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A Nickel–Iron Wall Against Contaminated Groundwater

New reactive-wall technology begins pilot study at Cape Cod military site.

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Deep beneath the sparse macadam landscape of the Massachusetts Military Reservation (MMR), known familiarly by its Cape Cod neighbors as Otis Air Force Base, lie at least 10 plumes of tainted groundwater that have contaminated large portions of the Cape's sole-source aquifer. Under pressure from EPA, the Massachusetts Department of Environmental Protection (DEP), and Cape Cod property owners, the Department of Defense must find a way to clean or contain these plumes before they further threaten the Cape's drinking water.

This fall, the Air Force Center for Environmental Excellence, the lead agency charged with remediating this Superfund site, began a test of a promising new technology designed to passively clean groundwater contaminated with chlorinated compounds. The technology: a permeable reactive wall made of zero-valent iron filings enhanced with nickel plating. Although a number of private and government sites around the nation have field tested reactive iron filing walls, the MMR test is the first to attempt to place such a wall so deep—to depths of 120 feet—and the first to test a nickel-plated iron wall in situ.

Reductive dehalogenation in aqueous solution, first reported in 1972 and further developed by Robert Gillham of the University of Waterloo, Ontario (*1*), is surprisingly simple: place a permeable wall made of iron filings across a contaminated groundwater plume. When halogenated methanes, ethanes, and ethenes—for instance, trichloroethylene (TCE), perchloroethylene, and vinyl chloride—contact the zero-valent iron filings, they are dehalogenated, ultimately producing chloride and nontoxic hydrocarbons (*2*). Contaminated water flows into the wall; water that meets regulatory standards flows out. Although cost data have yet to be collected on a large scale, the Air Force estimates that remediation costs of reactive technology are half those of pump-and-treat systems.

Several full-scale, pilot tests under way

Gillham founded EnviroMetal Technologies, Inc., in 1992 to commercialize the reactive wall technology. To date, five full-scale in situ treatment zones have been installed: two at commercial sites in California, one in Kansas, one in Northern Ireland, and, in June 1996, one at a U.S. Coast Guard site in Elizabeth City, N.C. Several pilot-scale studies were started in 1995 and 1996, and others are planned to begin by early 1997 (*2*).

The execution of permeable reactive wall technology is, of course, far more complex than the concept. Numerous variables must be tested at each site before walls can be built. Engineers are still experimenting with different emplacement techniques, and scientists are researching bi-metal technology and the proportions of iron to filler material, such as sand, that can be used.

So far, the results are encouraging. According to EnviroMetal's Larry Kwicinski, toxic compounds in the groundwater at a former semiconductor plant in Sunnyvale, Calif., the location of the first full-scale demonstration of the technology, were almost completely degraded. This 100% pure granular iron filing wall is 4 ft thick, 40 ft wide and approximately 20 ft deep (*2*). TCE levels of 30–68 parts per billion (ppb) in the groundwater entering the wall were reduced to < 0.5 ppb; *cis*-1,2-dichloroethylene (cDCE) levels of 393–1916 ppb were also degraded to < 0.5 ppb. Kwicinski reported similar results from a 1995 pilot-scale installation in New York.

These sorts of results excite environmental engineers like Ed Pesce, deputy program manager of MMR's Installation Restoration Program and project manager on the reactive wall test. "If this works in sandy or fairly permeable aquifers, this could work in many Department of Defense sites throughout the United States and the world. We're quite excited about its potential." Twenty U.S. military bases contain Superfund sites (*3*).

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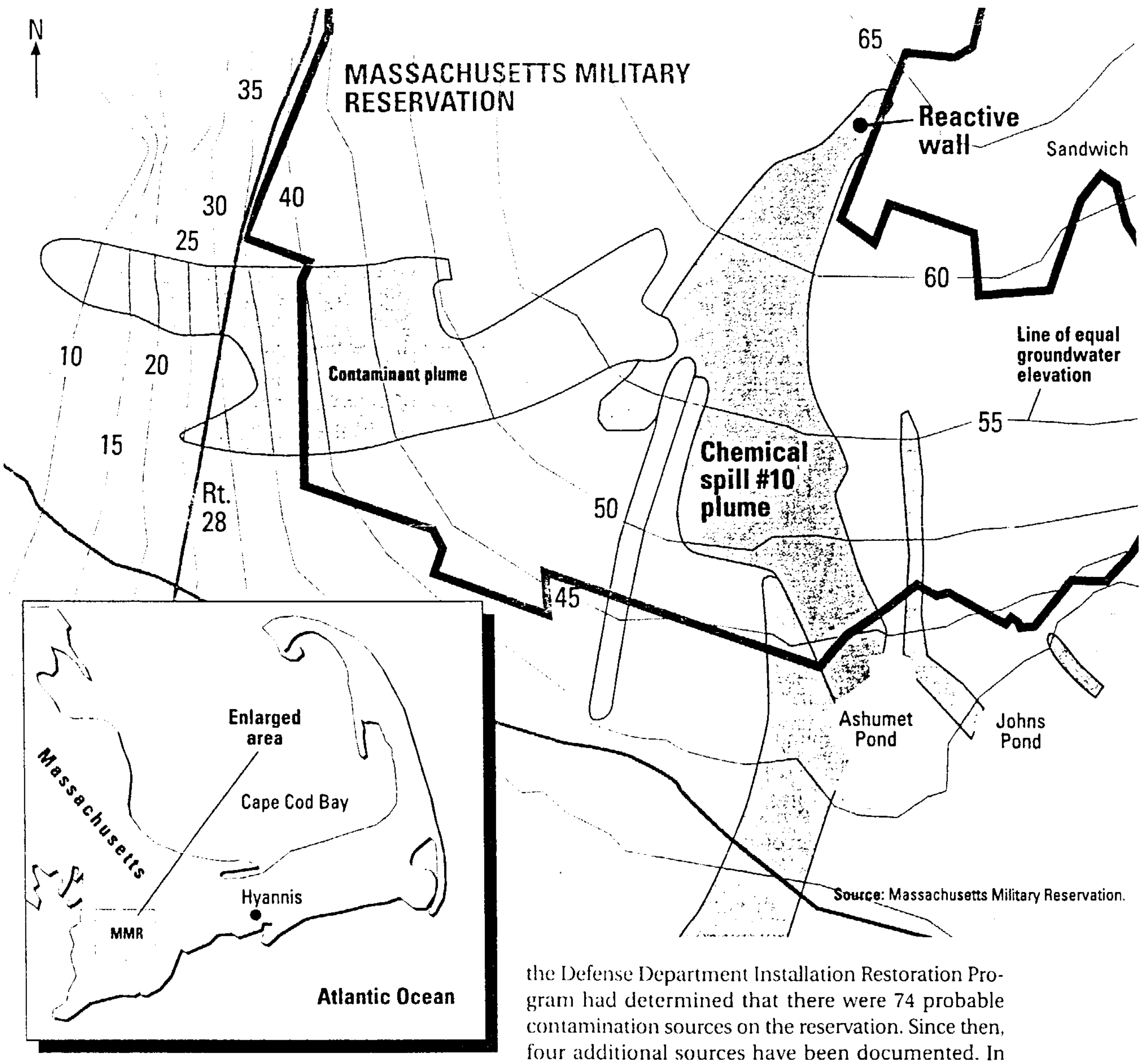


Source: Massachusetts Military Reservation.

A continuing public health threat

The 22,000-acre reservation, first established in 1935 on land just south of the Cape Cod Canal, has been home to the National Guard, the Air Force, and the Coast Guard. Contaminants at the site include jet fuel, degreasing solvents, and even radioactive wastes (*4*).

Today, the groundwater plumes, some more than 3 miles long, move an average of 1.5 ft per day, says Pesce. Daily, the plumes contaminate 8 million gallons of the Cape's drinking water, according to John Rodman, assistant secretary of environmental affairs for the Massachusetts DEP. The *Boston Globe* recently reported that scientists have documented 53 billion gallons of contaminated water, and many residents suspect the contamination is even more widespread (*5*). In August, the Department of Defense agreed to look for contamination in water beneath a firing range, the *Globe* reported.

Public health concerns surfaced in 1979 when the DEP closed a public well in the neighboring town of Falmouth, sparking an investigation into the quality of the area's groundwater. By 1981, scientists had determined the source of the well's contamination to be the base's wastewater treatment plant. By 1986, the Defense Department Installation Restoration Program had determined that there were 74 probable contamination sources on the reservation. Since then, four additional sources have been documented. In 1989, the MMR was added to the National Priorities List.

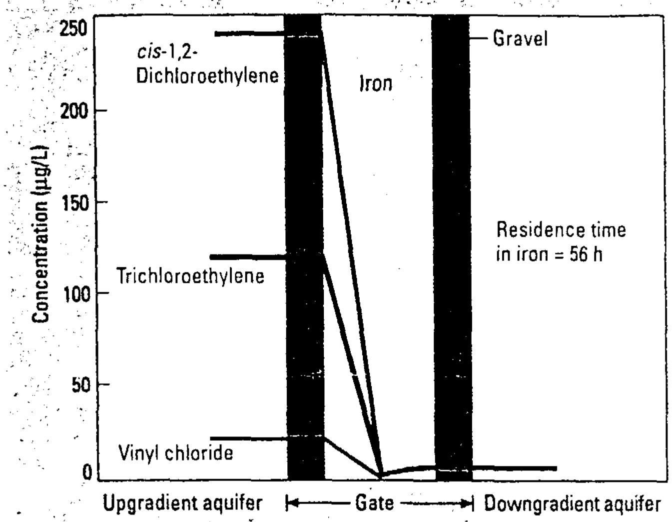
Over the past 15 years, the Defense Department has paid hundreds of citizens from the surrounding towns to shut private wells and convert to public water supplies. In early 1996, two public wells in Bourne, which are located near a benzene-contaminated plume generated by a capped landfill on the base, were closed.

The problem is critical for area residents. "The entire town of Falmouth gets its water supply right now from areas down gradient of the plumes," said Susan Nickerson, director of the Association for the Preservation of Cape Cod. "The [Mass.] DEP projected the flow path of these plumes over the next [several decades] and showed that huge areas of Falmouth will be affected if these plumes are not stopped."

In 1994, the Air National Guard, then leading restoration efforts, proposed a $250 million, 20-year plan to contain all known plumes. Much of the plan depended on a massive pump-and-treat operation that would remove 27 million gallons of water daily from the aquifer. But by 1995, with the design work 60% complete, Nickerson said, it became clear that removing that much water from the aquifer would dra-

Building on initial pilot-scale results

Previous tests of permeable zero-valent iron reactive walls have yielded encouraging results that researchers are hoping to improve upon at the Massachusetts Military Reservation (MMR) site. A 1995 in situ pilot project at an industrial facility in New York state significantly reduced groundwater VOC concentrations just half way through the 3.5-foot thick 100%-iron wall (2). This pilot used a funnel-and-gate design to concentrate the groundwater flow through the gate. Similar results are anticipated with an MMR wall just a few inches thick composed of nickel-coated iron filings.



matically alter the groundwater flow, potentially drying up ponds and private wells. The plan was abandoned.

Consequently, the Pentagon stepped in this April and moved management of the restoration effort from the Air National Guard to the Air Force. A new strategic document, released in July, proposed to clean up two plumes but recommended further study on the remaining eight. "We're at square one all over again," said Nickerson.

MMR staff, however, are more optimistic. "We're finishing up most of the investigation that needs to be done, and we're designing new systems," said MMR Installation Restoration Program spokesperson Douglas C. Karson. "We've already treated 35,000 tons of soils, capped a landfill, have one pump-and-treat system up, and have done a lot of monitoring at lots of sites. We have a firm schedule in place to construct [treatment] systems for the groundwater plumes. We would envision in the next four years to have all remedial action contracted."

Search for cost-effective solutions

The MMR reactive wall demonstration project is being performed in conjunction with EPA's Technology Innovation Office and Clean Sites, Inc., a non-profit public interest and research organization that manages public–private partnerships studying innovative remediation technologies. Although the two-year, $500,000 pilot test remains a small portion of the Air Force Center for Environmental Excellence's efforts at the MMR—this year the center will spend $40 million to $50 million there—it is representative of the Defense Department's interest in finding more cost-effective and less invasive remediation technologies. (The MMR is also testing other innovative technologies, including recirculating well technology.) By September, Pesce's team had dug 9 of 23 monitoring wells, and installation of the wall was tentatively scheduled to begin in November.

MMR is building two, parallel 50-ft reactive walls, 25 ft apart, perpendicular to the flow path of Chemical Spill No. 10 (CS-10), a 600-ft wide plume contaminated with 5–150 ppb TCE and tetrachloroethylene (PCE). Drinking water regulations here specify that TCE and PCE levels be no higher than 0.5 ppb, said Pesce.

In the first test of this technology on deep groundwater plumes, the walls will begin 80 ft below the surface, at the top of the plume, and extend downward to as deep as 150 ft. (The plume bottoms out at 110 ft below the surface, said Pesce.)

The depth of the aquifer poses problems not encountered where groundwater is shallower. In earlier in situ tests of reactive walls, engineers have used a "funnel-and-gate" configuration, building slurry or sheet metal walls that direct the contaminated water toward the wall in a V shape. When Pesce's team found that they couldn't drive sheet metal deep enough for a funnel-and-gate configuration, they went back to the University of Waterloo to explore other emplacement options.

Ultimately, Waterloo's Gillham recommended the use of a "vertical hydrofracture" technique, which has been used in the oil industry for installation of concrete or slurry walls. The technique requires engineers to bore holes 1 ft in diameter down to the top of the zone of contamination. They then induce a fracture that will be filled with iron filings combined with a slurry mixture downward and outward, creating a series of overlapping vertical planes that become a "continuous" wall. This is the first in situ test of a continuous permeable wall, says Pesce (6).

Whereas a funnel-and-gate system directs water toward a reactive wall, increasing its velocity, a continuous wall simply stands as a permeable barrier in the way of the groundwater's natural flow, reports Gillham. A continuous wall emplaced in this manner requires significant monitoring for breaks in the wall, but it also offers one potential advantage over funnel-and-gate systems, he says: Because it doesn't redirect the groundwater, a continuous wall requires no solid barrier at the bottom of the wall, as does a funnel-and-gate system. (MMR, working with the U.S. Geological Survey, will use bore-hole radar and other methods to verify the placement, continuity, and homogeneity of the wall.)

Nickel speeds degradation in lab tests

Pesce and Gillham are hoping that this first in situ test of a nickel-plated reactive wall will be as successful as laboratory trials. Gillham reports that in the lab, iron filings enhanced with nickel degrade compounds up to 10 times faster than do zero-valent iron filings alone. (Gillham has not yet published his findings concerning nickel.) For example, he says, the half-lives of TCE and PCE, in contact with zero-valent iron, are 30–40 minutes; in contact with nickel-plated iron, the half-lives "will be somewhere between 3 and 10 minutes." In practical terms, this means the groundwater requires less "residence time"—the time it is in contact with the reactive material—to degrade the contaminants. The nickel-plated wall planned at the MMR, for instance, would be only 2 in. thick; an iron-only wall would be about 10 in. thick, Gillham said.

Nickel promises yet another advantage, said Gillham. When degraded in contact with zero-valent iron, about 10% of TCE and PCE produces secondary volatile organic carbons, primarily vinyl chloride and DCE (2). These secondary products take additional residence time to degrade completely, a fact engineers must take into account when designing the wall. But compounds in contact with nickel create smaller concentrations of breakdown products, according to Gillham. "We're not sure why," he said. "We think that degradation follows a different pathway, so these degradation products may not be produced in the first place."

One potential drawback to using nickel is the possibility of adding harmful levels of the metal to the groundwater that passes through the wall. Gillham conducted lab tests on MMR groundwater to determine how much nickel leaches from the iron. "Nickel has fairly low drinking water limits itself, so we can't have large amounts of nickel in the water," he said. "In general, there's a relatively high initial rate [of leaching] but it drops below the drinking water limit very quickly."

Although Pesce is confident about using nickel-plated iron fillings at the MMR, other Defense Department engineers are skeptical about the technique. Mark Noll, director of field operations and research at the Air Force Groundwater Remediation Lab at Dover Air Force Base, Del., is planning to build a pilot-scale funnel-and-gate reactive wall the spring of 1997. The wall will be designed to materials that enhance the performance of zero-valent iron in degrading mixed chlorinated solvents, primarily TCE and PCE. Noll says his lab will probably test iron sulfide as an additive to the granular iron but is not likely to test nickel. "There needs to be more lab work done on the bi-metal systems, because there's a likelihood that a lot of the nickel may just leach off, and now you've got a nickel plume."

Interest high in industry, government

Several parties are watching this test closely, intent on seeing whether reactive walls can be used to treat such deep groundwater plumes. Gene Peters, director of technical services for Clean Sites, Inc., is overseeing the MMR demonstration project partnership. Participating in the demonstration is MMR; EPA Region I; the Massachusetts DEP; and industry partners, including DuPont, General Electric, Monsanto, Dow Chemical, Occidental Chemical, and ICI of Great Britain.

"Everybody is interested [in reactive wall technology]" said Peters. "GE is very interested in using the technology at their sites, and DuPont has done a great deal of research on installation technologies on their own," he added. The Defense Department funds the project, and the corporate partners contrib- their expertise. The project will produce a report assessing performance and cost of the technology.

GE, Dupont, Dow, Monsanto, and U.S. government agencies have also formed a "permeable barriers" workgroup under the auspices of the EPA Technology Innovation Office's Remediation Technology Development Forum. Although this group is not involved in the MMR test, it is helping to fund the test at Dover Air Force Base, says Rich Steimle, staff hydrogeologist with EPA's Technology Innovation Office.

"Our interest in the reactive wall is that it's something that can be put in place not only to contain [contamination] but to clean up," said Lt. Colonel John Selstrom, chief of the Air Force Environmental Restoration Division. He is cautious about endorsing any innovative technology until the results are in, however, saying that the chances of applying reactive wall remediation in full-scale cleanup situations are probably equal to those of recirculating well and other extraction technologies also being studied. "There's a level playing field, and we intend to evaluate what's best for the situation," Selstrom said.

Some experts, however, are skeptical about whether the vertical hydrofracture emplacement technique will work, because of complex geology more than 100 ft below ground. But, said Peters, vertical hydrofracturing "has the potential to provide an extremely cost-effective technology for sites having deeper contamination. Hence the [widespread] attention" this test is receiving.

Whether or not the MMR will select a permeable wall to clean CS-10 or any other plume at full-scale levels is a decision that is at least a year away, said Pesce. Should they decide to build a wall across the entire 600-ft plume, he estimates that it would cost $2 million to $3 million.

Nickerson of the Association for the Preservation of Cape Cod hopes the test works. "Right now, my confidence is waning in the ability of anybody to stop the forward progress of these plumes," she said. "So if the reactive wall were a successful technology and could be placed at the proper depth and could intercept the entire breadth and depth of each plume and release clean water on the other side, it would be many quantum leaps forward from where we are right now."

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