable membrane is used to preferentially separate different fluids or ions. Nanofiltration generally works for particle sizes over 10 angstroms (10^{-10} m), rejecting selected salts (typically divalent). Nanofiltration passes more water at lower operating pressure than RO systems, and thus requires less energy to perform the separation. Based on the size of the perchlorate ion, about 3.5 angstroms, nanofiltration may not prove to be effective for perchlorate removal.	No Applications		none		
Electrodialysis	Electrodialysis. Water is passed through channels of alternating semi-permeable and permeable membranes (to either anions or cations), while being exposed to an electrical field.	pilot scale - completed	7.4 gpm	Magna Water Co. , Utah . An electrodialysis reversal (EDR) pilot unit (7.4 gpm Ionics Aquamite III) was installed at an uncontaminated Magna Water Co. (Utah) well with high TDS (1300 mg/l) and silica (80 mg/l), and operated continuously for four days to evaluate perchlorate removal effectiveness. The extracted groundwater feed to the pilot unit was dosed to130 µg/L perchlorate.	Perchlorate removal rates stabilized in the low 70 percent range ; higher removal rates (94%) could be achieved with a four stage system	$1.10 to $1.50 / 1000 gal
CHEMICAL REDUCTION						
UV Light / Zero Valent Iron Reduction	Lab studies (Gurol, Mirat D., and Kyehee Kim, 2000) indicate that perchlorate can be reduced by iron (FeO) under anoxic conditions and that UV light can accelerate the reaction rate to levels for practical application. A patent (#6,531,065) was issued March 11, 2003. The patent also covers use of the iron metal with a catalyst and with phosphoric acid.	Laboratory Research		As of June 9, 2003, the San Diego State University Foundation, Office of Technology Transfer, was seeking funds to commence six months of field testing to develop a commercial prototype.		

Titanium +3 Chemical Reduction **Georgetown University**	Titanium +3 Chemical Reduction - Georgetown University has developed a technique using titanous ions (+3) to chemically reduce perchlorate. Several new organic ligands have been developed that have been shown to catalyze reduction of perchlorate by titanous ions (+3) ions to titanium dioxide and chloride in acidic aqueous media. A preliminary patent application has been filed.	Laboratory Research				
Electrochemical Reduction **Clarkson University** **City of Redlands, CA** **City of Riverside, CA** **(AWWARF-funded)**	A bench scale study of electrochemical reduction of perchlorate was conducted using two-chambered batch reactor systems. Cathodic and anodic compartments were separated by an ion exchange membrane, and electrodes consisted of titanium coated with a thin film of titanium dioxide particles. Initial perchlorate concentration ranged from 50 mg/L to 500 mg/l. Perchlorate reduction was limited due to the competition among anions for active sites on the electrode surface, with perchlorate being less strongly adsorbed than both sulfate and chloride. The time required for ions in the water to travel to the electrode surface is a design problem in developing a practical full scale system.	Laboratory Research				
ELECTROCHEMICAL						
Capacitive Deionization **Carbon Aerogel** **Lawrence Livermore National Laboratory**	Influent water containing salts enters space between two carbon-aerogel electrodes; electrostatic field forces ions into aerogel, where they are held, and purified water leaves the space between the electrodes. CDI systems potentially use 10 to 20 times less energy per gallon and achieve the same results as a convention electrodialysis or reverse osmosis system.	Research & Development		LLNL patented the carbon aerogel capacitive deionization technology in 1995 and has licensed the technology for commercialization to CDT Systems, Inc. (formerly FarWest Group, Inc.), based in Tucson, Arizona . CDT Systems, Inc. has a proposal to install a system to clean up brackish water at the municipal water treatment plant in Carlsbad, California.		
Capacitive Deionization **Flow Through Capacitor** **Biosource, Inc.**	The Flow Through Capacitor is made up of alternating electrodes of 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.	Research & Development		The Flow Through Capacitor technology is covered by a number of US patents. Biosource, Inc indicated in May 2004 that it had recently been awarded a contract to develop their water purification technology for for military use, and that it will be used in Iraq.		
PHYTOREMEDIATION						
Willow Trees	Willow Trees. In bench scale tests, willow trees successfully treated water contaminated with both perchlorate and TCE. Rhizodegradation accounted for most of the removal of perchlorate with little uptake into the plant. Plant uptake might be significant with high nitrate environments (a competing terminal electron acceptor).	Bench Scale				
Salt Cedar Trees	Trees. Salt Cedar trees are known to mine salt from the water. Stalks of the plant in the Las Vegas Wash picked up significant concentrations of perchlorate per gram of tissue	Research				

Containerized Wetlands **Lawrence Livermore National Laboratory**	The engineered use of plants to assimilate or degrade nitrate and perchlorate in water via the interaction of the contaminant with plant roots, and their associated rhizosphere microorganisms. The system consists of fiberglass tanks in series, which contain coarse aquarium-grade gravel and native wetland plants, such as bulrushes (Scripus), cattails (Typha) and sedges (Carex).	Pilot Study - completed		A containerized wetland system designed to remove nitrate and perchlorate from ground water was tested over a seven-month period at Lawrence Livermore National Laboratory.	Removal of Nitrate (as NO3 to <4 mg/L) and Perchlorate (to <4 µg/L)	

ION EXCHANGE

Anion exchange technology is the most commonly used physical chemical treatment method for perchlorate contamination. Anion exchange resins are commercially available to remove the perchlorate anion from aqueous wastestreams. A major concern with the use of ion exchange is the resultant brine wastewater that is high in both perchlorate and total dissolved solids (TDS), and must be disposed or somehow treated.

Ion exchange capacity for perchlorate is significantly reduced when treating waters with high total dissolved solids and especially with waters high in sulfates (each double negatively-charged sulfate ion will replace two chloride ions). In these cases more frequent regeneration of the resin bed is required and may not be cost-effective. Because perchlorate has ion exchange properties similar to nitrate, nitrate selective resins that were developed to preferentially exchange nitrates over sulfates may be used to remove perchlorate. These selective resins prevent sulfates from displacing or "dumping" nitrate or perchlorate as the bed reaches saturation.

A number of full-scale systems for treatment of contaminated groundwater for drinking water and remediation have been implemented in California and in other states. These include the Calgon ISEP® (Ionic SEParation) Continuous Anion Exchange and Regeneration system as well as fixed bed non –regenerable anion exchange systems developed by both Calgon and US Filter. With non-regenerable systems brine is not generated, but the resin bed must be replaced once bed capacity is reached, and the perchlorate-contaminated resin must be properly disposed.

In December 1999, the Department of Health Services accepted the Calgon ISEP® technology use in removing perchlorate from drinking water source waters. The approved system used a strong base anion, acrylic, type 1 gel resin developed by Purolite (Purolite A 850),

Perchlorate-Selective Resins

Oak Ridge National Laboratory (ORNL) and the University of Tennessee have recently developed bi-functional anion exchange resins that are highly selective for perchlorate. The technology has been licensed to Purolite to develop a commercial version of the resin (Purolite A-530E). The bi-functional resins consist of quaternary ammonium groups with large (C6) and small (C2) alkyl groups resulting in high selectivity and good exchange kinetics. The ability to select for perchlorate and not remove other anions means a significantly greater resin capacity for perchlorate. Additionally, the chemistry of the extracted groundwater is not negatively altered by the removal of other ions which can cause the treated water to be corrosive. Bi-functional resins are currently very expensive and can cost $1500/ft^3$ as compared to $200/ft^3$ for other anion exchange resins that are being used to treat perchlorate.

At the Stringfellow Site a 25 gpm has been installed and is now in continuous operation. During startup compounds not normally found in the groundwater plume, methyl ethyl ketone and tetrahydrofuran, were detected at significant concentrations. After further operation, these compounds were no longer being detected in effluent analyses. Whether these compounds were from the resin beds has not been determined.

Difficulty with regeneration of bi-functional resins has limited their use. ORNL has patented a process using a ferric chloride-hydrochloric acid displacement technique to regenerate bi-functional and other selective anion-exchange resins. Lab studies indicate a high recovery of ion-exchange sites can be achieved with the regenerant solution without affecting the resin's performance after repeated cycles.

Rohm and Haas Corporation has also developed a perchlorate-selective resin, Amberlite PWA2, which is NSF 61 Certified for potable use. A full scale 2000 gpm system using this resin has been installed and is operating at the Aerojet, Sacramento facility. Amberlite PWA2, is a non regenerable resin for "load and toss" applications.

Brine Treatment

The brine from regenerating an anion exchange resin bed contains high concentrations of perchlorate as well as high total dissolved solids (TDS). The brine stream may range from 1% to 5% of the volume of contaminated water treated, but is usually in the range of 1 to 2%. Approximately 10 pounds of salt is used to regenerate each cubic foot of resin. Technologies to treat the concentrated regeneration brine include:

- *Calgon ISEP+™ System.* The perchlorate and nitrate destruction module (PNDM) of this system is a catalytic chemical reduction process for treating perchlorate and nitrate ions in the waste regeneration brine. In this process, ammonium (a hydrogen source) is added as a reductant, and perchlorate is reduced to chloride ($ClO4^- + 8e^- + 8H^+ => Cl^- + 4H_2O$). The system operates at 250º C and is relatively energy intensive. Pilot study results indicate that the PNDM can effectively reduce both perchlorate and nitrate present in regeneration brine waste, and that the treated regenerant stream can be reused (i.e., recycled) to effectively regenerate the resin. The overall process waste from the pilot test system was about 0.16% of the feed volume. O&M costs are estimated at about two times the cost of a comparable biological treatment unit.

- *Oak Ridge National Laboratory*. ORNL has developed a method to degrade perchlorate in $FeCl_3$-HCl regenerant solutions using ferrous iron and/or non-toxic organic reducing agents (US patent pending). Results indicate that complete destruction of perchlorate to chloride and water can be achieved in less than one-hour residence time. While perchlorate is reduced, ferrous (Fe^{++}) ions are oxidized to ferric (Fe^{+++}) ions, which replenish or "regenerate" the $FeCl_3$ - HCl solution.

- *Applied Research Associates - Integrated Thermal Treatment Process.* Laboratory research demonstrated that perchlorate in regenerant brine could be thermally decomposed at elevated temperature and pressure with the addition of reducing agents and promoters.   Concentration of the brine with reverse osmosis would be necessary to make the process cost-effective. A patent application is pending.

BIOLOGICAL REDUCTION PROCESSES

Bioreactors: Fluidized Bed, Packed Bed, Fixed Film, etc.

Perchlorate can be anaerobically biodegraded under reducing conditions. In these reactions, perchlorate serves as an electron acceptor and is readily reduced to water, carbon dioxide and chloride in the presence of an appropriate food source (electron donor) and redox conditions. A number of microorganisms have been identified that have the capability to reduce both perchlorate and chlorate. Most identified bacterial strains that reduce perchlorate are denitrifying facultative anaerobes. Not all denitrifying bacteria can reduce perchlorate however, and in some cases the presence of nitrate can inhibit perchlorate reduction. Many reactor types have been investigated for perchlorate removal. Most of these systems are attached growth reactors using either granular activated carbon (GAC) or sand, and are able to remove perchlorate to very low levels. A variety of electron donors including ethanol, methanol, acetate, hydrogen and cheese whey have been utilized in these reactors. A total dissolved solids concentration above 20,000 to 30,000 mg/L generally inhibits perchlorate reduction. Microorganisms from saline environments may be able to degrade perchlorate at up to 5% salt concentrations. Fluidized bed reactors (FBR) as well as packed bed reactors (PBR) have been developed for treating perchlorate contamination and are commercially available. Fixed-bed systems use stationary sand or plastic media to support the biofilm while fluidized bed systems support biofilm growth on sand or GAC media suspended in the fluid by mixing and upward flow velocities maintained in the reactor. The disadvantage is the pumping cost to maintain the required flows. Fixed-bed systems require periodic backflushing to remove biosolids buildup and to prevent plugging. Fluidized bed systems have higher pumping/energy costs, but have high surface area for biomass attachment and growth, and low pressure drop across the bed. Other innovative systems to biologically reduce perchlorate are also being developed including a patented a hollow-fiber membrane biofilm reactor that utilizes hydrogen as the electron donor to biologically degrade perchlorate.

In April 2002 the DHS Water Treatment Committee recommended a conditional acceptance of biological treatment (fluidized bed reactor) for the removal of perchlorate in a drinking water supply. The recommendation is based on a treatability study of the full-scale FBR system treating perchlorate-contaminated groundwater at the Aerojet facility in Rancho Cordova. Biological treatment systems are being considered by the Castaic Lake Water District as well as in the San Gabriel Groundwater Basin, but to date DHS has not issued a permit to any facility that allows biological treatment for domestic water supply.

Biologically Active Carbon (BAC)

AWWARF-funded bench and pilot scale tests indicate that biologically active carbon filtration can effectively remove low levels of nitrate and perchlorate under anaerobic conditions with the addition of an electron donor. Nitrate reduction can also enhance perchlorate reduction kinetics, making BAC filtration particularly attractive for combined nitrate-perchlorate remediation.

In Situ Biological Reduction

In situ biological treatment of perchlorate contaminated groundwater involves essentially the same processes that above-ground bioreactors use to reduce perchlorate. Perchlorate-degrading microorganisms have been found to be widespread in the subsurface environment (indigenous, native bacteria) and present at many, if not most, perchlorate contamination sites. In the presence of an appropriate food source (electron donor) and redox condition these bacteria have the capability to reduce perchlorate into chloride, carbon dioxide and water. Injection or placement of a food/carbon source (electron donor) into the contaminated aquifer is necessary to promote growth of the desired bacteria and effect perchlorate degradation. Different remediation strategies have been used to supply the proper mixing and amount of food source into the contaminated aquifer. A system of injection wells or injection/extraction wells is typically used to inject and mix the carbon source into contaminated zone at the proper concentration. Selection of appropriate electron donor appears to be site specific. Injected carbon sources that have been used or considered include acetate, corn syrup and edible oils. Another approach is to use biologically active trenches or permeable reactive barriers (PRBs) to treat the contaminated groundwater plume as it flow through biologically active zone. Materials used to construct PRBs or "barrier" trenches have included composting materials, cotton seed meal and cotton seed. To effectively implement an in-situ biological treatment technology requires a comprehensive understanding of the subsurface contamination distribution and subsurface hydrogeology. in addition to an understanding of the microbiological processes. A system of monitoring wells to routinely monitor key biological and water quality treatment parameters is essential to a successful implementation. Key biological treatment parameters would include redox, dissolved oxygen, perchlorate and parent/by-product concentrations, carbon source concentration, microbiological growth, etc. Perchlorate can be biodegraded in situ under a mildly reducing environment. A highly anaerobic reducing environment is generally not desirable due to potential dissolution and/or release of compounds or metal ions that may adversely impact water quality (e.g., metal ions, sulfides, methane).

Contaminated Soil - Composting

Naturally occurring bacteria can effectively reduce perchlorate under anaerobic conditions when perchlorate-contaminated soil is composted with an organic carbon source (electron donor) such as steer manure, sawdust, alfalfa, corn syrup, alcohol, sodium acetate, etc.

GRANULAR ACTIVATED CARBON (GAC)

In general, aqueous-phase GAC has not been found to efficiently treat perchlorate. Standard untreated bituminous GAC has a low affinity for perchlorate removal and, once this capacity is used, perchlorate sloughing or dumping will occur causing perchlorate "spikes" in the effluent. However, there are several facilities where GAC has been used to treat VOCs that have had success in treating perchlorate as a co-contaminant. The removal mechanism is probably a chemical reduction reaction that occurs on the surface of the carbon, similar to other oxidants such as chlorine, bromate, and chlorite that have been studied.

U.S. EPA and the AWWARF are funding research on enhancement techniques such as pre-loading with an iron organic complex and regenerating with an anionic reducing solution. A Penn State University study will utilize existing full-scale GAC units installed at a number of water treatment facilities that process perchlorate contaminated water. Column studies indicate that 40-45% more capacity may be achieved by pre-loading with an iron organic complex, and that 50-74% of initial capacity could be restored by reducing regenerant solution.

US Filter is conducting research on a tailored or treated carbon where a polymer or monomer is added to the carbon pores. This tailored carbon behaves similar to an ion exchange resin. Using this approach, US Filter hopes to achieve a tenfold increase in the standard GAC capacity for perchlorate (i.e. typical 1500 to 2000 bed volumes for standard GAC versus 15000 to 20000 bed volumes for tailored GAC).

MEMBRANE FILTRATION

Membrane filtration technology such as reverse osmosis and nanofiltration are basically very fine filters that use a semi-permeable membrane to remove undesired dissolved ions in water. There is currently little available performance data on perchlorate removal using these technologies. The AWWARF is supporting an ongoing research project to investigate the feasibility of membrane filtration technology for perchlorate removal in water sources of different quality.

The primary drawbacks to membrane filtration technology would be the energy requirements and production of a brine, which can be as high as 15% to 20% of the groundwater volume treated. The brine containing high TDS and perchlorate concentrations would require treatment or proper disposal. Membrane fouling due to hardness or biological growth is another concern (silica, oil, clay, iron, sulfur and humic acids can be present in a very fine or colloidal form; calcium carbonate and calcium sulfate scaling present problems). Due to the high capital and O&M costs, membrane filtration technology may not be relatively cost effective.

Reverse Osmosis (RO)

Water is forced through a semi-permeable membrane. RO has long been used to treat groundwater and other water sources to remove high concentrations of total dissolved salts. It would also be expected to be effective in removing perchlorate ions although there is limited performance data, if any, to support this conclusion. Unselective removal of dissolved ions results in a more corrosive, lower pH effluent. There may also be an issue with degradation of the membrane in treating perchlorate.

Nanofiltration

A partially permeable membrane is used to preferentially separate different fluids or ions. The membrane pores in nanofiltration are typically much larger than the membrane pores that are used in reverse osmosis. Since it is not as fine a filtration process as reverse osmosis and requires less energy to perform the separation. Nanofiltration generally works for particle sizes over 10 angstrom (10^{-10} m), rejecting selected salts (typically divalent), and passing more water at lower operating pressure than RO systems. Based on the size of the perchlorate ion, about 3.5 angstroms, nanofiltration may not prove to be effective for perchlorate removal.

Electrodialysis

Water is passed through channels of alternating semi-permeable and permeable membranes (to either anions or cations), while being exposed to an electrical field. An electrodialysis reversal (EDR) pilot unit was tested at a facility in Utah and found to be effective at removing low concentrations of perchlorate in groundwater with high TDS.

CHEMICAL REDUCTION

***UV Light / Zero Valent Iron Reduction* -** Lab studies (Gurol, Mirat D., and Kyehee Kim, 2000) indicate that perchlorate can be reduced by iron (FeO) under anoxic conditions and that UV light can accelerate the reaction rate to levels for practical application. A patent (#6,531,065) was issued March 11, 2003. The patent also covers use of the iron metal with a catalyst and with phosphoric acid. As of June 9, 2003, the San Diego State University Foundation, Office of Technology Transfer, was seeking funds to commence six months of field testing to develop a commercial prototype.

***Titanium +3 Chemical Reduction* -** Georgetown University has developed a technique using titanous ions (+3) to chemically reduce perchlorate. Several new organic ligands have been developed that have been shown to catalyze reduction of perchlorate by titanous ions (+3) ions to titanium dioxide and chloride in acidic aqueous media. A preliminary patent application has been filed.

***Electrochemical Reduction* -** A bench scale study (AWWARF funded) of electrochemical reduction of perchlorate was conducted using two-chambered batch reactor systems. Cathodic and anodic compartments were separated by an ion exchange membrane, and electrodes consisted of titanium coated with a thin film of titanium dioxide particles. Initial perchlorate concentration ranged from 50 mg/L to 500 mg/l. Perchlorate reduction was limited due to the competition among anions for active sites on the electrode surface, with perchlorate being less strongly adsorbed than both sulfate and chloride. The time required for ions in the water to travel to the electrode surface is a design problem in developing a practical full scale system.

(Note: Several chemical reduction processes for perchlorate related to treatment of ion exchange brine are discussed under the section on ion exchange.)

ELECTROCHEMICAL

***Capacitive Deionization (CDI*)**. Influent water containing salts enters space between two porous carbon electrodes where an electrostatic field forces the ions into the carbon. The ions are held in the carbon and purified water is discharged from the space between the electrodes. The process appears more effective for monovalent ions. CDI systems have the potential to use less than a tenth the energy per gallon to achieve similar results as electrodialysis or reverse osmosis systems. There are several different patents involving this technology. LLNL patented their carbon Aerogel capacitive deionization technology in 1995 and has licensed the technology for commercialization. Biosource, Inc. has a number of patents beginning in 1995 related to their Flow Through Capacitor technology.

PHYTOREMEDIATION

Plants are known to uptake salts such as perchlorate when irrigated with water or grown in soils containing elevated concentrations of such compounds. Most notably, health concerns have recently been raised regarding reports of elevated concentrations of perchlorate in lettuce or other vegetables that have been irrigated with Colorado River water contaminated with perchlorate. Such properties in plants are under investigation as potential phytoremediation strategies:

- *Willow Trees.* In bench scale tests, willow trees successfully treated water contaminated with both perchlorate and TCE. Rhizodegradation accounts for most of the removal of perchlorate with little uptake into the plant. Plant uptake might be significant with high nitrate environments (a competing terminal electron acceptor).
- *Salt Cedar Trees*. Salt Cedar trees are known to mine salt from the water. Stalks of the plant in the Las Vegas Wash picked up significant concentrations of perchlorate per gram of tissue
- *Containerized Wetlands.* A containerized wetland is an engineered system that uses of plants to treat water, relying on the interaction of the contaminant with plant roots, and their associated rhizosphere microorganisms, to assimilate or degrade the contaminant. A system Lawrence Livermore National Laboratory developed to treat perchlorate and nitrate, consists of fiberglass tanks in series, which contain coarse aquarium-grade gravel and native wetland plants. Testing over a seven month period showed that this system can remove perchlorate to below 4 μg/L and nitrate to less than 4 mg/L.

COST

Table 2 presents relative cost information for a number of perchlorate treatment alternatives. Cost information in Table 2 is somewhat dated (1997 dollars) and site specific, but is provided to give a general indication of the magnitude and relative cost of identified alternatives. Additional cost information is also provided in Table 1 on specific technology projects where available.

Table 2 Summary of Cost Estimates

Treatment Alternatives	Total Capital Cost ($Million)	Annual O&M Cost ($Million)	Total Annual Treatment Cost		Normalized Treatment Cost
			($Million)	($/kgal)	
Biological with GAC/FB	35	3	6.6	0.6	1
Ion Exchange	28	5.5	10.4	0.95	1.6
Liquid Phase GAC	46	16	20.7	1.88	3.1
Electrodialysis	84	5	13.6	1.06	2.1
Reverse Osmosis	65	10	16.6	1.52	2.5
Capacitive Deionization	131	3	16.6	1.52	2.5

Notes:

1. Total annual treatment cost determined by adding annual O&M cost and total capital cost amortized over 20 years at 8%.
2. All costs are in 1997 dollars.
3. All costs are order-of-magnitude only accurate to within plus or minus 50 percent.
4. Costs of land and related environmental requirements are not included.

Source: Harding Lawson and Associates (HLA). 1997. Draft Technology Screening for the Treatability of Perchlorate in Groundwater, Baldwin Park Operable Unit, San Gabriel Basin. (As cited by Catts, 1997.)

REFERENCES

1. Roote, Diane S. "Technology Status Report, Perchlorate Treatment Technologies." 1st ed. Ground-Water Remediation Technologies Analysis Center, 2001.

2. Darrett, Michael; Touchi, Steven R. Perchlorate "Treatment Options for the Community Wellhead Treatment System Technical Memorandum, Revision 1.0" Department of Toxic Substances Control, March 28, 2002.

3. Urbansky, E.T. and M.R. Schock, 1999. "Issues in Managing the Risks Associated with Perchlorate in Drinking Water", in Journal of Environmental Management, Vol. 56, pp. 79-95., Article No jema.1000.0274, available at http://www.idealibrary.com.

4. Urbansky, E. T. 1998 . ''Perchlorate chemistry: Implications for analysis and remediation.'' *Bioremed. J.*, 2(2), 81–95.

5. Logan, Bruce E. "Assessing the outlook for perchlorate remediation." *Environmental Science and Technology* 35 (2001): 482A - 487A. (http://pubs.acs.org/doi/abs/10.1021/es012564o)

6. Interstate Technology Regulatory Council. A Systematic Approach to In Situ Bioremediation in Groundwater *Including Decision Trees on In Situ Bioremediation for Nitrates, Carbon Tetrachloride, and Perchlorate, Technical/Regulatory Guidelines*. August 2002. (http://www.itrcweb.org/Documents/ISB-8.pdf)

7. Communication with Ron Lewis, DTSC Stringfellow Branch on 2/11/03 re: perchlorate contamination Treatment Alternatives.

8. Communication with Leslie Ferry, LLNL on 4/2/03 re: perchlorate and nitrate groundwater treatment systems at Lawrence Livermore National Laboratory.

9. Communication with Sharon Wong, DHS Division of Drinking Water and Environmental Management on 2/25/03 re: drinking water systems approved for perchlorate treatment.

RELATED LINKS ABOUT PERCHLORATE AND TREATMENT

Technologies General:

U.S. Environmental Protection Agency (EPA) Perchlorate Home Page
EPA Office of Water - Ground Water and Drinking Water
http://water.epa.gov/drink/contaminants/unregulated/perchlorate.cfm

U.S. Environmental Protection Agency (EPA), Region IX Fact Sheet on Perchlorate
http://yosemite1.epa.gov/r9/sfund/r9sfdocw.nsf/8e90f9fb63154b3a882573290078b556/9e6bfbec3c658277882570070063c329/$FILE/perchlorate2_02.pdf

\CLU-IN.ORG Perchlorate Remediation Resources
http://www.clu-in.org/perchlorate

Defense Environmental Information EXchange (DENIX) –Chemical and Material Risk Management Directorate – Perchlorate, Evaluation of ESOH Related Mission Risks
http://www.denix.osd.mil/cmrmd/ECMR/Perchlorate/Evaluation.cfm

Awwa Research Foundation Projects Related to Perchlorate
Search > Research Topics > Water Quality > Inorganic Contaminants > Perchlorate
(list & project summaries only ; publications require membership)
http://www.waterrf.org/search/Default.aspx

Perchlorate News: Perchlorate sites and the treatment of Perchlorate contamination
http://www.perchloratenews.com/index.html (4/26/11: web page no longer available)

Information and Resources About Perchlorate And Treatment Options
(Sponsored by Calgon Carbon Corp. – presents case studies from Ground-Water Remediation Technologies Analysis Center 2001 report)
http://www.perchlorateinfo.com/perchlorate-overview.html (4/26/11: web page no longer available)

Slide Presentation: Ammonium Perchlorate Treatment Technology Development
James A. Hurley, Program Manager Air Force Research Laboratory
http://www.epa.gov/ogwdw000/ccl/perchlorate/pdf/hurley.pdf

Drinking Water Standards:

California Dept. of Public Health. Perchlorate in Drinking Water: Status of Regulations and Monitoring Results
http://www.dhs.cahwnet.gov/ps/ddwem/chemicals/perchl/perchlindex.htm

Anion Exchange:

Oak Ridge National Laboratory (ORNL) Highly Selective, Regenerable Anion Exchange Resins
http://www.esd.ornl.gov/~b26/perchlorate.htm
http://www.esd.ornl.gov/~b26/Perchlorate%20destruction.htm

Bi-functional Resin for Removal of Contaminants from Groundwater
Innovative Technology Summary Report DOE/EM-0634
(abstract only available on Mendeley web page)
http://www.mendeley.com/research/bifunctional-resin-removal-contaminants-groundwater/

Nitrate and Perchlorate Removal from Groundwater by Ion Exchange Pilot Testing and Cost Analysis
Lawrence Livermore National Laboratory, University of California UCRL-ID-135639
http://www.llnl.gov/tid/lof/documents/pdf/236620.pdf

Optimization Study of Nitrate and Perchlorate Removal by Ion Exchange
Environmental Restoration Division LLNL Fact Sheet
http://www-erd.llnl.gov/about/info/posters/Halden_Burge.pdf

Calgon Carbon Corp. ISEP® Ion Exchange Technology for Perchlorate
http://www.calgoncarbon.com/ion_exchange/documents/ISEPforPerchlorate_NitrateRemoval.pdf
http://www.envirofacs.org/Pre-prints/Vol%2039%20No%202/Papers/p25.PDF
http://www.sti.nasa.gov/tto/spinoff2002/er_6.html

Francis J. DeSilva, March 1999. "Essentials of Ion Exchange" presented at the 25th Annual WQA Conference.
http://www.resintech.com/pdf/EssentialofIonExchange-1.pdf

Proposed City of Monterey Park (City) Delta Treatment Plant (Delta), Notice of Intent to Adopt a Negative Declaration, December 2002
http://www.wqa.com/pdfs/DeltaNoticeOfIntent.pdf (4/6/11: no longer available on the web)

Water Technology, Volume 23, Number 11, November 2000, "Removing Nitrate by Ion Exchange"
http://www.enviroalternatives.com/waternitrate.html

Edwards AFB Pilot Test – ORNL Bifunctional Resin
http://www.clu-in.org/download/contaminantfocus/perchlorate/ORNL1.pdf
http://www.ornl.gov/~webworks/cppr/y2001/rpt/113238.pdf

JPL Pasadena, Perchlorate Treatment Pilot Tests (biological & ion exchange)
http://www.denix.osd.mil/edqw/upload/JPLFRTR.PDF
http://yosemite.epa.gov/r9/sfund/r9sfdocw.nsf/db29676ab46e80818825742600743734/1f90d484b35ee20f88257007005e93ea!OpenDocument#approach
http://jplwater.nasa.gov/NMOWeb/files/docs/rod/Perchlorate-Lit-Review.pdf

Thermal Decomposition of Brines:

EPA ORD NCER - Hydrothermal/Thermal Decomposition of Perchlorate
http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/1261/report/

Membrane Filtration:

Technical Manual Water Desalination TM 5-813-8 September 1986, Department of the Army
http://ec.europa.eu/echo/files/policies/evaluation/watsan2005/annex_files/USACE/USACE1%20-%20Desalination.pdf

Electrodialysis Reversal (EDR) and Ion Exchange As Polishing Treatment For Perchlorate Treatment
Pilot Project for Magna Water Company, Salt Lake City, Utah
http://www.desline.com/articoli/3931.pdf

Biological Treatment:

Ammonium Perchlorate Biodegradation for Industrial Wastewater Treatment
ESTCP Cost and Performance Report, June 2000
http://www.clu-in.org/download/contaminantfocus/perchlorate/ESTCP1.pdf

April 2, 2002 DHS Letter: Conditional Acceptance of Biological Treatment (Fluidized Bed Reactors) For The Removal Of Perchlorate During Drinking Water Production.
http://www.safedrinkingwater.com/community/Aerojetletter040222.pdf

NASA-California Institute of Technology Jet Propulsion Laboratory, Anoxic FBR
http://downey.kaiserpapers.info/jpl.html

JPL Pasadena, Perchlorate Treatment Pilot Tests (biological & ion exchange)
http://www.denix.osd.mil/edqw/upload/JPLFRTR.PDF
http://yosemite.epa.gov/r9/sfund/r9sfdocw.nsf/db29676ab46e80818825742600743734/1f90d484b35ee20f88257007005e93ea!OpenDocument#approach

Henderson Nevada – Las Vegas Wash, Colorado River Contamination Problem:

EPA Region 9 Perchlorate in the Pacific Southwest Nevada and Colorado River
Site-Specific Information Kerr McGee Chemical Corporation, Henderson/ Colorado River
http://www.epa.gov/region9/toxic/perchlorate/per_nv.html

Colorado River Basin RWQCB September 2002 Executive Officer's Report – Perchlorate Discussion
http://www.swrcb.ca.gov/rwqcb7/documents/eo_reports/eo_02-09-04.htm (4/26/11: web page no longer available)
http://www.waterboards.ca.gov/coloradoriver/board_info/board_minutes/2002/090402mins.pdf
http://www.waterboards.ca.gov/coloradoriver/board_decisions/adopted_orders/resolutions/2002/res02_0183_perchlorate.pdf