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Date: September 14, 2005
Refer to: ER2005-0682

Mr. James Bearzi
NMED – Hazardous Waste Bureau
2905 Rodeo Park Drive East, Building 1
Santa Fe, NM 87505-6303

SUBJECT: UPDATE OF PERMEABLE REACTIVE BARRIER IN MORTANDAD CANYON AND INFORMATION CONCERNING PERMEABLE REACTIVE BARRIERS AT OTHER SITES (LA-UR-05-7028)

Dear Mr. Bearzi:

In an August 25, 2005 meeting, Ms. Darlene Goering and Mr. John Young of your staff requested the submittal of information on (1) the status of the permeable reactive barrier (PRB) in Mortandad Canyon and (2) other PRBs that have been installed across the United States.

Background: A PRB was deployed in Mortandad Canyon during February 2003 as a pilot project to investigate the feasibility of removing perchlorate, nitrate, and strontium-90 from alluvial groundwater in that canyon. Details of the construction of this PRB and its effectiveness during the initial six months of operation are provided in a report by Kaszuba et al. (2004, 89661), which is available online (http://library.lanl.gov/cgi-bin/getfile?00639451.pdf). To summarize, the Mortandad Canyon PRB consists of the following four cells, ordered by their sequence of contact with groundwater: (1) a cell containing gravel-sized scoria, (2) a cell containing apatite, (3) a biobarrier cell containing pecan shells and cottonseed meal, and (4) a cell containing limestone to correct pH. The data indicate that the removal of perchlorate and nitrate is occurring within the two middle cells (cells 2 and 3), but that nitrate and perchlorate concentrations in cell 4 are roughly equivalent to the influent concentrations for a given sampling event. Sampling of the PRB has continued beyond the time of the report, and these analytical results are consistent with those outlined in the Kaszuba report.

Recent Developments: The surface of the PRB subsided up to three feet as a result of the infiltration of storm water along the PRB's southern edge during a March 2005 runoff event (see photographs in Attachment 1). The subsidence was isolated to the area overlying the two middle cells (see Figure 1 in Attachment 1) and resulted in the tilting of some of the PVC wells that monitor the performance of the barrier. Further sampling and investigation of the barrier have been put on hold until the safety associated with various activities within the footprint of the PRB can be ensured.

Path Forward: Los Alamos National Laboratory (LANL) and U.S. Department of Energy (DOE) personnel currently are developing a plan to determine the cause of the subsidence of the PRB and to diagnose any other issues associated with the barrier's construction. The ultimate goal is to develop a detailed lessons-learned document that will address the geochemistry, hydrology, and construction issues associated with the Mortandad Canyon barrier. The lessons learned from the investigation will be used in the design of any future PRBs that may be deployed at LANL.

Performance of PRBs at Other Sites: PRBs have been installed at numerous contaminated sites across the United States (see Attachment 2). Principal applications have been for chlorinated-solvent-contaminated waters in shallow (< 50 ft) aquifers, although PRBs have also been deployed to treat high explosives at the Cornhusker Army Ammunition Plant in Grand Island, Nebraska, and barium at a Dupont Corporation facility in Newport, Delaware (Attachment 2). Attachment 2 also includes a list of PRB projects installed across the United States by Shaw Environment and Infrastructure, Inc. In general, the performance of these PRBs has been excellent, resulting in the effective removal of contaminants with limited maintenance and operations costs. Many of these successful barriers have similar challenges to those presented at LANL and therefore provide a useful resource for lessons that can be incorporated into the implementation of PRBs at LANL.

If you have questions, please contact Don Hickmott at (505) 667-8753 (dhickmott@lanl.gov) or Lance Woodworth at (505) 665-5820 (lwoodworth@doeal.gov).

Sincerely,

David McInroy, Deputy Program Director
Environmental Remediation & Surveillance
Los Alamos National Laboratory

David Gregory, Federal Project Director
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Enclosures: 1) Photographs of the Mortandad Canyon PRB subsidence – March 2005
2) Report of "Potential Applications of PRBs to High Explosives and Barium at Nationwide Sites"

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Attachment 1

Photographs of the Mortandad Canyon
PRB Subsidence — March 2005

Figure 1. Subsided sections of the Mortandad Canyon PRB (view to the north)

Figure 2. Subsided sections of the Mortandad Canyon PRB (view to the east)

Attachment 2

Potential Applications
of PRBs to High Explosives and Barium at Nationwide Sites

1.0 OVERVIEW

After years of designing, manufacturing, and testing nuclear weapons, the U.S. Department of Energy (DOE) is faced with the challenge of cleaning up the waste left behind. Much of the experimental work supporting the development of nuclear weapons involved the use of high explosives (HE). Together with the many sites across the DOE and U.S. Department of Defense complexes that were involved in this effort, Los Alamos National Laboratory (LANL) must address HE and barium in soil, sediment, surface water, and groundwater at LANL's Technical Area (TA) 16.

Because HE and barium tend to persist on soil and in groundwater for decades, their remediation is a technically and economically challenging task. Currently deployed groundwater treatment methods are most commonly based on some form of active hydraulic manipulation and/or control associated with an *ex situ* treatment system. Pump-and-treat (P&T) systems are improving but remain problematic. P&T systems are frequently expensive to design and install, require significant hydrogeologic data to be successful, typically generate waste, and are difficult to operate and maintain for long periods of time. Furthermore, the medium used in P&T systems generally filters and concentrates the contaminant but does not actually destroy it. The medium usually requires subsequent handling, treatment, and disposal as a hazardous waste. Finally, permitting P&T systems can be time-consuming and costly.

Permeable reactive barriers (PRBs) operate passively, do not routinely bring the contaminants to the surface, and have the potential to operate for years with minimal maintenance. Unlike systems that are based on the active manipulation of the groundwater flow regime, PRBs may also require significantly less hydrogeologic and site characterization data for optimum design and effective performance. Further, the engineering design issues and associated costs are smaller for PRBs, and engineering solutions and field deployments, even for groundwater at greater subsurface depths, are less complex.

Compared with P&T methods, PRBs cause significantly less aquifer disturbance and, therefore, are less likely to induce cross-formational flow and the unanticipated spread of contamination. PRB treatment media frequently destroy the contaminant and, depending on site requirements and regulations, emplacements can be left in the ground, avoiding risks and disposal costs of surface treatment. The use of PRBs has been accepted by the U.S. Environmental Protection Agency (EPA), many state environmental agencies, and other regulatory authorities, and relatively few permitting issues are associated with PRBs.

DOE has applied PRB technology across the complex to treat a spectrum of contaminants in a variety of geologic settings. PRBs are in place at DOE's Oak Ridge National Laboratory, Rocky Flats Environmental Technology Site (RFETS), and the DOE facility in Monticello, Utah. All of these systems use zero-valent iron (ZVI) as the reactive medium.

At RFETS, Shaw Environmental, Inc. (LANL's subcontractor for the TA-16 corrective measures implementation) installed a PRB to treat volatile-organic-compound-contaminated groundwater underlying the Mound Site; treatment is ongoing. Shaw has also installed PRBs at the East Trenches Plume and Solar Ponds at RFETS to treat nitrates, volatile organic compounds (VOCs), and radionuclides.

Shaw designed and constructed a funnel-and-gate PRB at the DOE facility in Monticello, Utah. The treatment of radionuclides and metals has been successful and is ongoing.

Shaw installed PRBs at Oak Ridge National Laboratory's Y-12 Plant, where technetium, VOCs, metals, nitric acid, and uranium materials were released to the S-3 ponds disposal area. When the primary pond was removed from service, the pH was lower than 2.0. PRBs were installed in 1997, and treatment is ongoing. Table 1 summarizes these and other installations.

To date, 31 full-scale PRBs in this country use iron as a reactive material. Of these, 20 PRBs are continuous-reactive wall systems, eight are funnel-and-gate systems, and three are *in situ* reactive vessels. The performance data for these PRBs is consistently good.

Recently, researchers have demonstrated the applicability and technical merit of ZVI to the *in situ* treatment of HE constituents in groundwater. These laboratory-scale and field- scale experiments have focused on trinitrotoluene (TNT) and cyclo- trimethylenetrinitramine (RDX). Similar experiments in both laboratory and field settings have been conducted for barium treatment using calcium sulfate (gypsum). Results from these investigations are described in further detail below.

2.0 PRBS FOR HE

Laboratory studies have suggested that ZVI degrades RDX and TNT rapidly. Based on this finding, the Environmental Security Technology Certification Program (ESTCP) provided funding to install a pilot-scale ZVI PRB at the Cornhusker Army Ammunition Plant (CHAAP), a site that has a TNT and RDX plume emanating from its manufacturing area. GeoSyntec Consultants and Oregon Health and Science University joined forces on this project, with the former taking the lead on PRB design and installation and the latter leading the effort to assess the barrier wall's performance.

The 50-foot-long PRB at CHAAP was installed in November 2003 using trenching equipment and a biopolymer slurry that held the barrier wall open long enough for the installation team to emplace a sand/iron mixture into the trench. This installation technique—once regarded as novel—is now a well-accepted PRB emplacement technique. Installation was completed in one day; contractors worked into the night because they did not want to delay the backfilling process and risk encountering problems with trench stability. Monitoring wells and access tubes were installed during the PRB construction process.

Numerous groundwater samples were collected at the CHAAP PRB between November 2003 and August 2004 and were analyzed for TNT, sulfate, conductance, alkalinity, ORP, and pH. (RDX, which was present in very low concentrations, was not included in the analytical suite because the analytical methods available do not have sufficiently low detection limits.) To date, the results indicate (1) that the PRB is effectively degrading TNT, although it is unclear what is happening to the degradation products, and (2) that the vast majority of the groundwater is flowing through the PRB, although evidence suggests that some groundwater is flowing under it. Evidence suggests that the degradation products biodegrade more readily than their parent compounds do.

3.0 PRB FOR BARIUM

DuPont designed and installed a PRB to treat metals, primarily barium and zinc, from a landfill at the Newport, Delaware, Superfund site. For the first half of the 20th century, Dupont's Newport plant produced a barium-containing Lithopone pigment. Waste sludges were deposited in a landfill, the waters of which today contain barium that exceeds environmental standards. An EPA record of decision required the landfill to be remediated by *in situ* treatment. Dupont developed an innovative PRB for the treatment of barium and zinc in groundwater, which is less expensive and more protective of human health than other *in situ* methods. The PRB employs calcium sulfate to precipitate barium, and ZVI for the adsorption of zinc and other metals. Magnesium carbonate was added to suppress manganese solubility. To date, all data indicate that the PRB is effectively removing barium. The regulatory oversight of the project is provided by EPA under the Superfund program.

Table 1
Shaw's Current and Past PRB Projects

Site	Treated Contaminants	Scope of Services	Funnel-and-Gate Barrier	Continuous-Wall Barrier	Multiple Barrier	Geotechnical Investigation	Monitoring Well Installation	Hydrologic Modeling	Geochemical Modeling	Groundwater Sampling and Analysis	Engineering Design	Barrier Construction/Installation	Performance Monitoring
DOE, S-3 Pond, Oak Ridge, Tennessee	Nitrate, Radioisotopes, Metals, CVOCs, Common Ions	Designed and installed a funnel-and-gate reactive barrier system consisting of HDPE membrane walls, a treatment module containing porous media, and groundwater-collection piping. The barrier was installed using modular shoring and a biopolymer slurry. The treatment module is designed to allow for the testing of various treatment media.	√				√			√		√	
DOE, Mound Site, Rocky Flats Environmental Technology Site, Colorado	Chlorinated Organic Compounds, Metals, Radionuclides	Installed a funnel-and-gate reactive barrier system consisting of HDPE membrane walls, two treatment cells containing zero-valent iron, and a groundwater-collection system. The treatment cells are designed in such a way that the treatment media can be easily placed and retrieved to facilitate the regeneration or replacement of the media. The barrier was installed using an open-trench method with a track-mounted hydraulic excavator.	√			√	√					√	
DOE, East Trenches Plume, Rocky Flats Environmental Technology Site, Colorado	VOCs, Tetrachloroethene, Carbon Tetrachloride, Uranium-238	Designed and constructed a funnel-and-gate permeable reactive wall consisting of HDPE membrane walls and a subsurface groundwater collection system. The well was constructed using an open-ended trench box pinned with H-pile to shore the excavation. The treatment medium is granular zero-valent iron, which can be easily placed and retrieved from the cell.	√			√	√	√			√	√	
DOE, Solar Ponds, Rocky Flats Environmental Site, Colorado	Nitrates, Radioisotopes	Designed and constructed a funnel-and-gate permeable reactive wall consisting of a subsurface collection system and a two-stage treatment module. Stage 1 contains organic media and granular iron to induce denitrification and reduce nitrate. Stage 2 contains granular iron to remove radioisotopes by chemical reduction. The system was installed using a track-mounted hydraulic excavator.	√		√	√	√	√			√	√	

Table 1 (continued)

Site	Treated Contaminants	Scope of Services	Funnel-and-Gate Barrier	Continuous-Wall Barrier	Multiple Barrier	Geotechnical Investigation	Monitoring Well Installation	Hydrologic Modeling	Geochemical Modeling	Groundwater Sampling and Analysis	Engineering Design	Barrier Construction/Installation	Performance Monitoring
DOE, Monticello, Utah	Radionuclides, Metals	Designed and constructed a funnel-and-gate permeable reactive wall consisting of two impermeable bentonite/soil slurry wing walls and a zero-valent iron reactive section. The system was installed using steel sheet pile cofferdam construction.	√									√	
Shaw Air Force Base, Operable Unit 4, Sumter, South Carolina	VOCS, TCA, DCE, BTEX	Designed and constructed a permeable reactive barrier consisting of four continuous walls containing a 50/50 mixture of filter media and zero-valent iron. The walls were 275 ft long and 24 ft deep. The system was installed using a chain trencher.		√		√	√	√	√	√	√	√	√
U.S. Army Corps of Engineer, Denver Federal Center, Lakewood, Colorado	Chlorinated Organic Compounds	Designed and constructed a funnel-and-gate permeable reactive wall consisting of impermeable sections of sealable-joint sheet piling and four permeable treatment cells constructed by steel sheet pile cofferdam methods. The treatment cells consisted of zero-valent iron and pea gravel.	√			√	√	√	√	√	√	√	
Confidential Client, Southern California	TCE, Chromium+6	Designed, installed, and tested reactive sand fracturing as a method of installing permeable reactive barriers within fractured bedrock. Reactive components were pumped under high pressure into the fractures.		√		√	√	√		√	√	√	
Confidential Client, Oregon	TCE, VOCs	Designed and installed a funnel-and-gate permeable reactive barrier with a treatment cell containing zero-valent iron filings. The impermeable walls were constructed using a continuous-pass trencher and dry bentonite.	√			√	√			√	√	√	√
Confidential Client, Colchester, Vermont	CVOCs	Designed and installed a funnel-and-gate permeable reactive barrier with HDPE cutoff walls and four treatment zones consisting of iron filings mixed with sand. The system was installed using a continuous one-pass trencher and biopolymers to provide liquid shoring of excavations during construction.	√				√		√	√	√	√	√

Table 1 (continued)

Site	Treated Contaminants	Scope of Services	Funnel-and-Gate Barrier	Continuous-Wall Barrier	Multiple Barrier	Geotechnical Investigation	Monitoring Well Installation	Hydrologic Modeling	Geochemical Modeling	Groundwater Sampling and Analysis	Engineering Design	Barrier Construction/Installation	Performance Monitoring
U.S. Army Corps of Engineers, Kansas City, Missouri	Chlorinated Solvents, VOCs	Designed and constructed a permeable reactive wall consisting of an iron-and-sand mixture. A long-stick hydraulic excavator was used to excavate the trenches. Biopolymers were employed to provide liquid shoring of the excavation.		√		√	√	√	√	√	√	√	√

BTEX = Benzene, toluene, ethylbenzene, xylene

CVOC = Chlorinated volatile organic compound

DCE = Dichloroethene

DOE = U.S. Department of Energy

HDPE = High-density polyethylene

TCA = Trichloroethane

TCE = Trichloroethylene

VOC = Volatile organic compound