Peer Reviewed: Assessing the outlook for perchlorate remediation

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Assessing the outlook for perchlorate remediation

Promising technologies for treating this widespread water contaminant are emerging.

Perchlorate (ClO_4^-) may appear to be just another addition to a growing list of halogenated chemicals that persist in the environment, but the chemical characteristics of this inorganic anion make it quite unusual. Typical chlorinated aliphatic compounds, such as trichloroethylene (TCE), are relatively insoluble carbonaceous compounds, strictly used for industrial purposes. They are volatile, adsorb, and are reduced by metals such as zerovalent iron. In contrast, perchlorate is a highly soluble inorganic anion (2.09 kg/L for $NaClO_4^-$) (*1*) that adsorbs poorly to mineral surfaces and activated carbon and is not retarded during groundwater transport.

The resulting perchlorate contamination is difficult to treat. Compared with an average useful lifetime of 18 months for TCE removal, granular activated carbon (GAC) columns used at the Texas Street Well Facility in Redlands, CA, have an operational lifetime of about one month for perchlorate removal, making remediation of the anion uneconomical. This well facility and 29 others in California have been shut down until cost-effective methods are found for treating perchlorate-contaminated water (*2*).

The U.S. EPA has identified perchlorate users and manufacturers in 44 states and releases in 18 states (Figure 1), estimating that perchlorate affects the drinking water of 15 million people in the United States (www.epa.gov/safewater/ccl/perchlor/r9699fac.pdf). Widespread perchlorate contamination of groundwaters only became known when a new ion chromatography (IC) method lowered the anion's detection limit in water from 400 parts per billion (ppb) to 4 ppb. The first survey of perchlorate in groundwaters in California in 1997 using the new IC method found perchlorate in 109 of 428 wells—27% of those surveyed—and concentrations at 33 sites above the state's action level of 18 ppb. A more recent survey of 367 groundwater wells in 17 states found perchlorate in only 9 wells at <4–7 ppb (*3*).

Perchlorate is manufactured in large quantities as ammonium perchlorate, primarily for use as an oxidizer in solid rocket propellants. It is also used in fireworks, batteries, and automobile air bags. It occurs naturally in small concentrations in nitrate deposits in Chile and has been found in fertilizers derived from these deposits but not in other fertilizers (*4–6*). Major sites of perchlorate groundwater contamination are associated with nonregulated past releases of perchlorate salts by manufacturers located in arid regions in the western and southwestern United States. For example, a perchlorate concentration of 1680 ppb has been found in the Nevada wash, a storm drainage canal feeding Lake Mead, part of the Colorado River serving major cities in Utah, Arizona, and California. Perchlorate concentrations in Lake Mead as high as 165 ppb have been reported, and monitoring well data from manufacturing sites where perchlorate was produced show concentrations as high as 0.37% w/w (*3*).

The health effects debate
Perchlorate is unique because it has been used as a medical treatment for Graves' disease (hyperthyroidism). At high oral doses, perchlorate competes with iodide in the thyroid and reduces hormone production. The health impact of perchlorate at low doses is unresolved. On the basis of health effects of perchlorate that is administered therapeutically, EPA determined that the oral reference dose

(RfD) for perchlorate is 0.5 mg/kg/d. This is the level used by the California Department of Health Services to set a drinking water action level of 18 ppb.

EPA's National Center for Environmental Assessment prepared a draft toxicological review document for perchlorate in 1999. The final report was scheduled for release in June 2000 but has been delayed. The draft considers carcinogenic, neurodevelopmental, developmental, reproductive, and immunotoxic effects of perchlorate exposure. The anion is not genotoxic (2). The draft contains a tentative revised RfD of 0.9 mg/kg/d, but an EPA-funded review performed by a team of scientists concluded that further work is needed before a final RfD can be definitively established.

The drinking water standard could therefore be as high as 32 ppb based on the revised RfD (2), but at least one environmental group has advocated regulation down to a 4.3-ppb contamination level (7). It may be another 12 years before perchlorate can be federally regulated in a uniform manner (2). Meanwhile, states have been left to set their own limits, such as 14 ppb in Arizona and 22 ppb in Texas. Site-specific limits are being set near the undetectable limit by IC. A recent agreement between EPA (Region 9) and Aerojet at a Superfund site in Rancho Cordova, CA, calls for treating water to less than 5 ppb. EPA is regulating perchlorate levels in water down to a 1.5-ppb contamination level in Region 1.

Physical treatment options
Although there are many treatment options, there is no obvious treatment technology for removing perchlorate from water. Perchlorate can be removed using ion exchange (IX), but some resins remove all other anions before binding perchlorate, making the final product water too corrosive for use in water distribution systems without restoring water hardness. Perchlorate binds tightly to strong base anion resins so that very high salt concentrations (7–12%) are needed for resin regeneration (2). Disposing of these IX brines can be problematic because the perchlorate is concentrated but not destroyed. One commercially available IX treatment process includes a module that uses a high-temperature, rare-earth metal for perchlorate reduction to chloride (2). An improved method for resin regeneration using material that selectively binds perchlorate over other anions has been developed, but this technology has only been demonstrated in the laboratory (8). Additional IX resins for removing perchlorate are being developed, along with techniques that extend GAC bed life, through in situ resin regeneration.

Ambient temperature treatment methods using metals, such as zerovalent iron, which successfully remediate chlorinated aliphatic compounds, such as TCE, do not work for perchlorate. That perchlorate does not react with zerovalent iron is not surprising to most inorganic chemists. The anion is extraordinarily inert in aqueous solutions and is used by chemists to provide a constant ionic environment in otherwise reactive solutions. Perchlorate has long half-lives with transition metal complexes such as $[Ti(H_2O)_6]^{3+}$ (0.17 yr) and $[V(H_2O)_6]^{2+}$ (53 yr). The organometallic compound, methylrhenium trioxide, has produced a reasonably short half-life of 2.3 min, but this requires solution conditions quite different from typical groundwaters (2). Recent studies with rhenium catalysts and sulfides show greater promise for perchlorate reduction, although water treatment technologies based on these new catalysts are not available (9).

Microbiological degradation
Bioremediation of perchlorate-contaminated waters is promising (10, 11). Although perchlorate only occurs naturally in Chile, bacteria capable of perchlorate degradation appear to be widely distributed in nature at concentrations ranging from one to thousands of bacteria per gram of water, wastewater, sediment, and soil (12, 13). Perchlorate is used as an electron acceptor by some bacteria for cellular respiration and is degraded completely to chloride ion (Figure 2). The bacteria that degrade perchlorate are diverse. Almost all of them fall within new species' classifications based on a 16s rDNA classification scheme—a recombinant DNA methodology based on the 16s gene, which can be used to assess the

phylogeny of bacteria. Most perchlorate-respiring microorganisms (PRMs) are capable of functioning under varying environmental conditions and use oxygen, nitrate, and chlorate (ClO_3^-)—but not sulfate—as a terminal electron acceptor. Perchlorate can be successively degraded to chlorate and then chlorite (ClO_2^-) by a novel chlorate reductase respiratory enzyme. A chlorate-respiring bacterium was the first isolate shown to be capable of benzene degradation, although only under denitrifying, and not chlorate-reducing, conditions (*14*).

Because chlorite is toxic to bacteria, the key to bacterial growth using chlorate and perchlorate is the presence of chlorite dismutase, a nonrespiratory enzyme that catalyzes the disproportionation of chlorite to O_2 and Cl^-. Rates of chlorite disproportionation by chlorite dismutase are greater than chlorate reduction by chlorate reductase and oxygen utilization by cytochromes; the slowest step is perchlorate reduction. As a result, no intermediates ordinarily accumulate in solution during perchlorate biodegradation. The heme-based chlorite dismutase is produced in such large quantities by PRMs that the addition of chlorite to a concentrated cell suspension grown anaerobically on chlorate or perchlorate will produce visible frothing due to O_2 release. The release of small amounts of dissolved oxygen by the perchlorate degrader *Dechlorimonas agitatus* CKB using chlorite, but not chlorate, has been shown to support naphthalene degradation by *Pseudomonas sp*. JS150 (*15*).

Microbial reduction of perchlorate supports very high growth rates of some PRMs. Although kinetic data are scarce, the maximum observed growth rates of two isolates (*Dechlorosomas sp.* KJ and PDX) using perchlorate (0.14 h^{-1} and 0.21 h^{-1}, respectively) were found to be only slightly less than or equal to growth rates using oxygen (0.27 and 0.28 h^{-1}, respectively) or chlorate (0.26 and 0.21 h^{-1}, respectively) (*16*).

The reason why these bacteria are so widely distributed in the environment and can grow so quickly using perchlorate is unknown. It may be due to the relatively greater abundance of chlorate in the environment than perchlorate. Chlorate has been produced for many years by the pulp and paper industry from bleaching operations and was used as an algicide. Some bacteria can respire using chlorate but not perchlorate. Chlorate reducers are up to 50 times more abundant than perchlorate reducers in water and soil samples (*12, 13*). The maximum chlorate reductase enzyme reduction rate is 3 times faster with chlorate than with perchlorate (*17*). Thus, it appears that perchlorate degradation may be linked to the ability of some respiratory enzymes to substitute perchlorate for chlorate.

Engineering green degradation

Biodegradation of perchlorate in engineered systems offers the greatest potential for inexpensive and complete perchlorate degradation. Several reactor technologies have been shown to treat perchlorate, for which four patents have been obtained (*18-21*). Table 1 lists treatment methods and bioreactor systems for degrading perchlorate (*2, 22–29*).

Suspended growth systems were first used to treat the high concentrations of perchlorate produced from washing rocket casings during replacement of solid rocket propellant. Since then, research has concentrated on reducing perchlorate from the low-parts-per-million (ppm) and parts-per-billion levels to nondetectable concentrations. Two bioreactor types—fluidized- and fixed-bed reactors—have been used.

In a fluidized-bed reactor, the support medium (usually GAC or sand) is kept suspended and mixed in the reactor by using a high recycle flow rate. The biomass on the packing is kept uniform in the reactor by mixing, and biomass thickness is controlled by shear and particle collisions. The main system disadvantage is the pumping cost for maintaining high recycle rates. Fluidized beds have completely removed perchlorate under laboratory and field conditions at influent perchlorate concentrations of 6–13 ppm using an ethanol feed (*2*). In a fixed-bed bioreactor, the biofilm support medium (sand or plastic media) does not move during water treatment. Biomass buildup on the packing requires that the system be

periodically backwashed to prevent clogging.

Using biological treatment for processing drinking water is not new. Biological denitrification for drinking water pretreatment has been practiced in Europe for some time now and is used at one location in the United States. All recent studies reducing perchlorate concentrations in contaminated water to acceptable drinking water levels have used acetic acid/acetate or hydrogen gas as substrates. Acetic acid is relatively inexpensive but, unlike alcohols and sugars, it is not lost to fermentation. It remains to be seen if the public would accept this for addition to drinking water supplies. Packed-bed reactors using acetic acid have been extensively tested in the laboratory and are currently being evaluated in the field at the pilot scale.

The disadvantage of using an organic feed is that the unoxidized substrate could remain in the drinking water. Residual substrate can stimulate bacterial growth in water distribution systems and contribute to the formation of disinfection byproducts in water disinfected with chlorine.

Although residual organic matter can be biologically removed in aerobic filters, several investigators are looking at using hydrogen gas as an electron donor for perchlorate biodegradation. Like oxygen, hydrogen is only sparingly soluble in water. Little biomass is expected from unused dissolved hydrogen because of the gas's low solubility and experiments showing that biomass yields using hydrogen gas are low. To overcome low solubility, different methods have been used to supply hydrogen to perchlorate-degrading biofilms, including unsaturated water flow over biofilm particles in a partial (5%) hydrogen atmosphere, pressurized hydrogen gas injection into the feed, and membranes for gas sparging (_22, 23_). Hydrogen reactors for perchlorate degradation have only received laboratory-scale testing.

Perchlorate is completely removed in both acetate- and hydrogen-fed packed-bed reactors, but at rates dependent on the perchlorate concentration in feed water (_30_). There are now enough perchlorate bioreactor studies that engineers can scale the size of systems needed for perchlorate removal. Overall perchlorate removal rates are a first-order function of perchlorate concentration in the fixed-bed reactors. Thus, the most highly contaminated streams have the most rapid reaction rates in fixed-bed bioreactors.

In situ degradation
In situ bioremediation of perchlorate-contaminated waters eliminates the need for aboveground treatment. Anoxic conditions necessary for in situ perchlorate treatment can be established either by creating permeable reactive biobarriers containing high concentrations of organic matter, or by injecting substrates into the ground.

In one example, groundwater leaving a MacGregor, TX, site, at which soils contained 23–1,800,000 mg/kg perchlorate concentrations, was contaminating nearby surface waters. By digging trenches and directing the water flow through biobarriers containing gravel and organic amendments (compost, vegetable oil, or cottonseed), perchlorate was removed from a 27,000-ppb level down to nondetectable levels (4 ppb) (_31_). Adding lactate to perchlorate-contaminated soils achieves perchlorate removal in a few days under optimal laboratory conditions (_13_). Lactate can be dissolved in water or supplied as a polylactate compound that slowly dissolves (_32_). In Sacramento, CA, pulsed injection of acetate into a deep aquifer (100 ft) removed perchlorate from contaminated water from 12,000 ppb to below the detection limit. The hydrogen evolved from anaerobic fermentation of lactate and other substrates can also drive the reductive dehalogenation of chlorinated aliphatic compounds, such as TCE, which are common copollutants at perchlorate-contaminated sites (_32_).

Outlook and challenges

Despite the unique nature of the perchlorate anion, the outlook for remediating perchlorate-contaminated water looks promising. For small volumes of water, new IX technologies that selectively remove perchlorate from water show the greatest promise. Chemical methods can degrade perchlorate in regenerated systems that use NaCl brines, and it has recently been shown that perchlorate can be biologically degraded even in high salt solutions (11%), which are typical for these brines (*33*). For treating widespread contamination of drinking water, in situ and ex situ (see photo on preceding page) biological systems appear to be the most cost-effective solutions. These systems are in the developmental stage for drinking water applications, but successful laboratory and field tests demonstrate the potential that this technology has for treating perchlorate-contaminated

A pilot-scale study at the Naval Weapons Industrial Reserve Plant in McGregor, TX, evaluated ex situ treatment of perchlorate-contaminated soil and groundwater in a fixed-bed anaerobic bioreactor. ENSAFE, INC.

water and reducing contaminant concentrations to potable water levels. Although the full costs of these systems remain unknown, they are certain to increase current drinking water treatment costs.

Many sites contaminated with perchlorate also contain high nitrate levels and low concentrations of chlorinated aliphatics, such as TCE. Nitrate is removed along with perchlorate in bioreactors because most perchlorate reducers are denitrifiers. The effect of a perchlorate-reducing environment on TCE degradation and on downstream processes, such as those using GAC columns, also need to be investigated, although there appear to be no technical roadblocks for process trains using both bioreactor and GAC systems. Biological drinking water treatment systems, however, have not yet been approved for use for public water systems, and it remains to be seen if the public will accept the use of these treatment systems for degrading perchlorate. What does seem certain is that perchlorate will remain in groundwater sources used for drinking water supplies for a long time unless steps are taken to treat the aquifers or the water removed from these sources.

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