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Zero-Valent Metals Provide Possible Solution To Groundwater Problems

■ ***Permeable underground barrier containing iron is proving to be an efficient and cost-effective remediation technology***

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C&EN West Coast News Bureau

Real life isn't supposed to be this simple.

Two hundred twenty tons of iron filings, buried underground in a giant trough, have replaced elaborate machinery to clean up contaminated groundwater that has plagued a former Intersil semiconductor manufacturing plant in Sunnyvale, Calif., for more than a decade. The iron barrier is breaking down toxic trichloroethene into benign products, yielding water that passes muster with the Environmental Protection Agency. And where an aboveground pump-and-treat facility once stood, is a newly paved parking lot.

There are no parts to break, there is no need for electricity or maintenance, and, its creators say, the underground wall should last indefinitely. Soon, this system will begin saving Intersil more than $300,000 per year that the company was paying to operate, maintain, and manage the pump-and-treat facility. The property, which was deemed unusable for the life of the 30-year cleanup process because of the need for constant access and monitoring, can now be leased to other tenants.

The Intersil site is the first full-scale demonstration of this permeable barrier cleanup method that exploits zero-valent metals, a hot new topic in environmental chemistry.

Far from being skeptical of a field that appeared almost out of the blue three years ago, a host of government agencies and industries have joined academia in studying the use of iron and other zero-valent metals as a new addition to environmental remediation technology.

The concept is a new twist on the age-old corrosion process. When metal corrodes, the corrosive agents undergo reactions as well. Scientists are beginning to realize that these reactions may be used to remediate a slew of environmental scourges from chlorinated solvents to radionuclides.

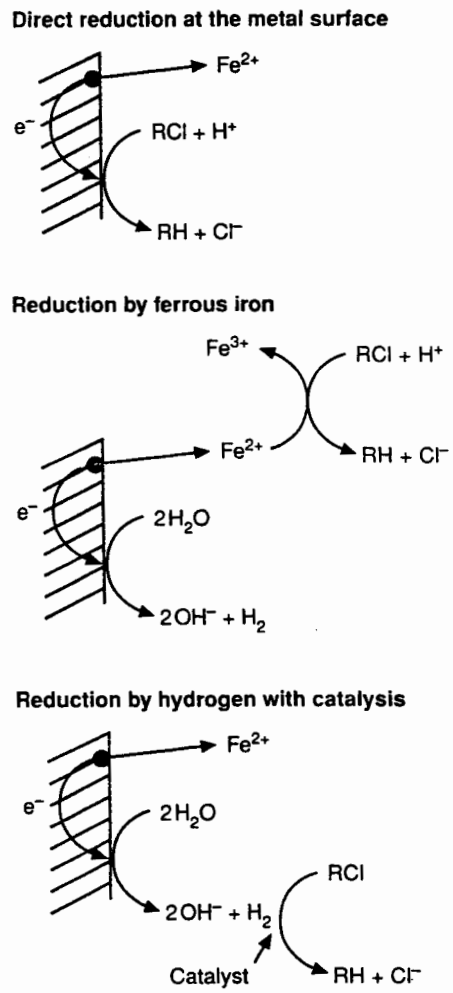
With thousands of hazardous waste sites around the country, the Environmental Protection Agency, the Department of Defense, the Department of Energy, the Air Force, and companies like General Electric and DuPont would save a great deal of money if the technology proves as useful as it is mind-bogglingly simple.

Ten years ago, at the University of Waterloo in Ontario, graduate student Glenn Reynolds was studying the corrosion of polyvinyl chloride, polytetrafluoroethylene, and metal pipes by water contaminated with chlorinated organics. He and his adviser, Robert W. Gillham, chairman of Waterloo's earth sciences department, noticed that the organics were disappearing from test bottles containing metals, "but our main interest was plastics, so we didn't pay much attention to it," Gillham says.

The potential environmental application seems obvious in retrospect, yet was something easily unrecognized, says Paul G. Tratnyek, chemistry professor at Oregon Graduate Institute of Science & Technology, in Beaverton. "If you had come to me five years ago and asked if metals could cause degradation, I would have scratched my head and said, 'Well, yes, but who cares,'" he says.

It was not until several years later that Gillham realized the degradation reaction could be exploited to clean up environmental contamination. Exploring earlier literature, Gillham found that in the early 1970s Keith H. Sweeney and J. R. Fischer had studied the phenomenon, even obtaining a patent for reductive dechlorination of halogenated pesticides.

Chlorohydrocarbons can be reduced by iron in three ways



But no peer-reviewed papers were published, and the idea never caught fire. "I suppose it was because concern about overchlorinated organics was at a low level," Gillham speculates. "The technology really got lost."

Gillham and colleagues tested the

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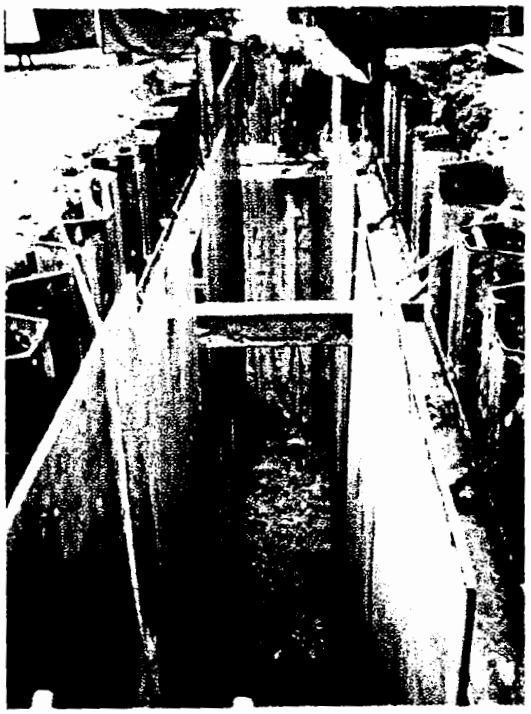


Treatment wall at a former Intersil semiconductor production site in Sunnyvale, Calif., is ready to be loaded with iron filings to treat groundwater contaminated with trichloroethene.

idea by using turnings from a machine shop at a contaminated site and found that water contaminants in the ground did indeed disappear. Gillham started a company, EnviroMetal Technologies Inc. (ETI), to test and market the technology. Gillham and ETI now hold several patents for the application.

"It provides a viable alternative to pump-and-treat," Gillham says. It doesn't require energy, it conserves water, and although installation costs may be comparable to other aboveground systems, the big payback is in operation and maintenance costs, he says.

Initially, the Waterloo work was met with some skepticism. "At a gut level, people couldn't believe it could be that easy," Gillham says.

Sponsors were demanding an explanation for iron's seemingly marvelous degradation of contaminants. "For a little while, it got the nickname 'magic sand,' but that started to be a liability because it implied something mysterious about the process," Tratnyek says.

Tratnyek began probing the chemistry of the reactions, and confirmed that the mechanism was simply corrosion with contaminant substituting for oxygen as the dominant oxidant. A chlorinated solvent, RX, oxidizes iron to Fe(II) and is dechlorinated in the process:

$$Fe^0 + RX + H^+ \rightarrow Fe^{2+} + RH + X^-$$

"It's kind of fun. Basically it's old-fashioned corrosion chemistry that everyone's had up to their eyeballs, and we're turning it around to be very useful," Tratnyek says.

In lab experiments, the mechanism looks like electron transfer from the metal surface to the adsorbed contaminant, but it is difficult to say how accurately this represents what goes on outside, under real environmental conditions, he says.

Many scientists are now studying the process. Among their findings so far: The rate of degradation increases with increasing ratio of iron surface area to solution volume. Iron appears to degrade many chlorinated aliphatics, although it has little effect on some serious environmental contaminants such as polychlorinated biphenyls. Iron is dissolved during the process, but researchers have concluded the metal disappears so slowly that remediation barriers likely will still be effective for many years, even decades.

As for the initial critics, Gillham says, "They have pretty well gone away."

The estimated combined cleanup cost of military, DOE, and Superfund sites around the country is about $650 billion, according to Steven C. McCutcheon, environmental engineer at EPA's National Exposure Research Laboratory in Athens, Ga. Hence, groups aimed at accelerating new remediation technologies are jumping on the zero-valent bandwagon. "It's pretty important with the horrendous costs," he says.

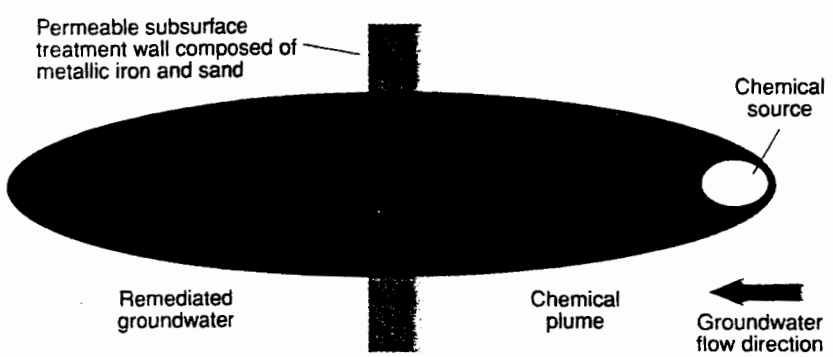
McCutcheon is a cochairman of a permeable barriers work group, along with Stephen Shoemaker of DuPont's corporate remediation department in Houston. The group consists of scientists and engineers throughout the country working furiously to get the wrinkles out of the technology.

The Solvents In Groundwater Research Program at Waterloo is sponsored by corporations such as General Electric, Boeing, Motorola, and DuPont. Through the consortium, industry and academia also facilitate zero-valent metals research.

Last March, at the American Chemical Society meeting in Anaheim, Tratnyek and Stanford University environmental engineering professor Martin Reinhard cochaired a symposium on zero-valent metals and contaminant remediation. The symposium, cosponsored by the Division of Environmental Chemistry and the Western Regional Hazardous Substance Research Center at Stanford, generated great interest: 40 papers were presented to more than 150 attendees, Tratnyek says. Additionally, many papers on zero-valent metals will be presented at the Emerging Technologies in Hazardous Waste Management symposium to be held in September in Atlanta (see page 46).

ETI is conducting feasibility studies at more than 25 industrial facilities across the U.S. ETI Manager John Vogan says the company is prepared to study at least 100 more sites. Most interested companies, Vogan says, hear of ETI by

Groundwater treatment wall purifies chemical plume



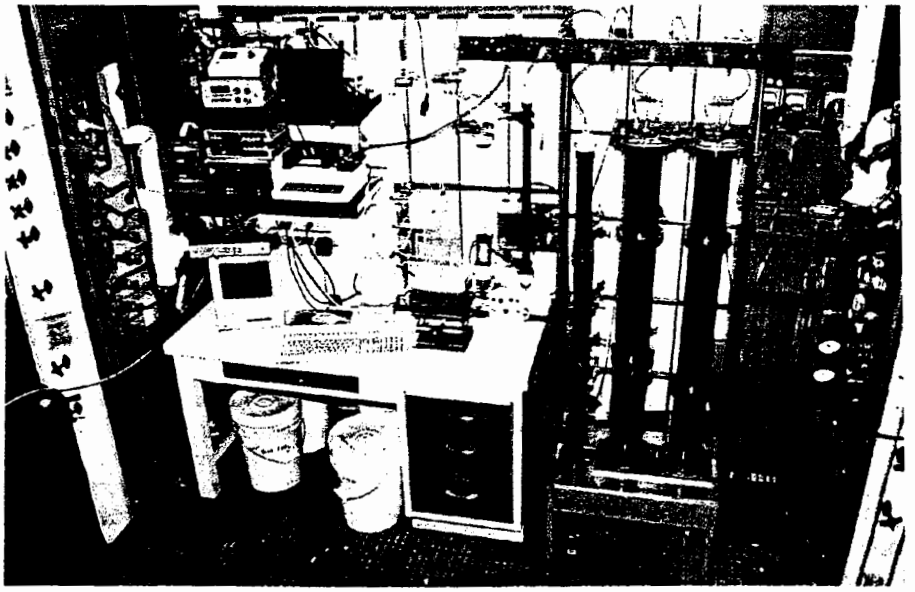
word of mouth. "With no aggressive marketing on our part at all, we've had no trouble locating [companies]," he says.

After several months of column tests of a particular site, pilot-scale field tests may take six months or a year. Then, a full-scale operation can be implemented.

Characterizing a ground site is very important when using permeable barriers, the engineers say. Misjudge the depth or speed of the flow and the contaminated water will sneak around or under the wall. Each site must be painstakingly researched. "The problem is we don't have a design manual that tells the engineers what to do," McCutcheon says. "Right now, most people are going by the seat of their pants."

The Intersil site in Sunnyvale, in operation since December, is the first full-scale operation in the country. The San Francisco-based environmental firm Geomatrix Consultants, in collaboration with Vogan, designed and built the underground wall for $1.5 million, after receiving a go-ahead from the California government.

"The groundwater was shallow, it was an industrial area, the quality of the groundwater was not high—it was an ideal site to try this technology out," says Deborah A. Hankins, executive vice president of engineering at Intersil. "I think we're breaking the ice."



Pilot-scale column studies of iron-promoted degradation of chlorinated solvents in groundwater is being carried out by General Electric corporate R&D in Schenectady, N.Y.

To accommodate the groundwater flow rate of 1 foot per day, the engineers designed a wall 40 feet long, 4 feet wide, and 20 feet deep. In the four days it takes for water to seep through the wall, a contaminant like trichloroethene degrades into products that are themselves degraded. The water seeping from the barrier meets EPA standards, the engineers say.

One area of debate among zero-valent metals researchers is the potential seriousness of precipitates. As the reaction proceeds, the pH rises locally, causing inorganics to precipitate, which could clog the porous wall. "There's a lot of research focused on identifying precipitates and looking at ways of removing them or preventing their formation in the first place," Gillham says.

According to McCutcheon, mixing iron with a substance such as pyrite lowers the pH and prevents precipitation. "If we just have reductive iron and some impurities and chlorinated solvents, the pH will drift on up to 10 or 11. That shuts down the reaction pretty well," McCutcheon says.

But other scientists say they have not found the same problems. At General Electric's corporate R&D division in Schenectady, N.Y., staff chemist Timothy Sivavec has been studying potential fouling mechanisms in column studies of zero-valent metals for four years.

Running columns at accelerated flow over a period of a year allows him to predict what will happen to a permeable wall in 10 years. In one such study, "we only lost about 10% of porosity," Sivavec says. "Also encouraging was [that] the dechlorination rates remained remarkably constant. So all is boding well."

Since operation began, the Sunnyvale site has not experienced precipitate problems, either, say Geomatrix scientists. "It is a concern, something we looked at extensively, but we estimated that it wouldn't be a significant enough problem to try doing anything about at this site," says John D. Gallinatti, principal hydrogeologist for Geomatrix.

In addition to chlorinated solvents, zero-valent metals appear to be effective against many other environmental ills.

McCutcheon says iron can degrade dye waste, and could possibly be used to clear up water tainted with dye effluents from textile mills, for example. Iron also may be able to degrade the now-banned pesticide toxaphene, which still contaminates soil where it was used for corn and cotton production.

Another possible use of iron remediation barriers is treatment of soil contaminated with other heavy metals. For example, highly toxic chromium(VI), although not as big a problem as chlo-

Iron degrades chlorinated hydrocarbons at varying rates

	Half-life (days)	Halogenated products
Trichloromethane	6.5	Dichloromethane (low concentration)
Tetrachloromethane	5.4	Trichloromethane, dichloromethane
Monochloroethene	14.9	None detected
1,1-Dichloroethene	55	None detected
cis-1,2-Dichloroethene	37	None detected
trans-1,2-Dichloroethene	6.7	None detected
1,1,1-Trichloroethane	5.5	1,1-Dichloroethane
1,1,2-Trichloroethane	7.8	Trace of monochloroethene
Trichloroethene	7.1	*cis*-1,2-Dichloroethene
1,1,2,2-Tetrachloroethane	10.2	*cis*-1,2-Dichloroethene, *trans*-1,2-dichlorethene
1,1,1,2-Tetrachloroethane	5.2	1,1-Dichlorethene
Tetrachloroethene	13.9	Trichloroethene, *cis*-1,2-dichloroethene
Hexachloroethane	6.1	Tetrachloroethene, trichloroethene, *cis*-1,2-dichloroethene, 1,2-dichloroethane
Tetrabromoethene	6.7	Tribromoethene, 1,2-dibromoethene

Source: EPA National Exposure Research Laboratory

rinated solvents, is a by-product of the plating industry and is targeted by EPA as a major environmental offender. Because of its mobility, Cr(VI) is hard to corral long enough to remove from soil.

Its reduced form Cr(III), however, is less harmful and insoluble. Iron, it just so happens, reduces the Cr(VI), says Robert W. Puls, senior research soil scientist at EPA's Robert S. Kerr Environmental Research Laboratory in Ada, Okla.

The reaction is quite rapid, occurring on the order of less than a minute, Puls says. The reaction is probably driven by several processes, including reduction at the surface of iron and in solution from the production of ferrous iron. The Cr(III) is immobilized in a precipitate of complex composition, Puls says, and stays put in the iron barrier, out of the running water.

Puls and colleagues started a field experiment for chromium remediation last September at a Coast Guard base in Elizabeth City, N.C. The test barrier, with a composition of 50% iron mixed with sand, has reduced chromate in the groundwater to below detection levels, Puls says.

The cost of a full-scale system, which Puls's group may be implementing soon, will be at least an order of magnitude cheaper than a pump-and-treat facility, he says—probably less than $500,000.

Iron's ability to reduce trace elements may also be used to rid soils of technetium, a radionuclide polluting several DOE sites, says Nic Korte, group leader of the restoration technology group at Oak Ridge National Laboratory's environmental science division in Grand Junction, Colo.

The reducing conditions of iron and water cause technetium to precipitate out into an immobile state, much like the process for immobilizing chromium.

Inexpensive and environmentally innocuous, iron is the metal of choice for most test sites, scientists say. But in the lab, other metals, particularly zinc and tin, can degrade compounds much more rapidly than iron. Palladium, with its catalytic ability, produces dramatic results as well. But the potential toxicity and expense prevent placing tons of these metals into the ground.

One variation includes adding small amounts of palladium to iron. A group at the University of Arizona led by chemistry professor Quintus Fernando is patenting its process of palladium-enhanced iron degradation (C&EN, April 24, page 50). Some important contaminants, such as *cis*-1,2-dichloroethene, remain resistant to degradation by iron. However, palladized iron dechlorinates the chemical within a few hours.

Korte says the technology, limited by palladium's expense, will probably be used in aboveground treatments. For example, 55-gal drums of carbonated waste are expensive and hazardous to dispose of. "But it's easy to hook up a 55-gal drum, destroy the contaminant with palladized iron, and rinse it with acid," Korte says.

Stanford's Reinhard also touts iron's potential for removing nitrates from soil. In a paper presented at the ACS meeting in Anaheim, Reinhard and colleagues described reducing nitrate to nitrite with iron with a reaction half-life of less than four minutes. "[Nitrate contamination] is a much more prevalent problem than chlorinated solvents worldwide, [especially] in agricultural areas where they use fertilizers," Reinhard says.

As with any new technology, there's plenty more to be explored in the field of zero-valent metals, Reinhard says. "We are just at the beginning of uncovering [new methods]," he adds, "and I'm convinced what we're doing now will look medieval in a few years." □

Ultrasonic cleaning cuts waste, energy use

The ultrasonic tubular resonator, a device for removing surface contamination, is making its way to chemical process tanks. Cleaning tanks and reactors with this device is less expensive, less energy intensive, and more environmentally friendly than with conventional cleaning methods, according to results of a demonstration project by DuPont Merck Pharmaceutical.

DuPont Merck has been testing the technology at its facilities in Deepwater, N.J., under a grant from the National Industrial Competitiveness through Energy, Environment & Economics (NICE^3) program. NICE^3 is a joint cost-sharing grant program of the Department of Energy and the Environmental Protection Agency.

The grant requires DuPont Merck to make available the results of the demonstration project. These results were presented in May at two seminars organized by the New Jersey Technical Assistance Program for Industrial Pollution Prevention.

Ultrasonic cleaning of reaction tanks and reactors is simple, says Angelo C. Piro, president of the U.S. subsidiary of Telsonic Ultrasonics, the Swiss producer of ultrasonic tubular resonators. A tank to be cleaned is filled with water, the water is heated to 150 °F, and 2% surfactant by weight is added. Ultrasonic power is applied for two to four hours, depending on tank size and contaminant type, and then the water is drained.

As environmental manager for DuPont Merck's R&D division until the end of April this year, Piro tested the tubular resonator in reactors ranging in capacity from 20 to 300 gal. Depending on tank size, one to three resonators were used, and cleaning times ranged from two to four hours. In Europe, however, trials have been carried out on 2,000-gal tanks, says Piro. For this capacity, six resonators were required.

Conventional cleaning requires refluxing of a solvent, usually methanol, inside tanks for four to eight hours, explains Piro. The vessel is half filled with solvent and then heated to the solvent's boiling point. At the end of the reflux period, the solvent is cooled and drained, and a sample is analyzed. The procedure is repeated until analysis shows an acceptable level of contaminants in the solvent. This process can take up to five cycles, says Piro. And spent solvent then has to be disposed of by incineration.

With the ultrasonic tubular resonator, cleaning usually takes only one cycle, DuPont Merck tests show. For a 300-gal vessel typically cleaned with methanol, savings amounted to almost $4,900 per cleaning, representing the cost of methanol, energy for refluxing, labor, and methanol disposal. Other savings due to reduced vapor emissions on site and fewer hazards to workers also are realized. For the same vessel, the cost of the tubular resonators—about $27,000—is paid off after six cleanings, says Piro.

Use of solvent is not completely eliminated, explains Mary F. Cooke, director of chemical process R&D facili-