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Permeable Reactive Barrier for Metals Treatment at the Newport, DE Superfund Site

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Abstract: DuPont has developed permeable reactive barrier (PRB) technology 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 Lithopone pigment ($BaSO_4$*ZnS) by roasting barium and zinc ores. Waste sludges were deposited in a landfill, the waters of which today contain metals that exceed environmental standards. An EPA Record of Decision required the landfill to be remediated by in-situ treatment. Innovative technology has been developed which reduces the cost from $17,000,000 for the ROD remedy to $5,000,000, while being more protective of human health. It employs a PRB using calcium sulfate to precipitate barium, zero-valent iron for the adsorption of zinc and other metals, and magnesium carbonate to suppress manganese solubility, in a matrix of local mortar sand. The key to a projected PRB life measured in centuries is a low-permeability cap over the landfill that reduces infiltration and subsequent groundwater flow leaving the landfill to extremely low levels. This minimizes reactant losses from reaction and solubilization. Development of the technology included laboratory batch and column tests and thermodynamic modeling. The final demonstrations were field tests in zones of different groundwater contaminant composition.

Introduction: PRB technology has been accepted by the U. S. EPA as a key component of the treatment remedy for the Newport South Landfill. It is designed to remove metals to below the following levels (ppb): barium 7,800, zinc 120, and manganese 1,000. Other metals of concern are already below their mandated levels (ppb): cadmium 4, copper 18, lead 15, and nickel 730. The 2,200-ft. long, 18-in. wide, 10- to 20-ft. deep PRB will treat all waters leaving the landfill. Wall life is extended by the installation of a low-permeability cap that permits only small quantities of rainfall to enter the landfill, and hence ultimately pass through the PRB.

Batch Scouting Tests: Batch tests were employed for screening reactive materials for use in a PRB. Two types of water were tested, representing areas of high barium or zinc concentration. Appropriate materials were used for each type of water -- for barium-rich water: $CaSO_4.2H_2O$ (gypsum), and for zinc-rich water: zero-valent iron, millscale, steel slag, and iron sulfide. These tests covered a broad range of concentrations for each reactive material to determine the level at which each would potentially become effective.

Barium concentrations were reduced from 290,000 ppb to less than 500 ppb by the addition of 0.5 weight percent of $CaSO_4.2H_2O$, through the precipitation of $BaSO_4$. This was substantially lower than the required 7,800 ppb standard. Zinc concentrations were readily reduced from approximately 1,000 ppb to less than 10 ppb (vs. standard of 120 ppb) by several materials, including zero-valent iron (ZVI; Peerless -8 +50 mesh), iron sulfide, steel-process mill scale, and steel slag, with the first two showing exceptional activity. The mechanism for ZVI is probably

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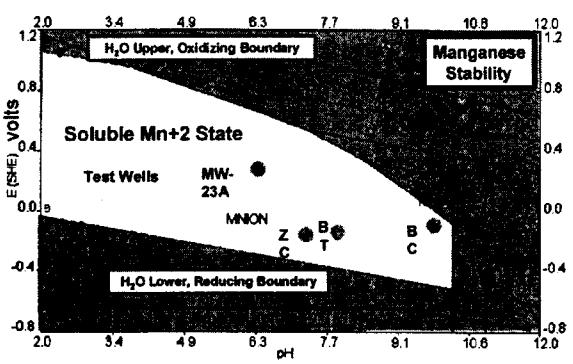
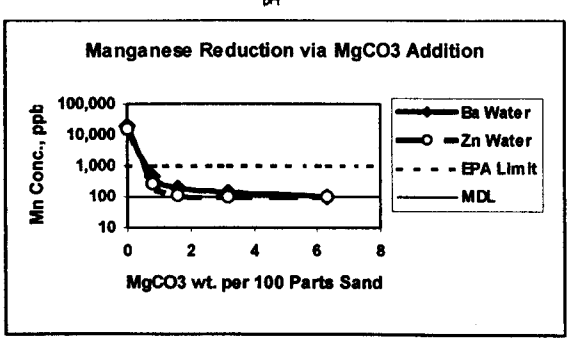
sorption onto surfaces of hydrous iron oxides. Manganese was generally not reduced by the materials, and in some cases showed increases, although remaining below the limit of 1,000 ppb.

Laboratory Column Tests: The composition of groundwater leaving the landfill at any point is not known with certainty, so it is not possible to delineate zinc-removal and barium-removal portions of the PRB. Consequently, one wall composition was chosen to accommodate both the worst-case barium and zinc levels. Delaware DOT mason sand was chosen as the PRB matrix material. It was determined that a 20 weight ratio of gypsum could be mixed with the mason sand and maintain a permeability (6×10^{-4} cm/sec) greater than that of the landfill material. Based on a projection of reactant needs and solubility losses, a mix composition was chosen with parts by weight of "sand : gypsum : ZVI :: 100 : 20 : 5." Two independent, continuous flow column tests were run, with barium-rich and zinc-rich feed waters. Each consisted of an eight-inch long, two-inch diameter column filled with the reactive mix, and a control column filled with sand. An upward flow of groundwater was maintained to give a six-hour residence time.

Barium removal was readily accomplished from both groundwaters throughout the one-month test. With the barium-rich feed, 500,000 ppb Ba was reduced to 1,000 ppb. With the zinc-rich feed, 70,000 ppb Ba was reduced to 100 ppb. With the zinc-rich feed (100 to 1,000 ppb Zn) zinc was consistently reduced to non-detect (25 ppb) in both the active and control columns. With the barium-rich feed water, no zinc was detected, consistent with the strong sulfide odor of this water, which implied that zinc had been precipitated in situ as the sulfide. Manganese concentrations were not reduced, and in some cases increased.

Flow pressure drops across the reactive columns were measured with manometers to determine whether there would be a decrease in permeability as a PRB ages. After 45 days of flow the hydraulic conductivities were essentially unchanged. No permeability decrease was thus observed over many simulated wall lifetimes, and wall plugging should not occur.





Manganese Treatment: The presence of manganese was the remaining issue. The accompanying Pourbaix Diagram shows the dominant solid phases and aqueous solution species as a function of pH and oxidation/reduction conditions. Under mildly oxidizing conditions Manganese is in a +4 valence state and forms an insoluble precipitate, MnO_2. Under natural reducing conditions the manganese is converted to the +2 valence state and is present as the soluble Mn^{+2} cation. The unshaded area is the region where the Mn^{+2} cation dominates. Test well samples are shown on the plot at the measured pH and oxidation/reduction conditions. It can be seen that several landfill conditions are conducive to the soluble Mn^{+2}, a condition that must be overcome to reduce manganese leaving the landfill.

Several options were evaluated to address the high-manganese levels. Ultimately the addition of $MgCO_3$ was effective, and was chosen to lower manganese concentrations to well below standards. In the laboratory, barium-rich and zinc-rich groundwaters were independently spiked with $MnCl_2$ and then treated with the proposed reactive mixture and $MgCO_3$ in a series of batch runs. Even at the lowest levels of $MgCO_3$ addition, manganese was below the required 1,000 ppb. No adverse effects were observed on the removal of other metals. Based on these results, the PRB composition was revised to "sand : gypsum : iron : $MgCO_3$: : 100 : 20 : 5 : 5."

PRB Field Demonstrations: At the landfill, two well clusters, each consisting of two control wells and one treatment well, were placed in locations exhibiting elevated levels of barium or zinc in the groundwater. Each 12-foot-deep well consisted of a 12-inch diameter column of material with a central one-inch PVC pipe screened over its lower five feet. The wells were spaced fifteen feet apart and constructed using either hollow-stem auger or sonic drilling, depending on the soil conditions. The first control well was backfilled with drill cuttings to obtain water in its most natural state. The second was backfilled with clean mason sand. The treatment wells were backfilled with the reactive mix consisting of "sand : gypsum : iron : $MgCO_3$: : 100 : 20 : 5 : 5." The barium-rich area had a second treatment well, with a weight ratio of "100 : 20 : 5 : 15." In the actual PRB, only the natural groundwater flow would pass through the wall. To accelerate wall usage for this test and simulate long-term wall aging, water was pumped from the wells using a peristaltic pump.

Groundwater sampled from the treatment wells showed reductions in contaminants compared to water sampled from the control wells. Zinc in groundwater from the zinc-rich wells was reduced from a range of 100 to 1,000 ppb to less than the 9 ppb detection limit. Barium in groundwater from the barium-rich control wells was reduced from a 4,000 to 8,000 ppb range to below 1,000 ppb. Manganese, detected between 6,000 and 26,000 ppb in groundwater from both zinc-rich and barium-rich control wells, was reduced to 100-300 ppb in barium-rich waters, and 500-900 ppb in zinc-rich waters.

Projected PRB Life: PRB life is determined by water flow through the PRB and the resulting depletion of gypsum and $MgCO_3$ by solubility and reaction, and of iron by reaching its sorptive capacity. The low-permeability (10^{-7} cm/sec) cap reduces the flow through the PRB to such a level that the residence time is measured in years. Based on the demonstrated field performance, the PRB life is conservatively estimated at 600 years, limited only by the duration of the test.

Costs: The cost of the PRB remedy, which also includes the cap and a slurry wall around part of the landfill, is approximately $5 million, which is considerably less than the approximately $17 million cost of the fallback ROD option of stabilizing the entire landfill with concrete.

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