BIOMAGIC – Summary of Progress and Recommendations

Introduction

Research at the University of Toronto and Boojum Research has focused on assessing the feasibility of an in situ BIOremediation of Mine Area Groundwater Inorganic Contamination (BIOMAGIC) process for South Bay, and elsewhere. It is a joint project, supported by NRC (the National Research Council of Canada) and has two components. The theoretical work is carried out at U. of Toronto, under contract from Boojum Research and the company carries out the field work, with field tests and scale up. The concept is based on using urea-degrading bacteria to increase the pH and alkalinity of acidic groundwater containing high concentrations of dissolved metals. This is intended not only to reduce the extent of acidification that normally accompanies the hydrolysis of dissolved metals in mine drainage, particularly ferric iron, but also to initiate the removal of dissolved metals through mineral precipitation and sorption reactions. Anticipated benefits include restoration of normal pH values and substantially reduced metal-loading in water that is apt to move off mine site property. Moreover, urea is produced as a bulk commodity agricultural fertilizer that is readily available.

The approach used in this preliminary evaluation of the potential use of urea-degrading bacteria for BIOMAGIC involved both geochemical modeling and microbiological investigations. Flow-through column work has also been undertaken to help in the assessment of South Bay hydrogeology, and to learn about the potential impact of bacteria on groundwater flow in porous geological media. Construction of the geochemical model using the MINEQL+ program was based on South Bay groundwater chemistry provided by Boojum Research. The objective of the modeling exercise was to determine (i) the extent to which groundwater pH would change in response to urea degradation, (ii) the minimum amount of urea that must be degraded to restore near-neutral pH, and (iii) the impact of anticipated pH changes on the aqueous chemistry and solubility of dissolved metals. Microbiological studies initially encompassed a survey of South Bay groundwaters to determine whether any urea-degrading bacteria existed in the mine site aquifer, and to identify specific locations with conditions favorable to their growth. Subsequent work involved single colony isolation of South Bay urea-degrading bacteria to compare their activity with that of a reference bacterial culture (*Bacillus pasturii*) from the American Type Culture Collection (ATCC). These pure culture studies are being done under anaerobic conditions in South Bay groundwater. All of this microbiological information is needed to determine where to initiate BIOMAGIC, and whether natural populations of bacteria might be used or, alternatively, whether a need exists to add urea-degrading bacteria to the groundwater system.

BIOMAGIC Feasibility

The predictive geochemical model that has been developed applies directly to peizometers along the hydraulic gradient and contamination plume that extends between the tailings and Mud Lake. Among the computational results, two key findings stand out. First, the Fe^{2+}/Fe^{3+} couple dominates the redox chemistry of the contaminant plume with Fe^{3+} concentrations decreasing, and Fe^{2+} concentrations increasing down gradient. This decrease in Fe^{3+} concentration and production of Fe^{2+} is likely the result of *in situ* anaerobic bacterial respiration. At the same time, SO_4^{2-} is the most thermodynamically stable sulfur species, implying that S^{2-} is highly prone to oxidation. It can be inferred from these results that groundwater emerging in Mud Lake is highly charged with Fe^{2+} that can be expected to undergo rapid oxidation and hydrolysis upon exposure to the atmosphere. This, in turn, contributes to the generation of low pH acid conditions because the alkalinity of the water is so poor.

The second key finding from computational work with the geochemical model is that only mM concentrations of urea need to be degraded to bring about and sustain a substantial increase in groundwater pH – even after oxidation of emergent reduced groundwater. The most important conclusion that can be drawn from this fundamental result is that, in geochemical and thermodynamic terms***, BIOMAGIC is highly feasible***. Moreover, because urea is very soluble, introduction of appropriate concentrations to recognize the benefit of BIOMAGIC is unlikely to be a problem for field application.

In addition to the increase in pH that is expected to accompany bacterial urea-degradation in South Bay groundwater, the geochemical modeling exercise revealed large changes in mineral saturation states. Although it is difficult to ascertain which minerals will precipitate based on thermodynamic data alone (i.e., the computational basis for geochemical modeling), kinetic constraints arising from differences in surface free energies anticipate, according to the Ostwald Step Rule, that the least soluble phase among a suite of related minerals is likely to precipitate first. In the case of iron oxides such as hematite, goethite, lepidocrocite, and ferrihydrite, the later is the least thermodynamically stable, yet generally precipitates first in most aquatic systems. This can be verified in laboratory and field experiments. **Field experiments are in progress and will be sampled in l999, to identify the minerals which have formed in the field experiment.**

The degree to which mineral precipitation occurs in BIOMAGIC is an important consideration for two reasons. On one hand, substantial mineral precipitation underground can dramatically decrease aquifer permeability and thus reduce water flow. Preliminary column experiments, for example, have confirmed that the hydraulic conductivity of iron oxide coated sand is less than clean sand. A reduction in hydraulic conductivity along the contaminant plume at South Bay would tend to lengthen the transit time of the water, and could increase dilution of contaminants beneficially through greater mixing with uncontaminated meteoric water. On the other hand, mineral precipitation generates solid phases that can both concentrate metals directly into their crystal lattice and capture dissolved metals through surface complexation (i.e., sorption) reactions. While this offers an effective way to remove contaminant metals from solution, considerable differences exist in the metal scavenging ability of different minerals. Again, this aspect of the BIOMAGIC process needs to be confirmed and quantified in laboratory and field experiments. **This is in progress, both with experiments and in the field test and will be confirmed in l999**.

Urea-Degrading Bacteria at South Bay

The microbiological survey of South Bay groundwater from peizometers between the tailings area and Mud Lake determined that urea-degrading bacteria, as well as other microorganisms, are indigenous to the aquifer. Their distribution, however, is not uniform as samples from peizometers with more acidic groundwater appeared to be less hospitable for urea-degrading bacteria. In comparative tests done thus far under anaerobic conditions with the ATCC *B. pasturii* culture, urea-degrading bacterial isolates from South Bay performed more slowly but still managed to substantially increase groundwater pH. These experiments have employed urea concentrations at mM levels as inferred from computational work with the geochemical model. This provides the first critical corroborative experimental evidence in support of the geochemical modeling effort, and the intrinsic feasibility of BIOMAGIC.

The apparent preference of urea-degrading bacteria for more neutral pH conditions, as observed in the initial microbiological survey, provides potentially useful insight on where to initiate BIOMAGIC in the field. Acid charged waters infiltrate into the aquifer in the immediate vicinity of the tailings, but become more neutral down gradient as the groundwater approaches Mud Lake. This is because of mixing with uncontaminated meteoric water, and because of *in situ* anaerobic bacterial processes, most likely Fe3+-reduction. In the down gradient area the groundwater, while at a somewhat higher pH, is still very acidic with poor buffering capacity. This is apt to be the best spot to initiate BIOMAGIC – just before the contaminated groundwater emerges in Mud Lake. The slightly elevated pH is supportive to the activity of urea-degrading bacteria that, in turn, could generate enough alkalinity to prevent further acidification of Mud Lake. Direct application of urea to the sediment of Mud Lake might also be considered, although some experimental work ought to be undertaken before this later option is explored in the field. **The 1999 field work will address these issues.**

The onset of mineral precipitation from ground water that occurs in response to urea degradation was readily apparent in the laboratory experiments with the South Bay bacterial isolate and *B. pasturii*. Both cultures exhibited very dramatic colour changes – from dilute iron oxide orange to black and green, respectively. Chemical analyses of the culture fluids revealed high levels of dissolved Fe^{2+}, implying that Fe^{3+}-reduction accompanied urea degradation. In addition, fluffy solid precipitates developed in both cultures. Examination of the precipitates by scanning electron microscopy and energy dispersive X-ray spectroscopy showed that they developed directly on bacterial cell surfaces (i.e., the bacteria served as heterogeneous nucleation templates for mineral precipitation), and were comprised largely of iron, implying an oxide mineralogy, probably ferrihydrite. Further studies employing a combination of X-ray diffraction, and high resolution transmission electron microscopy and selected area electron diffraction are needed to confirm the mineralogy. The precipitates were also found to contain detectable concentration of zinc, implying that the metal was very efficiently removed from solution by the solid phase precipitates. Note that the detection limit for energy dispersive X-ray spectroscopy is in the 1.0 weight percent range. Additional work is needed for quantification of solid phase metal partitioning as a consequence of the BIOMAGIC process. This scavenging of metals could be one of the most important side benfefits of BIOMAGIC.

Recommendations

Based on computational results from geochemical modeling establishing the feasibility of BIOMAGIC, and microbiological studies confirming that urea-degrading bacteria are active in South Bay groundwater, future development work ought to proceed alone three parallel lines of investigation. These include (i) implementation of exhaustive field testing; (ii) quantitative assessment of the impact of urea-degradation on solid phase metal partitioning (i.e., mineral precipitation and metal sorption); and (iii) construction of a reactive transport model – integrating groundwater flow parameters and rates of biogeochemical processes (from field and laboratory investigations) – to predict performance under realistic field conditions, and develop guidelines for full implementation. A model is being completed by Boojum Research and will be ready to be used in the next month , ie. April l999. With respect to the general recommendations outlined above:

- Microbiological investigations suggest that the BIOMAGIC field test should be conducted somewhere between the tailings area and Mud Lake where urea-degrading bacteria are likely to be more active.

- An infiltration gallery delivery system, for example a trench with a porous screen filled with fertilizer grade urea, needs to be designed and installed. It should probably extend into the contaminant plume.

- Close spaced monitoring wells (multi-level peizometers) may need to be installed down gradient of the urea delivery system to measure changes in groundwater chemistry on a regular basis within a reasonable time frame (week to month travel time of water between closest and farthest spaced monitoring wells). This would be an area with steepest possible gradient of hydraulic heads between wells. At least one full season of regular field sampling (weekly to biweekly) ought to be anticipated.

- The use of injection of dissolved urea solutions, followed by pumping to measure extent of urea degradation and groundwater chemistry changes, could be done on a wider scale at existing wells around the site. These tests could employ different lengths of time between injection and pumping to assess the combined influence of dilution by groundwater advection and bacterial urea-degration.

- The impact of urea additions to Mud Lake sediment and water ought to be investigated in laboratory microcosms, and macrocosms constructed in the field. If favorable results are obtained, Mud Lake might be restored to a more neutral pH level in a timely fashion.

- Studies on the products, and rate and extent of solid phase metal partitioning, that accumulate in response to bacterial urea-degradation should focus primarily on reduced groundwater from the contaminant plume, and Mud Lake water. These are places where BIOMAGIC is apt to be initiated with the least amount of difficulty.

- Solid phase metal partitioning induced by bacterial urea-degradation should be studied in solution, as well as sand filled microcosms, to ascertain whether any differences in process performance can arise because of attachment of bacteria to solid surfaces.

- A standard computer code for reactive transport modeling should be immediately identified, and input parameters clearly defined to establish what information is already available, and what additional information is needed, to construct and validate a predictive model.

NOTE: The rest of report of SB117 i.e. "A Computational Study of the Effects of Urea-degrading Bacteria on Groundwater Contaminated with Acid Mine Drainage" By Tracy L. Fleury can be found in SB78 PDF format.