United States
Environmental Protection
Agency

EPA/540/R-08/003
August 2008

SUPERFUND INNOVATIVE TECHNOLOGY EVALUATION

Demonstration Bulletin

Attenuated Anaerobic Dechlorination of Groundwater Using HRC®

MACTEC - Harding ESE

Technology Description: MACTEC's Harding Environmental Science and Engineering Division (Harding ESE) has designed an in situ Permeable Reactive Barrier Wall (PRBW) that utilizes Hydrogen Release Compound (HRC®) to treat groundwater contaminated with chlorinated compounds. HRC® is a hydrogen-generating compound based on a lactic acid/glycerine polyester that is able to generate free hydrogen under anaerobic conditions. The bacteria consume the HRC® (or hydrolysis products) and produce the hydrogen needed for dechlorination of contaminants. This process takes place along with other anaerobic degradation mechanisms which convert the HRC® to volatile fatty acids such as pyruvic acid, butyric acid, propionic acid, and acetic acid, which in turn are biodegraded by methanogenesis to ethane, methane, and carbon dioxide.

HRC® is manufactured by Regenesis Bioremediation Products of San Clemente, California, and is packaged and shipped in 4.25 gallon PVC buckets, each of which contains 30 pounds of HRC®. At room temperature its consistency is that of a sticky gel (i.e., cold honey). Regenesis advises heating unopened buckets of HRC® in a hot water (130-170°F) tank to 95°F for 20-30 minutes. When heated to 95°F, the buckets are transferred to a pump hopper and the desired dose of the fluidized gel is pumped into each well. By pumping the viscous HRC® under pressure into a network of injection wells (**Figure 1**), installed perpendicular to the flow of the groundwater and screened at the anticipated depth of the plume, HRC® can be placed to form a PRBW perpendicular to the plume.

Although HRC® can be used as a stand-alone treatment, Harding ESE and Regenesis have in the past used a two staged approach involving Oxygen Release Compound (ORC®) (magnesium peroxide). This oxygen source is injected into the formation either downgradient of injected HRC® or at a later time. ORC® is formulated to convert the environment to one that is aerobic and oxidative where daughter products, such as cis-1,2-dichloroethene (DCE) and vinyl chloride (VC), are more rapidly destroyed than occurs in anaerobic environments.

The PRBW technology generates essentially no waste streams above-ground. HRC® is reported by Regenesis to be non-toxic; composed of a polylactate ester (lactic acid) and food grade magnesium phosphate. Residuals that could be generated during a full-scale PRBW treatment are contaminated drill cuttings, purge water, and PPE.

Waste Applicability: According to Harding ESE, their attenuated anaerobic dechlorination process is applicable to groundwater plumes contaminated with chlorinated ethenes, particularly tetrachloroethene (PCE) and trichloroethene (TCE). Little or no supplementation (nutrients, ammonia,

phosphate) is needed since the soil/groundwater matrix usually provides enough of these amendments. The soil must be sufficiently porous to allow groundwater flow through the PRBW and the groundwater must be in an anaerobic state or readily convertible to anaerobic conditions (which is helped by the presence of the HRC® hydrogen production capability). Previous studies have demonstrated that dechlorination is optimum when the Oxidation/Reduction Potential (ORP) of the groundwater is in the -100 to -150 millivolt (mV) range; lower potentials (greater than -150 mV) encourage methanogenesis and sulfate reduction.

Demonstration Results: A demonstration of Harding ESE's PRBW was conducted near the Fisherville Mill brownfields site in South Grafton, MA. The original plan was to implement a two-stage treatment within a groundwater plume having relatively high concentrations of TCE. HRC® was to be injected across a section of the plume, followed by introduction of ORC® at a later date, if necessary. However, when a fire destroyed the existing plant, an alternate off-site demonstration location was selected.

The evaluation was initiated in June 2000 with the installation of a series of HRC® injection wells and monitoring wells downgradient of an existing well which was designated as a "pseudo source" of contamination. The injection wells were spaced in order to provide overlap of HRC® when injected into the aquifer at 40-50 ft below ground surface (bgs). In this manner, a PRBW was to be established perpendicular to the flow of the groundwater from the pseudo source well. The areal extent of the pilot-scale treatment system's injection and monitoring wells was approximately1,200 ft^2.

Two rows of monitoring wells were installed for tracking HRC® and contaminated groundwater. The first row of monitoring wells was installed 12-15 feet south of the pseudo source well and were used for early monitoring of the treated plume (they could also be used as wells where ORC® could be introduced if that became desirable). The second row of monitoring wells were situated about 30 feet south of the pseudo well to allow time (and distance) for the HRC® to move into the aquifer and accelerate growth of existing anaerobic bacteria capable of degrading the chlorinated ethenes. Additional monitoring wells were located to both sides of the expected plume and further downgradient to provide control data on the movement of HRC® and degradation of the chloroethenes.

The primary objective of the demonstration was to determine the effectiveness of the PRBW in eliminating TCE and its degradation products from the groundwater plume. Specifically, the developer claimed that 90% of the samples collected from the downgradient "critical" wells would meet the Massachusetts groundwater criteria (GW-1), after a reasonable period (about 4 months). GW-1 criteria for the target contaminants are as follows: TCE (5 ppb), cis and trans-1,2-dichloroethene (70 ppb-combined) and VC (2 ppb).

The demonstration was initially expected to last about 6 to 9 months, which was anticipated to be ample time for determining if the primary objective had been met. In fact, the demonstration was extended to over 24 months as TCE concentrations were found to decrease more slowly than expected. Water level measurements indicated the project area to be very flat. Although this would suggest low flow of water, analysis of various parameters indicated that movement of HRC® and other constituents was occurring. Concentrations of VOCs and other parameters varied in adjacent wells throughout the evaluation, possibly due to non-uniformity in the formation; nevertheless each well showed similar trends in VOC changes.

After a few months of contact with the HRC® there was clear evidence of conversion of TCE to cis-1,2-DCE (DCE). Although the treatment did achieve extensive conversion to DCE (~80%-95%+ in individual critical wells) the GW-1 criteria were not achieved at the downgradient monitoring wells even though the treatment was allowed to continue for about two years. In fact, DCE continued to increase for most of that time before production of VC became apparent; VC concentrations were still increasing when the project was considered complete.

The second stage of the investigation, the introduction of ORC® to accelerate the degradation of DCE and VC, was never undertaken for several reasons. The primary reason was Harding ESE's expectation that large concentrations of HRC® (relative to TCE concentrations) would enable the dechlorination to proceed to completion (ethene). Funds and time were also considerations.

The results of well monitoring are consistent with the hypothesis that extensive anaerobic dechlorination occurred in the groundwater as it moved downgradient from the injection area. Secondary parameters also indicated that HRC® had been forced into the upgradient "source" well, allowing dechlorination to begin upgradient of the actual HRC® injection wells. Very low groundwater flow gradients over the two years may have confounded the results.

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