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SITE
SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

Emerging Technology Summary

Handbook for Constructed Wetlands Receiving Acid Mine Drainage

A treatment technology based on constructed wetlands uses natural geochemical and biological processes inherent in the aqueous environment and designs a system to optimize processes best suited to removal of contaminants specific to the site. Key features of this wastewater technology are that it is a passive treatment system, the cost of operation and maintenance is significantly lower than that for active treatment processes, and the removal methods try to mock rather than overcome natural processes. In this study, the contaminant waters were metal-mine drainages with low pH (<3.0) and high concentrations of metals (Al, Mn, Fe, Ni, Cu, Zn, and Pb).

From studies done at constructed wetlands at the Big Five Tunnel near Idaho Springs, Colorado, the important process for raising the pH and removing metals was found to be bacterial sulfate reduction followed by precipitation of metal sulfides. By optimizing the process and determining how to properly load the wetland with contaminant drainage, the following results were achieved:

- pH was raised from 2.9 to 6.5.
- Dissolved Al, Cu, Zn, Cd, Ni, and Pb concentrations were reduced by 98 % or more.
- Iron removal was seasonal with 99% reduction in the summer.
- Mn reduction was relatively poor unless the pH of the effluent was raised above 7.0.
- Biotoxicity to fathead minnows and *Ceriodaphnia* was reduced by factors of 4 to 20.

Once it was found that microbial processes were primarily responsible for contaminant removal, a staged design process comparable to the design process used for other wastewater treatment technologies was devised. Laboratory studies determine whether in principle contaminants could be removed and the best substrate combination for their removal. Bench scale studies determine the optimum loading capacity and treatment system configuration. From these studies design of a reasonably sized module that is specific to the site can proceed with the expectation that it will successfully treat the contaminanted water.

This summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the SITE Emerging Technology Program that is documented in a separate report (see ordering information at back).

Introduction

In response to the Superfund Amendments and Reauthorization Act of 1986, (SARA), the U. S. Environmental Protection Agency's (EPA) Office of Research and Development (ORD) and the Office of Solid Waste and Emergency Response (OSWER) have established a formal program to accelerate the development, demonstration, and use of new or innovative technologies as alternatives to current containment systems for hazardous wastes. This program is called Superfund Innovative Technology Evaluation or SITE.

The SITE program is part of EPA's research into cleanup methods for hazardous waste sites throughout the nation. Through cooperative agreements with developers, alternative or innovative technologies are refined at the bench-scale and pilot-scale level and then demonstrated at actual sites. EPA collects and evaluates extensive performance data on each technology to use in remediation decision making for hazardous waste sites.

The report summarized here documents the results of laboratory and pilot-scale field tests on the applicability of sulfate-reducing bacteria operating in the anaerobic zone within a wetland constructed to remove contaminant metals associated with mine drainages. These metals can include Al, Mn, Fe, Co, Ni, Cu, Zn, As, Ag, Cd, Hg, and Pb. In the mine drainage water used in this study, Mn, Fe, Cu, and Zn are the primary contaminants in the water. Also, most mine drainages have an acidic pH that causes concern and has to be increased to effect treatment. In the water used in this study, the average pH is 3.0.

The Concept of Constructed Wetlands

Ecologists have long understood that soils in wetlands are often foul because they naturally accumulate contaminants by:

- filtering of suspended and colloidal material from the water;
- uptake of contaminants into the roots and leaves of live plants;
- adsorption or exchange of contaminants onto inorganic soil constituents, organic solids, dead plant material, or algal material;
- neutralization and precipitation of contaminants through the generation of HCO_3^- and NH_3 by bacterial decay of organic matter;
- destruction or precipitation of contaminants in the aerobic zone catalyzed by the activity of bacteria; and
- destruction or precipitation of chemicals in the anaerobic zone catalyzed by the activity of bacteria.

With so many possible removal processes, a wetland, such as depicted in Figure 1, is the typical contaminant treatment system in a natural ecosystem. In addition, it operates in a passive mode requiring no additional reactants and no continuous maintenance.

In the last decade, engineers began to use wetlands to remove contaminants from water. In some instances, natural wetlands were used. A natural system however, will accommodate all the above removal processes and probably will not operate to maximize a certain process. A constructed wetland, on the other hand, can be designed to maximize a specific process suitable for the removing of certain contaminants. Engineering and ecological reasons lead to using a constructed wetland for contaminant removal rather than using an existing natural ecosystem.

As an example of constructing a wetland to maximize specific removal processes, consider the bacterial processes that are items 6 and 7 in the above list. Typical microbially mediated reactions that are possible in the aerobic zone of a wetland include:

$$4\ Fe^{2+} + O_2 + 10\ H_2O \longrightarrow$$

$$4\ Fe(OH)_3 + 8\ H^+$$

$$2\ O_2 + H_2S \longrightarrow SO_4^{=} + 2\ H^+$$

$$2\ H_2O + 2\ N_2 + 5\ O_2 \longrightarrow 4\ NO_3^- + 4\ H^+$$

Typical microbially mediated reactions that are possible in the anaerobic zone of a wetland include:

$$4\ Fe(OH)_3 + CH_2O + 8\ H^+ \longrightarrow$$

$$4\ Fe^{2+} + CO_2 + 11\ H_2O$$

$$5\ CH_2O + 4\ NO_3^- + 4\ H^+ \longrightarrow$$

$$2\ N_2 + 5\ CO_2 + 7\ H_2O$$

$$SO_4^{=} + 2\ CH_2O \longrightarrow H_2S + 2\ HCO_3^-$$

In these reactions, "CH_2O" is used to symbolize organic material in the substrate.

It is apparent that the anaerobic reactions are approximately the reverse of the aerobic reactions. Both zones exist in a wetland. If removal involves aerobic processes, then the wetland should be constructed so the water remains on the surface. If removal involves anaerobic processes, then the wetland should be constructed so the water courses through the substrate. In a natural wetland, the water primarily remains on the surface.

In the important area of microbially mediated removal, the wetland must be constructed to maximize removal reactions and minimize competing reactions. When removing contaminants from acid mine drainage, the removal processes should consume hydrogen ions and, consequently, anaerobic processes are emphasized. The research and development at the Big Five Tunnel site in Idaho Springs, Colorado has concentrated on understanding the chemistry and ecology involved in removal and designing structures from readily available materials that maximize these processes.

Although this appears to be "low technology", an intense interdisciplinary effort and creative engineering skills are needed to design and perfect systems that maximize natural processes. For more details on what should be considered, The full report cites recent references.

The Big Five Pilot Wetland

The research reported here has involved studying removal processes from a pilot constructed wetland designed to receive metal mine drainage from the Big Five Tunnel in Idaho Springs, CO. The chemistry from the adit drainage is reasonably constant throughout the year and is summarized in Table 1. After a number of modifications of the pilot cells, removal results were excellent.

Table 1. *Contaminant Concentration, Big Five Tunnel Drainage, Averages.*

Constituent	*Concentration,mg/L*
Mn	*31*
Fe	*38*
Co	*0.10*
Ni	*0.15*
Cu	*0.73*
Zn	*9.4*
Cd	*0.03*
Pb	*0.03*

Figure 2 shows the removal trends for a 2-year period as outflow concentrations over influent concentrations. Cu and Zn are completely removed; Fe removal changes with the seasons.

During this 2-year period, analysis of chemical data accumulated at the site led to the conclusion that microbial reduction of sulfate to sulfide followed by precipitation of heavy metal sulfides is the predominant process accounting for the removal of over 90 % of the Fe, Cu, and Zn and the rise in the pH from below 3 to above 6. Procedures for construction of wetland cells that emphasize anaerobic removal processes has been considered. Another consideration is how to employ knowledge of the biochemistry of sulfate reduction in the wetland design process. This has been done by using two ideas particularly suited to wetlands-ideas that employ anaerobic removal processes such as sulfate reduction: The limiting reagent concept, and staged design of wetlands.

The Limiting Reagent Concept

In the design of wetlands for wastewater treatment, there is a strong emphasis on determining the loading factor which gives an indication of how large a wetland should be to remove the contaminants of concern. This can be stated as the amount of square feet of wetland per gallon per minute of water to be treated or as the grams of contaminant removed per day per square meter of wetland. In our experiences at the Big Five site, typical measures of loading factor do not seem to explain the removal of metals even though heavy metals such as Cu and Zn are

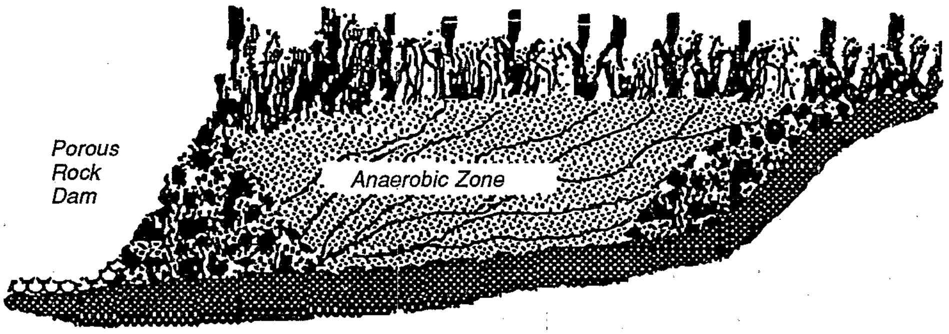

Figure 1. *Diagram of a typical wetland ecosystem that emphasizes subsurface flow.*

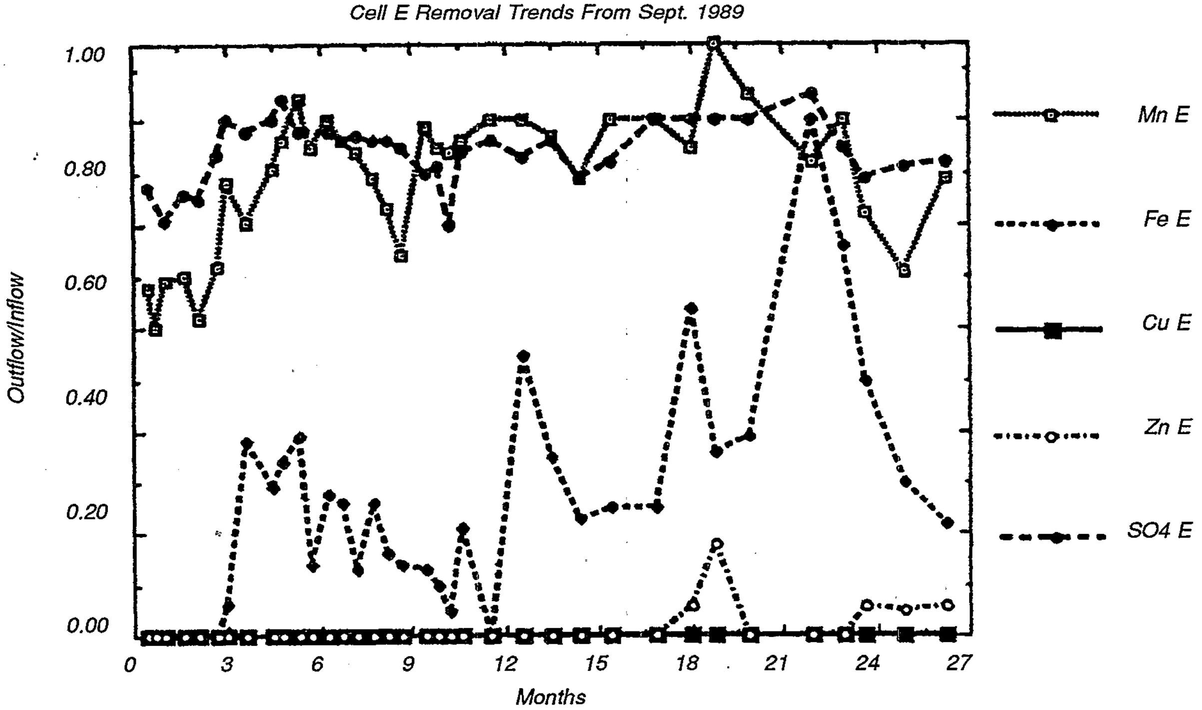

Figure 2. *Two year removal trends for a subsurface wetland cell located at the Big Five Tunnel in Idaho Springs, Colorado.*

reduced by greater than 99 %. We have discovered that a key factor in sulfate reduction is to insure that the optimum microenvironment for sulfate-reducers is maintained. The most important environmental conditions are reducing conditions and a pH of around 7. Since the wetland cell is receiving mine drainage with pH below 3 and Eh of above 700 mV, the water can easily overwhelm the microenvironment established by the anaerobic bacteria. This leads to the limiting reagent concept for determining how much water can be treated, as an alternative to the use of typical loading factors.

Consider the following precipitation reaction:

$$Fe^{2+} + S^{=} \longrightarrow FeS$$

At high flows of mine drainage through the substrate, sulfide will be the limiting reagent, the microbial environment will be under stress to produce more sulfide, the pH of the microenvironment will drop, and removal will be inconsistent. At low flows of mine drainage through the substrate, iron will be the limiting reagent, the excess sulfide will insure a reducing environment and a pH near 7, the microbial population will remain healthy, and removal of the metal contaminants will be consistent and complete. Using this idea, loading factors should be set to insure that the heavy metal contaminants are always the limiting reagents. The question then is how much sulfide can a colony of sulfate-reducing bacteria produce per cubic centimeter of substrate per day?

Studies by the U. S. Bureau of Mines wetlands group suggests that a reasonable figure for sulfide generation is 300 nanomole sulfide/cubic cm/day. This number, the volume of the wetland cell, and the metals concentrations in the mine drainage are used to set the flow of mine drainage through the wetland cell. Using this concept in a subsurface wetland cell to determine the loading factor has resulted in year round complete removal of Cu and Zn (Figure 2).

Staged Design of Wetlands

After determining that precipitation of metals by sulfide generated from sulfate-reducing bacteria is the important process, it was realized that establishing and maintaining the proper environment in the substrate is the key to success for removal. This means that processes operating on the surface of the wetland are not that important. In particular, plants are not necessary in a wetland emphasizing subsurface processes. If this is so, then a large pilot cell, such as was built at the Big Five site, is not necessary to determine whether a wetland that emphasizes anaerobic processes for removal will work. Consequently, the study of wetland processes and the design of optimum systems can proceed from laboratory experiments to bench scale studies to design and construction of actual cells. We call this "staged design of wetland systems".

In current laboratory studies, culture bottle experiments are used for fundamental studies on how to establish simple tests to determine the production of sulfide by bacteria, and of what substrate will provide the best initial conditions for growth of sulfate-reducing bacteria. In these experiments, laboratory production of sulfide at 18 °C has been 1200 nanomole/gm of dry substrate/day.

Culture bottle tests have shown that in the case of cyanide, sulfate reduction was retarded until the concentration of total cyanide was below 10 mg/L and that Cu concentrations above 100 mg/L would kill or retard sulfate-reducing bacteria. However, other culture bottle tests have also shown that sulfate reduction was still vigorous at Cu and Zn concentrations above 100 mg/L.

For bench scale studies, plastic garbage cans are used to conduct experiments to provide answers necessary to the design of a subsurface cell, e.g. determining the optimum loading factor, substrate, cell configuration, and substrate permeability. In a recent study, garbage cans filled with substrate were used to determine whether using the sulfide generation figure of 300 nanomole sulfide/cm^3 of substrate/day could be used to set the conditions for treating severely contaminated drainage that flows from the Quartz Hill Tunnel in Central City, CO. Contaminant concentrations are shown in Table 2.

Using the limiting reagent concept described above and the amount of substrate contained in the garbage can, flow could not exceed 1 ml/min to ensure that sulfide would always be in excess. Contaminant concentrations from the outputs of three different bench scale cells are shown in Table 2. For cell A the mine drainage was passed through the cell with no delay. For cell B the substrate was soaked with city water for one week before mine drainage started passing through the cell. For cell C, the substrate was inoculated with an active culture of sulfate-reducing bacteria and soaked with city water for one week before mine drainage started passing through the cell. Preparations on cells B and C were done to ensure that there would be a healthy population of sulfate-reducing bacteria before mine drainage flowed through the substrate. All cells were run in a downflow mode of the mine drainage through the substrate. In all three cells removal of Cu, Zn, Fe, as well as Mn is greater than 99%. The increase in pH is from about 2.5 to above 7. These results were consistently maintained for over ten weeks of operation.

The substrate used was a mix of 3/4 cow manure and 1/4 planting soil. The results from cells B and C show that the cow manure has an indigenous population of sulfate-reducing bacteria that are quite active. Inoculation with an active culture of bacteria is not necessary in this case. Also, since the results from cell A are comparable to those of cells B and C, the population of sulfate reducers can withstand immediate exposure to severe mine drainage and still produce sufficient quantities of sulfide. The key to good initial activity is to ensure that the flow of mine drainage is low enough that its low pH does not disturb the micro-environment established by the bacteria.

These bench scale systems also serve as permeameters and thus can provide important information for others aspect of wetland design. Determination of soil conductivity and how this physical property changes with time is found to be an important geotechnical parameter for the design of subsurface constructed wetlands.

Conclusions

Using constructed wetlands for wastewater treatment is still a developing technology. The results from the Big Five Pilot Wetland study, however, show promising removal of heavy metals and increase of pH for acid mine drainage. Conclusions from the project include:

- Toxic metals such as Cu and Zn can be removed and the pH of mine drainage can be increased on a long term basis.
- The major removal process is sulfate reduction and subsequent precipitation of the metals as sulfides. Exchange of metals onto organic matter can be important during the initial period of operation.
- A trickling filter type of configuration achieves the best contact of the water with the substrate.
- Removal efficiency depends strongly on loading factors. In the Big Five wetland and in bench scale studies, flow of water should not exceed the 300 nanomoles/cm^3/day of sulfide that can be generated by the microbes in the substrate.

- Permeability of the substrate is a critical design variable for successful operation. Using laboratory and bench-scale tests, a good indication of the soil permeability in a constructed wetland can be determined.
- As with any other wastewater removal technology, design of a constructed wetland or passive bioreactor is specific to the site and the water to be treated.
- A staged design and development sequence can be used where laboratory studies are used to determine the best conditions and substrate, bench scale experiments help to determine loading factors and substrate properties, and pilot modules test the performance of a typical field module.

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***Table 2.** Constituent concentrations in mg/L in the Quartz Hill Tunnel mine drainage and in effluents from the bench scale tests*

Sample	*Days Operated*	*Mn*	*Fe*	*Cu*	*Zn*	*SO_4*	*pH*
Mine Drainage	*24*	*80.0*	*630.0*	*48.0*	*133.0*	*4240*	*2.4*
Cell A	*24*	*0.94*	*1.6*	*0.06*	*0.27*	*450*	*7.4*
Cell B	*24*	*0.91*	*1.9*	*<0.05*	*0.17*	*70*	*7.5*
Cell C	*24*	*0.99*	*1.0*	*<0.05*	*0.16*	*412*	*7.4*
Mine Drainage	*43*	*80.0*	*640.0*	*50.0*	*135.0*	*4300*	*2.5*
Cell A	*43*	*0.97*	*0.87*	*<0.05*	*0.18*	*1080*	*7.2*
Cell B	*43*	*0.64*	*0.96*	*<0.05*	*0.24*	*660*	*7.4*
Cell C	*43*	*1.6*	*0.46*	*<0.05*	*0.14*	*1180*	*7.2*
Mine Drainage	*71*	*70.0*	*820.0*	*70.0*	*101.0*	*NA*	*2.6*
Cell B	*71*	*0.48*	*0.40*	*<0.05*	*0.21*	*NA*	*8.0*
Cell C	*71*	*1.6*	*0.40*	*<0.05*	*0.25*	*NA*	*7.9*

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The complete report, entitled "Handbook For Constructed Wetlands Receiving Acid Mine Drainages," (Order No. PB93-233914AS; Cost: $36.50, subject to change) will be available only from:

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