

ANAEROBIC REDUCTION OF PERCHLORATE-IMPACTED SOILS IN AN ENCLOSED CELL

William Smith, P.G. Principal Hydrogeologist,
Kevin A. Morris, Bioremediation Specialist (kmorris@envalliance.com)
(Environmental Alliance, Inc., Wilmington, DE, U.S.A.)

ABSTRACT: The anaerobic reduction of perchlorate is an electron donor/carbon rate driven, microbially mediated, oxidation-reduction reaction capable of degrading perchlorate to the final end products, chloride, oxygen and water. Several studies have indicated that perchlorate may be the perfect tracer and there is little published information related to adsorption values for perchlorate in soils. Therefore, a perchlorate release in soil must be addressed almost immediately to prevent the perchlorate ion from leaching through the soil and eventually contaminating groundwater. Few conventional treatments exist to treat perchlorate-impacted soils. Those that are available, such as dig and haul, only serve to transfer the problem from one source to another, potentially impacting landfills receiving any excavated/impacted soils. Once in groundwater, perchlorate, having a solubility in water of approximately 18.5% at 15°C, becomes very difficult to treat. Therefore, the ability to rapidly respond to the presence of impacted soil is critical in minimizing groundwater impacts and thus significantly lowering the overall cost to remediate the release of perchlorate to the environment. The anaerobic reduction of perchlorate in soils utilizing the biocell technology was successfully implemented for pilot testing and full-scale operation at an industrial facility with perchlorate-impacted soils in excess of 100 mg/kg.

INTRODUCTION

Several in situ and ex situ pilot tests were initiated to determine the applicability and effectiveness of stimulating the indigenous anaerobic microbial treatment of perchlorate-impacted soils and groundwater via the introduction of carbon-based electron donor substrates at an industrial facility.

The ex situ pilot test activities were focused on the treatment of excavated, perchlorate-impacted soils in a contained cell. The soil was excavated from a known perchlorate source area emanating from a sump that collected perchlorate-impacted wash water. The sump was located approximately four to six feet below ground surface (bgs) and is within the seasonally fluctuating (as much as ten feet) groundwater table. The sump was in the ground for approximately twenty years and may have acted as a continuing source of perchlorate impacts to the surrounding soils and groundwater before being removed during excavation.

The four main geologic strata identified at the site include: silt/clay, silty sand, gravel with sand, and loose fine sands underlain by a clayey aquitard zone. The confining clay zone beneath the surface aquifer has been identified across the site and appears to be acting as an aquiclude that appears to have limited the migration of perchlorate.

The ex situ pilot test specifically addressed the excavated silt/clay, shallow, vadose zone soils (8 to 12 below ground surface [bgs]), that were impacted from the sump. Soil data collected before and during the excavation indicated elevated levels of perchlorate in the silt/clay soils within the seasonal water table that increased with the increasing depth of the samples. The excavation was conducted during a time of year that the water table was at its lowest level (15 to 17 feet bgs) to prevent groundwater intrusion during the excavation.

Methods and Materials

The biocell consisted of approximately 100 cubic yards of soil taken from the known perchlorate source (sump) area excavation. Prior to transportation of the excavated soil to the biocell location, hardwood sawdust was added as a bulking agent and to increase the inherent porosity and permeability, at an approximate ratio of 10:1 soil to sawdust. Increasing the permeability of the silty clay material was essential to maximize the distribution of substrate and bacteria into the soil particles and to insure complete treatment. The augmented soil was then transported to the area proposed for biocell construction and placed on the bottom 18-mil polyethylene liner. The new soil was mixed with actively composting soil from the previous biocell pilot test to introduce additional substrate and active perchlorate-reducing bacteria. Calcium magnesium acetate (CMA) was added to the biocell to test the feasibility of using this additional carbon source to promote anaerobic activity in the biocell. Shredded and rotting prairie hay was also added as an additional carbon source. The soils added to the biocell were thoroughly mixed and leveled with a trackhoe, then, a 20-mil UV resistant polyethylene liner was placed on top (Refer to Figure 1 for overview of biocell).

The design and construction of the biocell liner and cover material is particularly important in an anaerobic treatment process. First, the liner must be durable to allow for the operation of the mixing equipment in loading the cell and remixing the amended soil material. Second, the liner must be UV resistant, waterproof, and adequately sealed from the ambient atmosphere to minimize the oxygen and water penetration from the surrounding environment. Third, the liner must reflect the design criteria for the biocell. In some applications a more durable liner may be required should the cell be designed to accommodate multiple treatment batches. Prior to selecting the liner material, the design objectives must be determined and reflected in the final design.

Field screening of soil during excavation using the ion selective electrode (ISE) method guided the selection of soil to be placed in the ex situ biocell. A composite sample of 34 field screening soil samples was collected and sent to a laboratory for analysis by ion chromatography (EPA Method 314.0) as a confirmatory baseline sample.

Upon completion of biocell construction activities, approximately 200 feet of three quarter-inch diameter rubber sprinkler hose was placed across the top of the biocell. The hose was used to facilitate the addition of substrate and water (as needed to maintain the proper moisture content of approximately 40% required to support the anaerobic biodegradation process) without uncovering the biocell. Prior to placing the 18-mil plastic cover over the biocell, all groundwater generated during pilot test activities were added to the biocell for treatment and to assist in maintaining moisture levels within the biocell. Water from the existing biocell sumps was also used to thoroughly saturate the new biocell to achieve the desired moisture level by pumping water from the two-inch

screened pipe located in the sumps to the sprinkler hose on top of the biocell. Moisture and temperature probes were placed within the interior of the biocell and connected to a data logger to monitor the interior biocell environment. The top cover was placed over the biocell such that at least three feet of the cover overlaid the retention berm. Landscaping timbers were laid end to end to keep the cover in place. Except for periodic sampling, turning and water addition to maintain desired soil moisture levels, the biocell was left covered and undisturbed to promote the establishment and maintenance of anaerobic conditions necessary for the reduction of perchlorate.

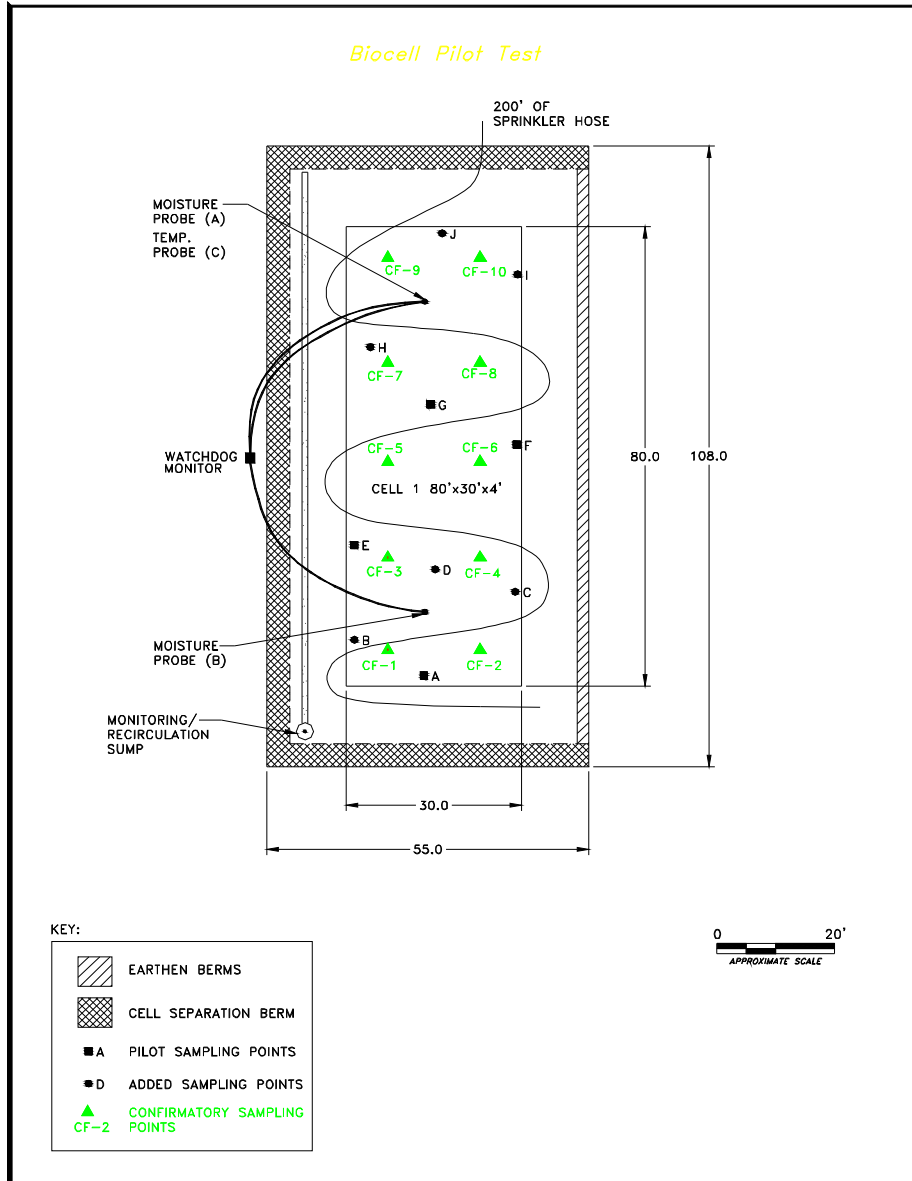


Figure 1. Biocell As-built Overview and Sampling Locations

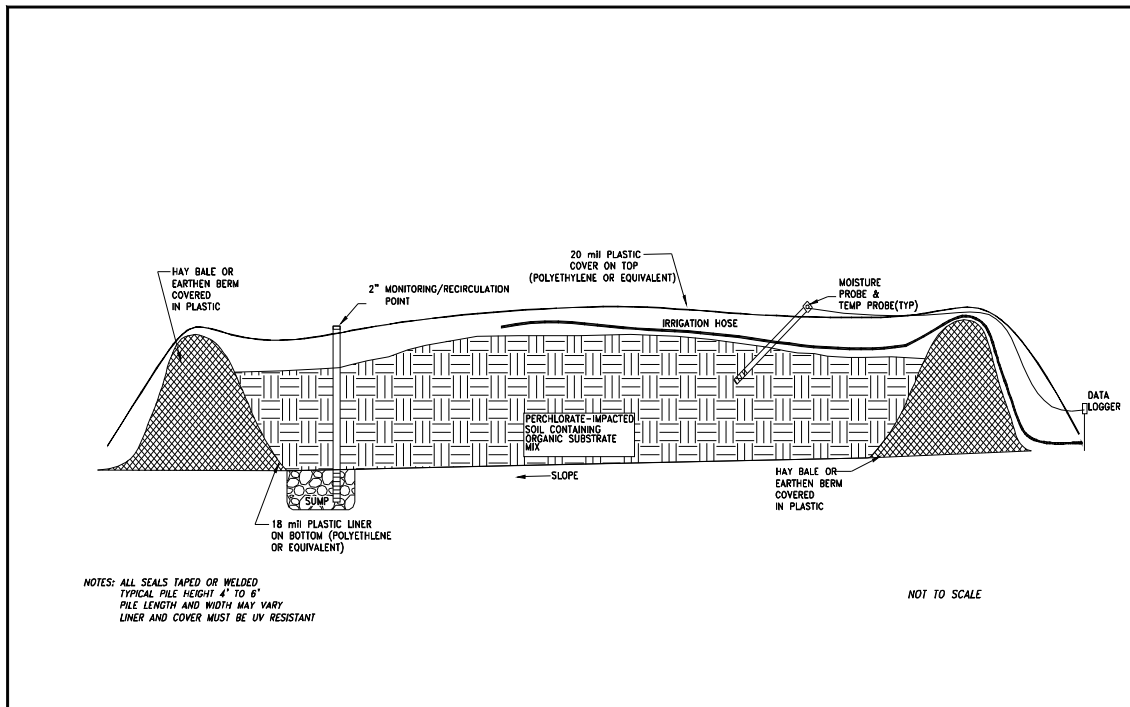


Figure 2. As-Built side-view of Biocell Indicating Sump Locations

RESULTS AND DISCUSSION

The composite sample collected during the field screening of the excavated soil yielded an initial perchlorate concentration of 42 mg/kg. Prior to placing the top liner over the biocell, soil samples were collected using a hand auger at four locations (i.e., A, B, C, and D) at depths of six inches and two-feet (surface of and interior of the biocell, respectively). This sampling event represented the baseline laboratory analysis for the biocell soils.

All sampling locations had measurable levels of perchlorate except for location B. The average perchlorate concentration for the samples collected from the other locations (i.e., A, C, and D) was 37.3 mg/kg (Figure 1). The non-detect analyses for both soil intervals at sampling location B for that event may be attributed to an excess of bulking agent/substrate (hay) in the soil samples. After six months of operation the laboratory analytical data (IC) reported perchlorate concentrations to be below an average of 0.030 mg/kg and no detectable perchlorate in the biocell sump water with a detection limit of 0.004 mg/l (Please refer to Figure 2 for sump sampling locations).

During the spring sampling event, the biocell was observed to be noticeably drier on the exterior. Since bacterial activity requires moist conditions, it was determined that the biocell needed to be rehydrated. The sump water beneath the biocell liner was the most logical source of water containing potential perchlorate-reducing bacteria. A sample was collected to determine if any perchlorate could be detected in this water. The laboratory analysis report indicated no detectable concentration of perchlorate, so the sump water was deemed suitable for use to rehydrate the biocell. Approximately 3000

gallons of sump water were recirculated over a three-month period. To improve the distribution of moisture and substrate within the perchlorate-impacted soils and accelerate perchlorate degradation, remixing (turning) of soil in the biocell was also conducted. After approximately twelve months of operation the laboratory data indicated no detectable perchlorate in the biocell soils with a detection limit in soil of 0.010 mg/L.

The initial data collected from the dataloggers indicated a temperature that was at least ten degrees above the ambient temperature and a moisture level of 37%. After collection of the first data set the data loggers failed, due to the extreme heat during the summer months.

In the twelve months of operation of the biocell, all sampling locations exhibited fluctuations in perchlorate concentrations ranging from a high of 307 mg/kg to non-detect at several locations. However, when the perchlorate concentration data sets are averaged, a significant decreasing trend was observed, from the initial composite concentration of 42 mg/kg to the last sampling event indicating no detectable perchlorate concentrations in the biocell soils (i.e., less than 0.010 mg/kg) (refer to Figure 3). This data represents an estimated 100 % decrease in perchlorate concentrations.

The variability of the concentration of perchlorate in the soils may have been due to the initial heterogeneous distribution of perchlorate in the excavated soils and the inherent variability of collecting soil samples over time. Taking this heterogeneity into account we theorize that, while perchlorate may not readily adsorb to soils, the perchlorate ion may be trapped in water that is itself trapped in the interstitial spaces of the silt/clay matrix that was excavated. This may help to explain why elevated levels of perchlorate were found several feet above the water table and that this residual perchlorate may be acting as a continued point source impacting the groundwater as it rises into the impacted zone.

In addition, the perchlorate in soil extraction technique as well as the analytical method for this particular silt/clay soil may be problematic. To date, there is no EPA recognized method for determining perchlorate concentrations in soil, so a modified EPA method 314.0 was used. A solution is prepared using a measured amount of the soil sample and an equal amount of an ionic strength adjustor. The solution is then thoroughly mixed, usually by hand to attempt to create a homogenous solution and “wash the soil” of the perchlorate. The elluent is decanted and is then analyzed via ion chromatography (method 314.0). This silty/clayey soil has a tendency to form tight clumps that can present problems when trying to create the homogenous solution during the soil washing that is required for the laboratory analysis of perchlorate in the soil.

While conducting the biocell pilot test we also became aware of potential difficulties in analyzing perchlorate in soil that contained elevated amounts of organic acids. The anions in the substrate along with possible biological contributions (organic acids, etc.) from the anaerobic degradation process created interference during the perchlorate analytical (IC) process. The interferences were significant enough to damage several ion exchange columns even when they were equipped with a filter designed to prevent such damage from occurring.

To obtain a final confirmation of the last sampling event indicating no detectable perchlorate at a detection limit in soil of 10 ug/kg a split sample was sent to a lab for analysis via a new method, a modified EPA method 8321a using ion/liquid

chromatography and mass spectrometry. Both analytical methods indicated no detectable perchlorate.

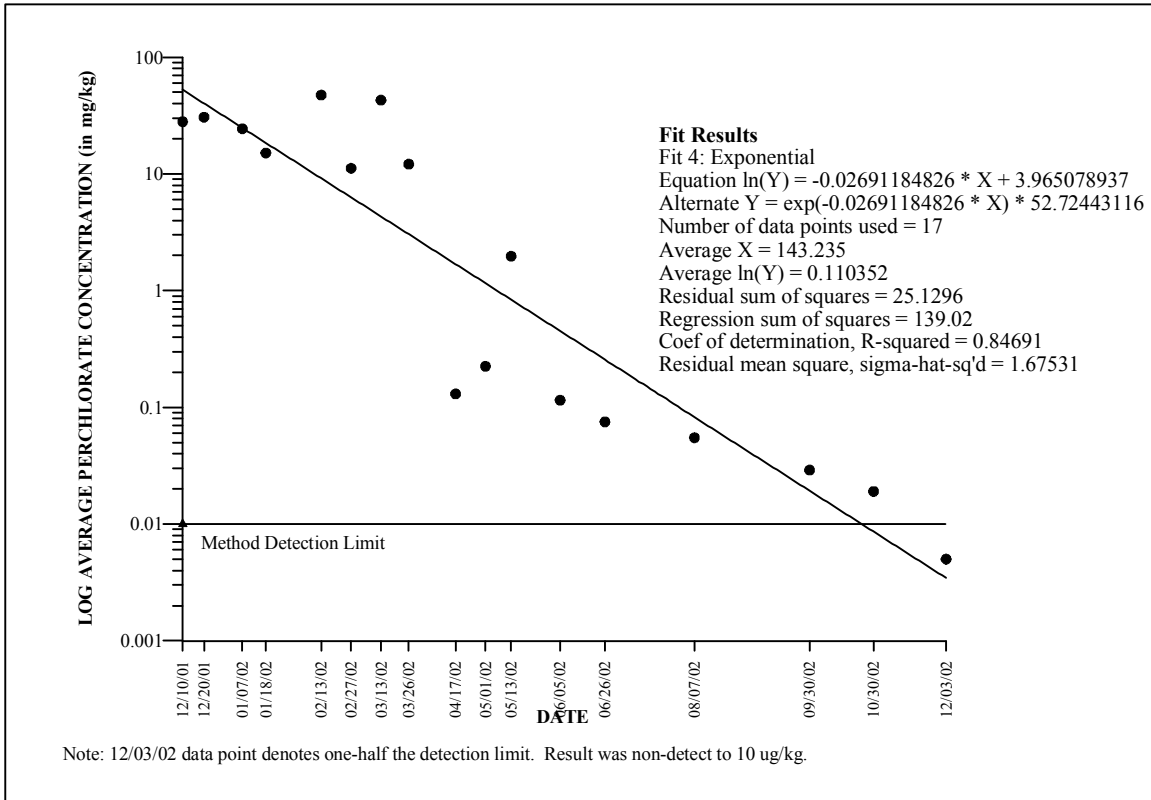


FIGURE 3. Average perchlorate concentration in soil over time for biocell

CONCLUSIONS

As with any soil treatment technology the variability in permeability and porosity must be addressed to insure treatment is completely attained. In some cases the need to augment, pre-treat and or homogenize the soil to improve substrate penetration is required. Perchlorate may not readily adsorb to soils but there is a potential for certain soil matrices (particularly clays) to capture perchlorate in water trapped in the interstitial spaces and act as a point source.

Additionally, the operation of the biocell requires adequate monitoring and maintenance to adapt to changing conditions in moisture levels, substrate distribution requirements, and potential re-mixing of treated soils to improve treatment effectiveness. As demonstrated by the pilot test and full-scale application, the use of on site ex situ biocell technology can be an effective technique to address soils contaminated by perchlorate.

The laboratory analytical problems that developed during this pilot test raised several issues that need to be addressed before accurate investigations or even remedial strategies related to perchlorate can occur. A consistently repeatable and accurate industry-standardized laboratory analytical method for detecting perchlorate in matrices more complex than water would provide an invaluable tool for determining perchlorate point sources and ultimately aid in perchlorate remediation.

Based on data collected during the biocell pilot test, including a new potentially more reliable analytical method for perchlorate in soils, ex situ anaerobic composting (biocell) has proven to be an efficient and cost-effective method for the treatment of perchlorate-impacted soil. This pilot test and full-scale application has demonstrated the possibility of treating heavily perchlorate-impacted soils using a properly maintained ex situ biocell within a timeframe of 6 to 12 months with no impacts to the surrounding soils or groundwater. This technology may also be applicable to soils impacted with other contaminants that are amenable to anaerobic reduction such as chlorinated solvents, HMX/RDX, pesticides, etc. The treated soil, with regulatory approval, is then available for use as clean fill and/or as starter substrate for the creation of additional biocells to treat additional perchlorate-impacted soils.

ACKNOWLEDGEMENTS

The author would like to thank the participating members of the Environmental Alliance, Inc. field staff for their efforts in the collection of samples and data from the biocell. The author would also like to thank the office support staff at Environmental Alliance, Inc. for their assistance in pilot test documentation and reporting activities.

REFERENCES

Coates, J. D., U. Michaelidou, S. M. O'Connor, R. A. Bruce, and L. A. Achenbach. 2000. "The Diverse Microbiology of (Per)chlorate Reduction". Chapter 24 in: Perchlorate in the Environment, E.T Urbansky (Ed.). Kluwer Academic/Plenum Publishers, New York

Cox, E. E., E. Edwards and S. Neville. 2000. "In Situ Bioremediation of Perchlorate in Groundwater," Chapter 21 in: Perchlorate in the Environment, E.T Urbansky (Ed.). Kluwer Academic/Plenum Publishers, New York

Nzengung, V. A., J. Kastner, K. C. Das, and A. G. Browder. 2001. University of Georgia, Athens, Georgia, "Pilot Scale In-Situ Bioremediation of Perchlorate-Contaminated Soil." The Sixth International Symposium on In Situ and On Site Bioremediation, San Diego, CA.