USE OF A UNIQUE BIOBARRIER TO REMEDIATE NITRATE AND PERCHLORATE IN GROUNDWATER

Betty A. Strietelmeier[1], Melissa L. Espinosa[1], Joshua D. Adams[1], Patricia A. Leonard[1] and Evangeline M. Hodge[2]

Abstract: Research was conducted to evaluate a multiple-layer system of volcanic rock, limestone, Apatite®II mineral and a "biobarrier" to impede migration of radionuclides, metals and colloids through shallow alluvial groundwater, while simultaneously destroying contaminants such as nitrate and perchlorate. The "bio" portion of this Multi-Barrier system uses highly porous, slowly degradable, carbon-based material (pecan shells) that serves as an energy source and supports the growth of indigenous microbial populations capable of destroying biodegradable compounds. The studies, using elevated nitrate concentrations in groundwater, have demonstrated reduction from levels of 6.5-9.7 mM nitrate (400-600 mg/L) to below discharge limits (0.16 mM nitrate). Perchlorate levels of 4.3 µM (350 µg/L) were also greatly reduced. Elevated levels of nitrate in drinking water are a public health concern, particularly for infants and adults susceptible to gastric cancer. Primary sources of contamination include feedlots, agriculture (fertilization), septic systems, mining and nuclear operations. A major source of perchlorate contamination in water is ammonium perchlorate from manufacture/use of rocket propellants. Perchlorate, recently identified as an EPA contaminant of concern, may affect thyroid function and cause tumor formation. A biobarrier used to support the growth of microbial populations (i.e. a biofilm) is a viable and inexpensive tool for cleaning contaminated groundwater.

Aquatic ecosystems and human populations worldwide are affected by contaminated water supplies. One of the most frequent contaminants is nitrate. Remediation of nitrate in groundwater and drinking water by biodegradation is a natural solution to this problem. Microbial processes play an extremely important role in *in situ* groundwater treatment technologies. The assumption of carbon limitation is the basis for addition of carbon-based substrates to a system in the development of bioremediation schemes for nitrate-contaminated groundwater. The biobarrier concept typically involves construction of a wall of porous carbon-based material that is placed in a trench perpendicular to the direction of groundwater flow that extends at least the width and depth of the contaminant plume. A biobarrier can be used as a stand-alone system when biodegradable materials are the only contaminants, or it can be used along with other barriers, as has been done in the LANL Multi-Barrier system, designed to remediate multiple contaminants. The groundwater system must be reasonably well characterized in terms of direction of flow, width and depth of plume, concentrations along the plume, flow velocity and hydraulic conductivity. Barrier technology is largely applicable to shallow, alluvial plumes (less than 20 feet deep), although permeable reactive barriers (PRBs) have been placed at much greater depths, up to 70 ft. deep. Under these conditions, a barrier could be placed across the plume downstream from the source to prevent migration from a controlled site.

The most effective barrier materials are natural waste materials of high porosity, resistant to degradation, that will not require removal or replacement with time. Pecan shells are a

[1]Group E-ET, Los Alamos National Laboratory, Los Alamos, NM 87545
[2]Group FWO-WFM, Los Alamos National Laboratory, Los Alamos, NM 87545

significant waste problem in pecan-growing areas. The most commonly used solution is land disposal. Use in biobarriers provides a desirable alternative. Pecan shells are composed of cellulose and lignin, and they degrade very slowly, providing a "time-release" carbon source. If left uncrushed, they provide a high porosity material. Fishbone is a waste product made of calcium phosphate, or hydroxyapatite, which is very resistant to deterioration. Apatite®II effectively removes dissolved metals and radionuclides from groundwater (Conca et al. 2000). The precipitates formed with metals and radionuclides are highly insoluble and very unlikely to leach subsequently from the barrier. The residual tissue associated with the fishbones provides nutrient materials that contribute to formation of a microbial population as an additional benefit.

We have investigated denitrification and perchlorate reduction processes within a biobarrier. We performed batch and column studies. The batch studies involved comparison of two potential carbon-based biobarrier support materials: pecan shells alone and pecan shells mixed with dog food in a 10:1 ratio. The results of the column studies have been reported elsewhere (Taylor et al. 2000, Habas et al. 2000, Taylor et al. 2001). The column studies were used to confirm that the microbial reactions occurring under denitrifying conditions in the batch studies are not altered dramatically under flowing conditions with the introduction of oxygenated groundwater. The objectives of these studies were to: 1) determine the effectiveness of the materials in development of a biofilm, and in destruction of nitrate, 2) quantify microbial populations present in batch systems, 3) determine amounts of nitrite and ammonia produced, and 4) determine pH conditions produced by the microbial activity in the biobarrier. An additional objective was to determine if these systems are effective at reducing the level of perchlorate.

Experiments with levels of nitrate from ~0.5 to 9.7 mM of nitrate produced effective degradation to below detection using both the pecan shell and pecan shell/dog food systems. The primary difference in our experimental results lies in the length of time required to fully degrade the nitrate. The batch experimental degradation rate can be used as a predictor of the rate expected in the field system. However, the ratio of water to solids (10:1) in the batch system was selected in order to have adequate solution for analysis. The actual liquid/solid ratio in the field will be much lower. Therefore, the batch results can be viewed as a conservative estimate of the degradation rates since the amount of nitrate present at a given time will be smaller. A second difference between the two systems was an increase in the levels of ammonia produced in the process in the presence of dog food. Figure 1 displays results from one experimental system at 9.7 mM nitrate.

The results presented in this paper demonstrate the effectiveness of a biobarrier design using pecan shell waste for reduction and elimination of nitrate in a dilute groundwater contaminated with multiple contaminants, including radionuclides, heavy metals, nitrate and perchlorate. The results indicate that an active biofilm is developing within and on the biobarrier support materials, and that this biofilm is effective in destroying nitrate in the groundwater. A biobarrier can be used in conjunction with other barrier materials and can be configured as a Multi-Barrier (such as that under development at Los Alamos National Laboratory). Thus, a technology is created that can be used to clean up many different mixtures of contaminants in a more cost-effective, highly efficient and less-intrusive manner than can be provided by other available technologies.

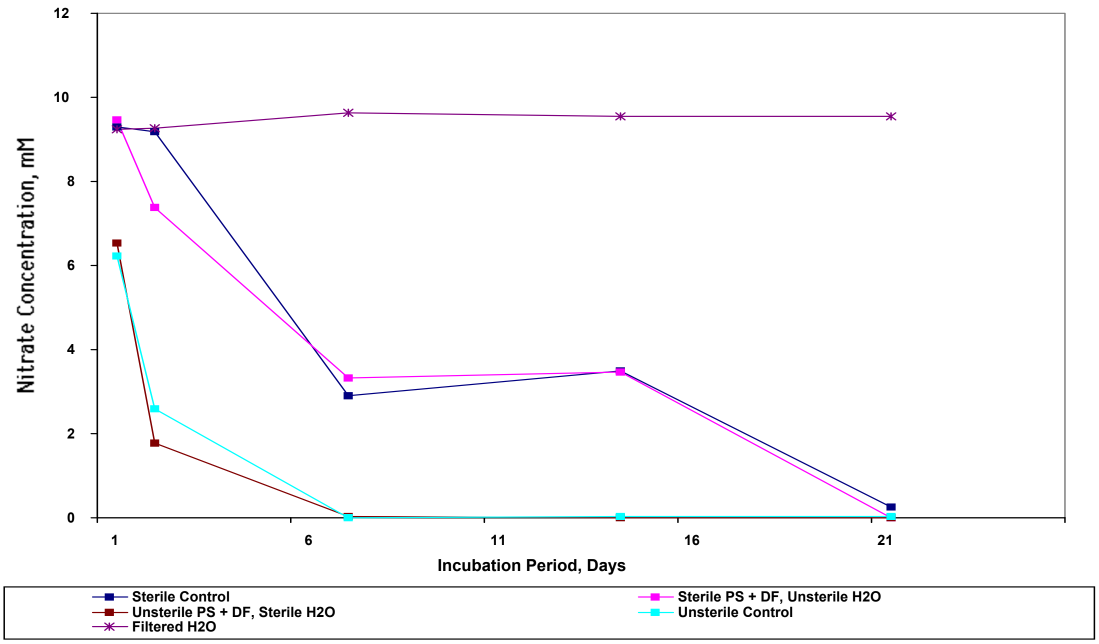

Figure 1. Biodegradation of nitrate in Mortandad Canyon groundwater supplemented with 9.7 mm nitrate using a pecan shell and dog food biobarrier material.

As was expected, the addition of dog food to the pecan shells as a source of micronutrients and protein produced a more rapid rate of destruction of nitrate in the Mortandad Canyon groundwater.

We have produced evidence that the pecan shell biobarrier is able to destroy perchlorate as well. Those studies are continuing in an attempt to eliminate analytical problems and provide valid results. The Multi-Barrier system developed at Los Alamos National Laboratory is capable of removing nitrate, perchlorate, colloids, metals and radionuclides. The results of experiments with the last three groups of contaminants are discussed elsewhere.

REFERENCES:

1. Conca, J.L., N. Lu, G. Parker, B. Moore, A. Adams, J. Wright and P. Heller, "PIMS – Remediation of Metal Contaminated Waters and Soils" in Proc. 2nd Intl. Conf. on Remediation of Chlorinated and Recalcitrant Compounds (2000).
2. Taylor, T.P. and N.N. Sauer, "Remediation of Inorganic Contaminated Groundwater Using Multi-Barrier Reactive Treatment Wall Technology," Gordon Research Conference, Modeling of Flow in Permeable Media, Andover, NH (2000).
3. Habas, S.E., T.P. Taylor, N.N. Sauer, J.L. Conca, B.A. Strietelmeier, J.P. Kaszuba, M.L. Espinosa And S.D. Ware, "Multiple Reactive Barrier Wall Technology for Remediation of Inorganic Contaminated Groundwater," Robert A. Laudise, ACS Symposium, Union College, NY (2000).
4. T. P. Taylor, N. N. Sauer, J. L. Conca, B. A. Strietelmeier, J. P. Kaszuba, M. W. Jones & S. D. Ware, 2001, Reactive Barrier Treatment Wall Technology For Remediation Of Inorganic Contaminated Groundwater, Groundwater 2001 Conference, Sheffield, England.