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Abstracts

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ABSTRACTS

LOW-PROFILE STRIPPING OF ORGANIC POLLUTANTS

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We have demonstrated the feasibility of effectively removing organic pollutants in aqueous solutions using a Shallow-tray, low-profile air stripper. In particular, we evaluated the effects of water flow, air flow, volumetric air-to-water ratio, and concentrations of the organic compounds in solution on stripping rate constants and steady state stripping efficiencies. Unlike conventional packed-tower air strippers, which create a number of operating and maintenance problems due to clogging, low-profile strippers have no packing materials and offer easy access for removal of scale and other fouling agents. They are also capable of operating at very high air-to-water ratios (greater than 1,000:1 on a volume basis), which is desirable for high treatment efficiencies for more-difficult-to-strip compounds.

In this paper, we report laboratory results for benzene, toluene, ethylbenzene, xylene (BTEX), trichloroethylene (TCE), methyl-tert-butyl ether (MTBE) and acetone. These results are obtained by sampling and analyzing the stripper's inlet and outlet water streams using a UV/VIS spectrophotometer (DU 7500, Beckman) set at wavelengths of 210-190 nm. We have found that the rates of contaminant removal and efficiencies of these strippers are significantly affected by the air-to-water ratios, initial aqueous-phase concentrations of contaminants, and temperature. Unfortunately, the low molar absorptivity these compounds (e.g., MTBE), limits the sensitivity of our spectrophotometric technique. Current efforts of this study include the use of EPA Method 602 (a purge and trap GC method) to evaluate stripping efficiencies at low initial concentrations (ppb levels), destruction of stripped organics in the gas phase with UV photolysis (using advanced ultraviolet flashlamps), characterization of reaction products with gas chromatograph/mass spectroscopy (GC/MS) and determination of mechanisms of decomposition.

TREATMENT OF RUBBER THREAD MANUFACTURING INDUSTRY WASTEWATER USING AN UPFLOW ANAEROBIC FILTER

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Wastewater from the rubber thread manufacturing industry is acidic in nature with pH ranging from 3.6 to 4.7 and contains high concentrations of COD, BOD, Total-N and Zn (5900, 5000, 222 and 286 mg/L respectively). The high BOD to COD ratio (0.78 to 0.9) indicated that the wastewater is biodegradable. However as the wastewater contained high concentration of Zn which could inhibit the anaerobic digestion process, it was pretreated by chemical precipitation/flocculation. The treatment using a combination of sodium sulphide (precipitant) and polyelectrolyte LT 27 (flocculant) at concentrations of 800 and 5 mg/L respectively is the most effective system for removing Zn from the wastewater.

After Zn removal an upflow anaerobic filter which contained polyurethane foam as the packing media could be used effectively to treat the wastewater to reduce other parameters like BOD, COD etc. to within the Department of Environment standard for industrial effluent discharge. The optimum loading rate and the HRT obtained were about 8 g COD/L/d and 1.5 days respectively. In view of cost of operation, the wastewater treatment using the upflow anaerobic filter, which is the common method used for rubber industry wastewater, is best at about 35^0C within a pH range of 6.0 to 9.0 although the highest biogas production was at 50^0C. The study further showed that by increasing the organic loading rate from 2 to 14 g COD/L/d, the specific biogas yield decreased from 0.250 to 0.069 L CH_4/g COD added. Simultaneously, the amount of N and P utilized by anaerobic microorganisms also decreased from 1.25 to 0.55 mg and from 0.13 to 0.09 mg for each 100 mg of COD consumed respectively. On the effect of micronutrients, the study showed that the addition of Ni and Co improved biogas yield of the process. Attached biomass in the upflow anaerobic filter (versus free floating) contributed to more than 70% of the COD removal in the treatment of rubber thread manufacturing industry wastewater.

EXTRACTION OF POLLUTANTS FROM SOIL WITH ORGANIC SURFACTANTS

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This paper presents a simple, effective, and economical method of remediating soil contaminated with benzene, toluene and xylene (BTX), and other petroleum hydrocarbons. The gasoline and diesel contaminated soil at the A&T farm was chosen as the source of soil. Different soil samples collected from different points and depths of the contaminated area were subjected to different laboratory analyses to ascertain some essential physical and chemical properties. Physicochemical properties obtained include hydraulic conductivity, bulk density, porosity, particle size distribution, pH, organic matter and composition of essential nutrients (phosphates, ammonium, nitrates etc.). Samples of the soils were washed or thoroughly mixed with solutions of selected nonionic surfactants (Surfynol 465, Surfynol 486, Poly-Tergent SL-62, and Industrial Basic-I). Surfactant/water solutions of 1/50, 1/75, 1/100, 1/125, 1/150, 1/175, and 1/200 concentrations were prepared by mixing 1 ml of surfactant with 49, 74, 99, 124, 149, 174, or 199 ml of water respectively. The soil/surfactant solution mixtures were filtered and concentrations of the pollutants in the filtrates were determined by UV spectroscopy. Since BTX absorb UV light in the range of 340-220 nm, UV spectroscopy was also used to optimize the conditions of the extraction process. These variables include the concentration of the surfactants in water, the agitation gas flow rate, and the mixing time between the soil and the surfactant/water mixture. In general, the results indicate that all organic surfactants tested gave comparative performance under identical conditions. Comparing absorbency results at the similar conditions, surfonyl 465 appears to have a slight advantage.

SUPPORTED TIO2 CATALYST FOR PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS

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Photocatalytic oxidation using TiO_2 has been shown to be an effective technique for degradation of organic pollutants in waste streams. Although a vast amount of work is available in the literature on the mechanisms and conditions governing the photocatalytic reactions, a feasible technology for continuous photocatalytic detoxification is still not available. A major obstacle in commercializing the process involves the lack of an efficient design of the catalyst system. TiO_2 is generally used in the form of a slurry, and although it is very effective in degradation of common organic chemicals, it poses some problems in having to be filtered out of the purified water.

In this project, a new procedure has been developed to support the catalyst as a film on thesurface of polypropylene beads. A very stable film is obtained that is not affected appreciably upon multiple usages. The film thickness and morphology is characterized by high magnification optical microscopy.

The effectiveness of the catalyst is demonstrated by successful degradation of trichloroethylene and 4-chlorophenol in a batch reactor. The performance of the new catalyst is compared with the equivalent reaction rates in the TiO_2 slurry. Although not as large as in the slurry, sufficiently high degradation rates are reported for the catalyst supported on the beads. To further demonstrate the utility of the catalyst, a continuous photocatalytic reactor has been designed. Performance studies on the catalyst are continuing in the new reactor. In particular, the objective is to obtain optimized reactor parameters for detoxification of chlorinated organics to safe levels.

EFFECTS OF CLAY ON TRANSPORT OF CONTAMINANTS: GOVERNING EQUATIONS VIA HMT

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Clay soil is characterized by particles consisting of a solid (clay mineral) and vicinal liquid which may swell or shrink due to mass transfer of liquid or changes in the pH or ion concentration. This in turn affects the permeability of the soil and the transport of contaminants. In this talk, recent results on the modeling of clay soils using Hybrid Mixture Theory (HMT), an approach based on fundamental thermodynamic principles, are discussed. The resulting governing equations are found to be generalized versions of what is standardly used (i.e. Darcy's law and the definition of chemical potential) in order to account for the swelling nature of clay.

Hybrid mixture theory consists of classical mixture theory applied to a multiphase system with volume averaged field equations. Averaging each field equation (e.g. conservation of mass, momentum balance, energy balance, and entropy inequality) produces macroscopic variables which are precisely defined in terms of their microscopic counterparts. A three-phase porous medium (e.g. solid, and two immiscible fluids) with N constituents per phase is thus viewed as $3N$ overlaying continua with each macroscopic variable for each constituent of each phase defined spatially everywhere. Constitutive restrictions and near-equilibrium expressions are obtained by exploiting the entropy inequality using the Coleman and Noll method.

A RANDOM PROCESS MODEL FOR CONTAMINANT TRANSPORT

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Modeling the process in which a contaminant migrates through groundwater has been the focus of a great deal of research over the last few decades. In particular, accurate models which have the ability to predict the migration of a contaminant over a specified period of time are desired. Such a model would greatly aid efforts to remove or reduce significantly the level of contamination in groundwater.

Traditional approaches for modeling a miscible contaminant in the saturated zone of an aquifer rely upon either deterministic methods (partial differential equations) or stochastic methods (stochastic differential equations). Herein, we present a scheme that is a hybrid of these two approaches. That is, the contaminant moves and spreads in a deterministic manner but the parameters used in the transport model are generated through random processes with statistics sampled from the site in question.

This approach is very appealing in that typically data from a site is very sparse and difficult to extrapolate over the entire domain (as is required for deterministic models). Also, this approach offers an alternative model for hydrodynamic dispersion that does not suffer from scale dependent parameters, a situation which is typical of traditional methods. The analysis herein includes mathematical theory and numerical implementation, as well as computational examples to demonstrate the feasibility of our method.

SUBSTITUTION POLLUTION PREVENTION

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The reduction of toxic materials in the environment may be accomplished by substituting materials and processes that are less polluting. Products have a typical life cycle beginning with material selection and production, their manufacture, followed by their application, and concluded with their disposal. At any point in this cycle, toxic elements can be released to the environment with little regard to the utility of the product or its ultimate application.

Such is the case for cadmium (Cd) and chromium (Cr). Although both metals have been identified and characterized for their intrinsic toxicity, their usefulness in supporting our quality of life is well recognized. How do we keep the good and get rid of the bad? We look for different materials that will do the same or better job with much less risk to our populations.

The purpose of this paper is to discuss an investigation to confirm the opportunity for minimizing hazardous materials (Cd and Cr) in the supply chain maintained by the Defense Logistics Agency. The mission of Hazardous Waste Minimization (HAZMATMIN) is one of compliance with environmental regulations, recognition of opportunities for cost reductions and savings, and identification of materials and technologies that are commercially available for service qualification and support.

Substantial amounts of Cd and Cr, in appropriate formulations, are distributed worldwide by Defense Supply Centers in support of customers' captive plating operations. The associated risks have been recognized as: 1) toxic materials/solutions/wastes from plating operations, 2) toxic wastes from machining and shaping operations, 3) toxic weathering and corrosion products during service, and 4) the concentration of toxics in massive disposals and/or the elevation of toxic backgrounds. Industrial and commercial organizations have a tendency to recognize and address only risks that reduce their profits. For example, since 1977 when EPA recognized that Cd should be replaced by acceptable substitutes, platers have reported that their customers are not calling for a substitute -- they continue to use the familiar. With little driving force in the civilian economy for safer substitutes, the military has been given the mandate to lead the way in minimizing environmental risks.

The case at hand involved the investigation and qualification of high purity aluminum (Al) deposited electrolytically on metal substrates and with different surface treatments as an environmentally and commercially viable alternative. This investigation has established the feasibility and has confirmed both the electrolytic process and the quality of the plated material as a commercially available and suitable substitute for Cd and Cr in typical applications.

THE SELECTIVE CATALYTIC REDUCTION OF NO BY PROPYLENE OVER Pt/Al_2O_3 AND Pt/SiO_2

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The selective catalytic reduction (SCR) of nitric oxide (NO) by hydrocarbons has received a lot of attention over the last few years because of its potential use in commercial emission control applications. Noble-metal-based catalysts are the most promising candidates for this reaction due to their hydrothermal stability and low-temperature activity. However, an understanding of the fundamental chemistry involved in this reaction is rather limited and warrants further investigation.

Our work in this area, involves detailed kinetic and *in-situ* FTIR studies of the selective catalytic reduction of NO by propylene (C_3H_6) over supported platinum catalysts, and more specifically Pt/Al_2O_3 and Pt/SiO_2.

The results of our kinetic studies over 1% Pt/Al_2O_3 and Pt/SiO_2 catalysts indicate the presence of two kinetically distinct regions below and above the temperature of maximum NO conversion as a result of the two competing reactions of propylene with NO and oxygen. The Pt/Al_2O_3 catalyst exhibits a maximum NO reduction temperature of 300°C whereas, the corresponding temperature for Pt/SiO_2 is 280°C. The two catalysts exhibit similar kinetic behavior indicating that the reaction proceeds, on both, through the same mechanism.

During *in-situ* FTIR studies, adsorbed carboxylates (1300 – 1600 cm^{-1}), cyanide (-CN) (2150 cm^{-1}) and isocyanate (-NCO) (2245 cm^{-1}) species were detected on Pt/Al_2O_3 under reaction conditions. Additional adsorption and reaction studies were carried out over a wide range of temperatures in an attempt to identify the origin and investigate the reactivity of these adsorbed species. These were also complemented by isotopic studies with ^{15}NO. The stability of the various adsorbed species was investigated. The results suggest that the surface isocyanate is a reaction intermediate, whereas, the other adsorbed species are "spectators" that do not participate in the SCR process.

LOW LEVEL MIXED WASTE MANAGEMENT

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ABSTRACT

Throughout the United States, mixed waste has become one of the most important and difficult issues facing those in waste management. Mixed waste is considered one of the most difficult types of waste to dispose of and manage because it falls under the authority of two different regulatory agencies. Mixed waste is subject to a dual regulatory framework under the Resource Conservation and Recovery Act (RCRA), as administered by the U.S. Environmental Protection Agency (EPA), and the Atomic Energy Act (AEA), as administered by the U.S. Nuclear Regulatory Commission (NRC). Because of the complexities involved in managing and treating mixed waste, many disposal sites have stopped accepting it. As a result, there are large volumes of mixed waste in storage. The need to provide LLMW treatment capacity has been driven by changes in RCRA Land Disposal Restriction (LDR) requirements and the need to reduce current stockpiles RCRA requires hazardous waste to meet LDRs prior to disposal in a land based unit. LDRs include treatment technology standards and concentration based standards.

Practically all of the commercially generated mixed waste is composed of low-level radioactive waste (LLRW) and hazardous waste and is called Low Level Mixed Waste (LLMW). Radioactive and hazardous materials are commonly used in medical and academic institutions for diagnostic testing and research, industrial facilities for pharmaceutical and biotechnology development, irradiator manufacturing, fuel storage and fabrication, waste processing, and pesticide research, nuclear power plants for operations and maintenance, health physics, and laboratory and radiochemical processes.

The DOE has stored low-level mixed waste for years in violation of the RCRA, primarily due to the nonexistence of treatment technologies. The Federal Facility Compliance Act (FFCAct) of 1992 waived sovereign immunity for the DOE and required DOE to develop plans and facilities for achieving RCRA compliance under a constrained schedule. The high cost of treating and disposing of LLMW provides incentives to DOE and others to develop optimized mixed waste treatment technologies based on life-cycle costs. The variety of sources and types of mixed waste demands the evaluation of numerous efficient and innovative alternatives or combinations of alternatives to satisfy all disposal problems. Other factors such as volume reduction, health risk, simplicity, resource recovery, and energy efficiency should also be considered when considering process options.

The overall objective of this analysis is to develop a waste stream life-cycle model for designing preliminary LLMW treatment systems based on performance and other criteria. A series of mixed waste treatment technologies developed from engineering experience alone may not represent the optimum treatment system, especially when good design alternatives are overlooked. The use of the BIE algorithm in this analysis enables planners and decision makers to consider alternatives that fall within the specified range of costs, as well as being different with respect to other selected decision variables. The availability of useful and cost efficient treatment alternatives contributes to facility compliance. The Oak Ridge K-25 site, where 32,000 drums of mixed-waste sludge were stored, was used as an example in illustrating the application of the model.

AN OPTIMAL ESTIMATION SCHEME FOR SUBSURFACE CONTAMINANT TRANSPORT MODEL

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ABSTRACT

The Kalman-Bucy (KB) filter in the sequential estimation theory has the potential of being applied to data interpolation-assimilation process for groundwater contaminant models. It can improve the accuracy of the prediction which may greatly affect the reliability of risk assessments in a wide range of environmental interests. The KB estimation scheme can include, explicitly, the model dynamics, and keep optimizing predictions from the running model by combining any additional knowledge about the fate and transport process at any irregular time and spatial points. The KB scheme is one of the most robust data assimilation methods because of its four-dimensional assimilation capabilities as well as its general operational property with respect to data type and model dynamics.

A methodology for developing a data assimilation scheme using Kalman-Bucy (KB) filter for an applicable subsurface model has been proposed and illustrated. A numerical scheme was constructed using C language and MATLAB routines. Preliminary results of a hypothetical two-dimensional contaminant plume indicate that the numerical model with KB filter reduces the deviation of model predictions by 60%. Sensitivity tests were also conducted to demonstrate the robustness of the estimation scheme. This paper concentrates on the sensitivity of the model and the optimal estimation with incomplete or insufficient data set.

BIODEGRADATION OF EXPLOSIVES FROM CONTAMINATED SOIL

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Soils from the former Pantex Munitions Facility in Amarillo, Texas were examined for biological removal of nitroaromatic contaminants, principally RDX. Although RDX levels are very high in portions of the Pantex soils (up to 10,000 mg/kg in isolated "hot spots"), solubility in groundwater is about 40 mg/L, limiting availability for biological conversion. TNT (up to 100 mg/kg) and HMX were also found in soils sampled for this study.

Bench-scale shaken flask and bottle reactors were used to test treatability of soil slurries, extracts of soil contaminants, and nitroaromatic reagent solutions. Results of these and numerous control reactors were analyzed to determine: relative differences in the rates of RDX desorption and transformation; extent and rate of biotransformation under nitrate-reducing, sulfate-reducing, fermentation, and aerobic respiration conditions; effect of TNT and HMX on RDX bioconversion; and nitro-group reduction by bisulfide. Slurries of soil contaminated with approximately 10-100 mg/kg RDX indicate that the rate of biotransformation by acclimated native microorganisms is significantly slower than the rate of desorption. Therefore even in the presence of bioconversion, no measureable change in soluble RDX concentration occurs for some time. In reactors fed aqueous extracts of these soils, significant biotransformation of RDX has been observed under nitrate-reducing and sulfate-reducing conditions. Experiments with reagent solutions have shown RDX conversion rate to be fastest under sulfate-reducing conditions, with bisulfide production. Conversion has been minimal in aerobic reactors. Results indicate that removal of TNT (and possibly other nitroaromatics) must be essentially complete before RDX biotransformation proceeds. This observation is significant for treatment of any soil contaminated with such mixtures of munitions residues.

We are quantifying the relative effects of these variables on RDX biodegradation, patterns of intermediate product formation, and subsequent biotransformations. Experiments with small amounts of soil are establishing sorption and desorption effects. Results may be applied to enhance bioremediation of RDX-contaminated soils in soil slurry reactors.

REMEDIATION OF MTBE CONTAMINATED GROUNDWATER WITH HIGH ENERGY ELECTRON BEAM INJECTION

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The Clean Air Act Amendments of 1990 mandate the use of oxygenates in gasoline, either seasonally (i.e. oxygenated gasoline) or year-round (i.e. reformulated gasoline), in specific parts of the United States where concentrations of carbon monoxide in the winter or ozone in the summer exceed established air-quality standards, respectively. Methyl tert-butyl ether (MTBE) has been used as an octane enhancer in gasoline in the United States since the late 1970's. MTBE is the most widely used fuel oxygenate. In 1995, 8.0 billion kilograms were produced in the United States, and it is now in the top 20 chemicals produced in the US annually. Environmental contamination of MTBE may result from leaking underground storage tanks, spills, and air-water interaction, i.e. volatilization and condensation, and storm water discharges. The solubility of MTBE in water (4.8% by weight) suggests that once in the subsurface environment and in contact with groundwater it will move with groundwater. That, coupled with the fact that the rate of bio-degradation is relatively slow, could lead to widespread contamination of groundwater. This paper will describe the results of laboratory experiments and large scale studies (100 gallon per minute) which show that the innovative electron beam process is effective in treating MTBE contaminated groundwater. The treated water was analyzed for formaldehyde and formic acid, which are expected reaction by-products, and both compounds were below detection limits. We have also developed a kinetic model that accurately describes MTBE destruction and can be used to predict removal from groundwater. Preliminary economic analysis suggests that this process is a cost effective alternative compared to conventional treatment systems.

MAPPING CONTAMINATED WELL SITES IN GUILFORD COUNTY, NORTH CAROLINA, USING GIS TECHNOLOGY

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Abstract

A Geographic Information System can be defined as a computer assisted information management system of geographically referenced data. This system integrates the acquisition, storage, analysis and display of geographic data. The application field and objectives of a GIS can be varied, and concern a great number of questions linking social and physical problems, (transport and agricultural planning, environment and natural resources management, location/allocation decisions, facilities and service planning (education, police, water, sanitation, and marketing).

Generally, the objective of a GIS is the management, analysis, and display of geographic data. Even if a few general concepts are presented, the GIS discussed in this small-scale project will be seen from an environmental health perspective. Therefore, GIS can be used as a tool to assist public health officials in the planning, monitoring, and evaluation of the Contaminated Well Sites in Guilford County.

The components of a well that prevent contamination are its surface sanitary seal, annular seal, and well casing. If the annular seal is too shallow, the casing is ruptured, or if the surface seal is broken, by holes or missing gaskets, contaminants can enter the well. If a well is located too close to a source of contaminants, these may enter through one of these routes or percolate down through the ground, and enter the well, therefore causing contamination.

The Contaminated Well Site Data used in this project was obtained from Guilford County Public Records. The data contains a total of 42 contaminated well sites, across Guilford County. Of the 42 contaminated sites, 35 were contaminated with petroleum. Eight were contaminated with other volatile organic chemicals. After verifying the list against the State Public Health Lab Reports results, 21 lab reports revealed contaminants that were listed under the EPA's National Primary Drinking Water Standards, which are regulated by the EPA

However, the objective of this project is to apply simple GIS technology to convert non-spatial contaminated well site data into a spatial map layer, that would display the distribution of the contaminated well sites throughout Guilford County, North Carolina.

An exposure-time model for metabolic lag effects on *n situ* bioremediation

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The fate of materials undergoing transport and reactions in natural porous media sometimes depends on the time of exposure of the conveyed material to other materials present in the system. One example is illustrated by the exposure of resting-state microorganisms in the subsurface to novel substrate occurrence. The transition from oligotrophic to eutrophic conditions is often associated with a time lag in the development of the microorganisms' capability to degrade the substrate. When the microbes occur as an immobile phase in the porous matrix, it is possible to incorporate this lag in metabolic potential in the kinetics of degradation. However in the presence of transport and non-equilibrium partitioning of microbes to and from the immobile phase, conventional non-equilibrium reactive transport models are incapable of representing the effect of a lag in metabolic potential, because the microbes at any point in space and time in general reflect a mixture of metabolic potentials. A solution to this problem is proposed, by treating the components as a mixture of overlapping continua and developing evolution equations for the mixture material densities in the new dimensions of space, time, and exposure-time. The result is a set of nonlinear integrodifferential equations describing the evolution of each component of the mixture, coupled through the reactions terms. Application of the same approach to problems involving chemical heterogeneity and the distribution of groundwater age is discussed.

Application of Flow Reversal in Membrane Flux Enhancement: A Theoretical and Experimental Study of Ultrafiltration of BSA

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ABSTRACT

The effect of flow reversal on permeate flux in crossflow ultrafiltration of bovine serum albumin (BSA) has been investigated experimentally and theoretically. BSA is a well-studied model solute in membrane filtration known for its notorious fouling and concentration polarization capabilities. Ultrafiltration experiments were performed with BSA feed solutions in a hollow-fiber membrane module. The BSA feed concentrations ranged from 0.01 to 5 weight percent and were ultrafiltered at a transmembrane pressure range of 20 to 35 psia. Permeate flux was determined both with the use of flow reversal and without for each concentration. These experimental results indicate that under flow reversal condition the permeate flux is enhanced significantly when compared with runs without flow reversal. The effect of flow reversal on flux enhancement is very pronounced for dilute BSA solutions. A mathematical model has been developed to evaluate the performance of the hollow-fiber membrane module under flow reversal conditions. Besides the effect of osmotic pressure and axial pressure variation, the model considers the convective-diffusive mass transport without decoupling the momentum equation from the solute continuity equation. Model equations were solved by an implicit finite difference method as part of an iterative method. The experimental results compared favorably with the theoretical predictions. In this presentation, the experimental results along with theoretical predictions will be discussed to show the potential benefits of flow reversal in flux enhancement of ultrafiltation processes.

FIELD GC/MS, HPLC AND EDXRF FOR REMEDIAL INVESTIGATIONS AT FORMER ARMY ORDNANCE PLANT

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Many former military facilities have been returned to public and private sectors for multiple uses. Unfortunately, some past practices left environmental contamination behind long after the military rendered these bases obsolete. Rapid assessment of these Former Utilized Defense Sites (FUDS) allows for the remedial investigation and cleanup of these properties to go forward at a faster pace than traditional environmental assessments. The utilization of field transportable analytical instrumentation to direct the investigation and remediation of these sites is a critical element in the successful assessments.

The determination of explosives (nitroaromatics and nitroamines), metals and solvent chemicals was made possible using field transportable analytical instrumentation. Rapid analytical techniques allow the investigation team to make real time decisions in placement of sampling points, delineation, placement of monitoring wells and contaminate boundaries.

Explosives in soil and sediments were determined using a Rapid Extraction Method (REM) coupled to a HPLC equipped with a multiple wavelength diode array ultraviolet detector (HPLC-DAD). Metals and organometallic compounds in soil and sediments were investigated using Electron Dispersive X-Ray Fluorescence (EDXRF) detector. Solvents in soil, sediments and soil gas were identified and quantified using purge-trap-desorb GC/MS.

Samples were provided to the chemist within minutes of collection; samples were prepared immediately and analyzed rapidly along with method blanks, replicates matrix spikes and second source laboratory control samples. Quality Assurance parameters utilized to monitor the accuracy and the precision of the data generated will be discussed.

Definitive (court defensible) level data was generated for use by the USACE and other federal and state government agencies to determine the extent of contamination and rapid removal of contaminates. The paper will discuss the resources required to deploy and utilize a GC/MS, HPLC and EDXRF and the advantages and pitfalls of this type of remedial action support.

MOBILE LABORATORY DETERMINATION OF NATURAL ATTENUATION FOR REMEDIAL INVESTIGATIONS AND ACTIONS

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The United States Environmental Protection Agency (USEPA) defines natural attenuation as (OSWER, 1996):

> *The term "Natural Attenuation" refers to naturally-occurring processes in soil and groundwater environments that act without intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media. These in-situ processes include biodegradation, dispersion, dilution, adsorption, volatilization and chemical or biological stabilization or destruction of contaminants.*

To support the assessment process of natural attenuation as a possible avenue for remediation an field analytical program was established to provide near real time measurement of the indicator parameters. To support remediation by natural attenuation, one must scientifically demonstrate that attenuation of site contaminants is occurring at rates sufficient to be protective to human health, biosystems viability and the overall environment. Three lines of evidence can be used to support natural attenuation of chlorinated aliphatic hydrocarbons, including:

1) Observed reductions in contaminant concentrations along the flow path downgradient from the source of contaminants.

2) Documented loss of contaminants mass at the field scale using:

    a) Chemical and geochemical analytical data including;
        - decreasing parent compound concentrations
        - increasing daughter compound concentrations
        - depletion of electron acceptors and donors
        - increasing metabolic byproduct concentrations

    b) A conservation tracer and a rigorous estimate of residence time along the flow path to document mass reduction and to calculate biological decay rates at the field scale.

3. Microbiological laboratory or field data that support the occurrence of biodegradation and give rates of biodegradation.

This paper will highlight what parameters are measured to determine the evidence of natural attenuation. Near real time results are made that allow the investigation team to optimize the field data collection and analytical determinations. Discussion will be made of Hydrogen in water measurements, Methane, Ethane and Ethene determinations, Volatiles Organic Compounds (VOCs), ferrous iron, eH (oxidation-reduction) and other time critical elements of the natural attenuation monitoring program. Quality assurance guidelines and goals required for a successful monitoring program will be discussed.

Information Resources Workshops for Consulting Engineers and Project Managers

Finding the shortest path to information on innovative technologies for site characterization and remediation

The U.S. Environmental Protection Agency is committed to increasing the development and promoting the use of innovative technologies for the characterization and remediation of contaminated waste sites. We have recognized the problem for consulting engineers, contractors, and Federal and State Project Managers in locating adequate, reliable information on innovative technologies. This Technology Workshop is an opportunity for this audience to learn how to identify and better understand resources and tools to support the selection and use of innovative technologies. In previous deliveries, the workshop has been co-sponsored by the Hazardous Waste Action Coalition, the Navy's Naval Facilities Engineering Command, and North Carolina DENR - Hazardous Waste Division. The next delivery is being co-sponsored by the New Jersey Water Environment Federation. TIO is willing to work with interested parties to tailor the course to meet the specific needs of State and not-for-profit organizations and their audiences. Previous deliveries have ranged from 1 hour sessions to full day workshops.

The short 1-2 hour session covers the use and availability of information resources, both in print and electronic format, which assist in the selection of innovative site characterization and clean-up technologies. The presentation follows a step by step approach, answering the most common questions a project manager might be asking throughout a site cleanup process. The internet is the primary source of the information and tools covered in the presentation, and where possible live Web access is used. Specific site characterization and remediation information resources to be covered in greater depth include in the Vendor Field Analytical Characterization Technologies System (VFACTS), the Vendor Information System for Innovative Treatment Technologies (VISITT), and the on-line Remediation Technologies Screening Matrix and Reference Guide. Participants are provided with a personal resource guide designed in the same format as the material is presented in. The combined knowledge acquired through the presentation and the resource guide should greatly reduce the effort required to collect the information needed to make a technology selection decision.

AEROBIC BIOREMEDIATION OF METHYL TERTIARY BUTYL ETHER (MTBE)

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The presence of the gasoline oxygenate, methyl tertiary butyl ether (MTBE) in aquifers presents a complication in the remediation of underground storage tank (UST) sites. Many UST properties have already addressed the dissolved benzene, ethylbenzene, toluene, and xylenes (BTEX) problems with traditional remedial options, Risk Based Corrective Action (RBCA) and Natural Attenuation (NA). The MTBE issue is difficult to address via RBCA due to the limited information on toxicity and carcinogenicity characteristics of the compound. Also, MTBE fate and transport characteristics are currently being evaluated to support NA efforts.

Regenesis has been collecting data from numerous sites where Oxygen Release Compound (ORC) was being used to biodegrade BTEX and MTBE. The MTBE bioremediation phenomenon identified in these data could not be attributed to adsorption, volatilization, dilution or chemical destruction. Data from across the country indicate MTBE half-life ranges from approximately 5 to 61 days in the presence of ORC. This is more efficient than the published half-life of 30 to 182 days under aerobic conditions.

The MTBE biodegradation rates appear to increase after the BTEX concentrations are reduced via ORC treatment. The presence of background hydrocarbons interfere with the metabolism of MTBE. Data has been gathered from other researchers in the field supporting the observation that BTEX is often consumed preferentially to MTBE in contaminated aquifers. Laboratory experiments using microbial isolates capable of utilizing MTBE as a sole carbon source showed that the metabolism of MTBE can be inhibited by adding BTEX. The MTBE metabolism rate fell upon BTEX addition, and the MTBE degradation resumed as the BTEX was removed from the culture.

Another factor affecting the rate of MTBE biodegradation is dissolved oxygen (DO) concentration. The rate of MTBE biodegradation was shown to be proportional to the concentration of DO in the water by Dr. Mark Deshusses at the University of California Riverside Department of Civil and Environmental Engineering. The experimental data showed that MTBE uptake followed Michaelis-Menton kinetics with respect to DO. Relatively high DO concentrations can be established in aquifers treated with the ORC technology (20 to 30 mg/ml), and may be responsible for the observed enhanced MTBE degradation.

THE USE OF OXYGEN RELEASE COMPOUND (ORC®) AND HYDROGEN RELEASE COMPOUND (HRC™) FOR ENHANCED BIOREMEDIATION

Patrick Hicks and Stephen Koenigsberg
Regenesis Bioremediation Products

Oxygen Release Compound (ORC®) is a patented formulation of time-release magnesium peroxide that releases oxygen slowly when hydrated. ORC treatment represents a "low intensity" approach to site remediation. It provides a simple, passive, low-cost and long term enhancement of aerobic natural attenuation and has been shown to cost-effectively reduce time to site closure. ORC is now a proven technology as evidenced by its use on over 3,700 sites in 50 states and 9 countries and the existence of a full body of independent, peer reviewed literature on its performance. In addition to the use of ORC in the remediation of BTEX, successful applications have been made to an array of other aerobically degradable compounds such as VC, PCP, PAHs and MTBE. ORC is sold as exchangeable filter socks or as a loose powder. Filter socks are placed in an array of wells or trenches, in which contact with ground water facilitates release of oxygen. ORC powder can be made into a slurry for permanent applications in the saturated zone, or dispersed as free powder for the in-situ or ex-situ treatment of soil. A broad array of treatment points, in which ORC slurry is backfilled or injected, can be implemented with low-cost, small-bore technologies to directly "cauterize" the source areas. Loose powder is traditionally used in the remediation of residual contamination at the bottom of tank excavations.

Regenesis has recently introduced Hydrogen Release Compound (HRC™) as a simple, passive, low-cost and long term option for the anaerobic bioremediation of chlorinated aliphatic hydrocarbons (CAHs). HRC is a proprietary, food grade, polylactate ester that, upon being deposited into the subsurface, slowly degrades to lactic acid. Lactic acid is then metabolized to hydrogen which drives reductive dechlorination. HRC is a moderately flowable, injectable material, that facilitates passive barrier designs for enhanced natural attenuation. Evidence suggests that a low concentration of hydrogen favors reductive dehalogenators and starves out methanogens. The slow hydrolysis rate of lactic acid from the ester keeps hydrogen concentrations low which may favor reductive dechlorination over methanogenesis. Results from laboratory and field studies will be presented.

ASSESSMENT OF METAL REMOVAL FROM COAL PILE RUN OFF WATERS

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This studies addressed a critical metal contamination from coal pile run off waters at sites found in many parts of the country including such sites at the Department of Energy's Savannah River Site. The biogeochemical oxidation of pyrite present in coal results in a run off with low acidity (<2) and rich in dissolved toxic metals. This run off water flow into catchment basins where the dissolved toxic metals pollute the surrounding ecosystem and groundwater. The objectives of our research include (1) to conduct pilot-scale treatment of coal pile run off water using specific microbial biomass, and (2) to evaluate the effects of changing environmental parameters (pH, redox, conductivity, temperature, and dissolved oxygen on metal sequesterization and microbial growth dynamics. The results of our bioremediation strategy were effective in changing the pH of the wastewater from <2 to > 8 and dissolved metal concentrations were reduced by 50-100%. In addition, the metabolic reactions of the microbes changed the redox conditions from 278 mV to – 50 mV. Consequently, a chemical environment was generated, which supported the precipitation of the metals from solution. These results have two significant regulatory implications: (1) It established the use of relatively simple parameters (pH, conductivity and redox) as diagnostic tools for monitoring metal mobility, and (2) the bioremediation strategy was effective in reducing metal concentrations in the wastewater below drinking water standards.

PROTOCOL FOR TESTING PORTABLE CORD CONNECTED IN ROOM AIR CLEANERS

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ABSTRACT

Respirable suspended particles (RSP) specially less than $3\mu_m$ in size present in indoor air environment are retained by pulmonary (lower) portion of the human respiratory system.

Adverse health effects such as bronchitis and lung cancer are associated with chronic deposition of particulate matter in this region of the lungs. To address this issue, strategies such as natural or mechanical ventilation, central air-cleaning, and portable in-room air cleaning are currently being used to reduce indoor exposure to dust particles. In residential applications portable air-cleaning systems are probably most common for removing dust particles. The effectiveness of these units is affected by their location, fan size, fan shape and the air movement in the space. Unfortunately, the performance of these units has not been listed for commercially available residential units. Currently there is only one test procedure prescribed by the Association of Home Appliance Manufacturers (AHAM). Under this procedure the units are located in the center of an empty room and are run at the highest fan speed. These are unrealistic conditions for residential applications. The AHAM testing procedure is modified for this proposed research. Tests are performed for selected samples of in-room cleaners to determine the test location and height of an in-room air cleaner within a typical residential room. The results of this study will be focus on this paper.

The study will focus to develop a testing protocol, test air-change effectiveness, estimate the reduction of respirable suspended particles, test the ability of the units to remove respirable suspended particles at various heights and locations, develop suggested guidelines for the application and placement of these units in residential applications.

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COMPARATIVE STUDY OF BIODEGRADABILITIES OF FUEL SYSTEM ICING INHIBITORS

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The current fuel system icing inhibitor (FSII) used for commercial and military aircraft is diethylene glycol monomethyl ether (DiEGME). Fuel deicing additives are mandatory in military fuels and optional in commercial fuels. However, the toxicity and environmental loading of DiEGME are of increasing concern. Recently at George Mason University, new FSII's were synthesized from acetals and ketals from the reduced sugar mannose. These compounds are believed to be less toxic and more environmentally benign than DiEGME.

The biodegradabilities of two of the synthesized FSII's, namely 2,2-dimethyl-1,3-dioxolane-4-methanol (M-1) and 2-methyl-1,3-dioxolane-4-methanol (M-3), and DiEGME were studied and compared. Standard 5-day BOD tests were conducted for all three compounds in an aerobic respirometer (Challenge Environmental Systems) at 20°C and neutral pH. Pure cultures of the bacillus bacteria OR-2A-A were isolated at the Oak Ridge National Laboratories from glycol-contaminated soil obtained from Alaska. The cell growth and decrease in substrate were monitored throughout by extracting samples periodically and analyzing them using a spectrophotometer (Spectronic Instruments) and 6890 GC/5973 MS (Hewlett Packard). Concentrations of 0, 2, 5, 10 and 50 mg/l of substrate were studied.

The oxygen consumption patterns showed similar trends for all three compounds. M1 showed the least oxygen consumption and maximum cell growth. For the concentrations studied, 86-98% of M1 was degraded, whereas only 56-75% of DiEGME and 65-79% of M3 were degraded. The compound 1,3,5-trioxane,2,4,6-trimethyl (paraldehyde) was found in mixture with M-3. Only about 38-58% of paraldehyde was degraded. The half-lives of DiEGME, M1, and M3 were found to be 34-53, 7-20 and 23-69 hours, respectively. Paraldehyde had a higher half-life (>105 hours). Earlier studies indicated the formation of formaldehyde on decomposition of M-3 at mildly acidic conditions. This could be due to the presence of paraldehyde in M-3. Maximum growth and rate of reaction occurred at substrate concentrations between 5 and 10 mg/l.

MODELING EM-ENHANCED AGGREGATE REMEDIATION

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Abstract

A model is presented to help determine if "old contamination" aggregate remediation can be significantly improved by the application of electrokinetics. "Electrokinetics" (EK) is a class of phenomena that can be used in remediation to induce fluid flow, induce ion migration without fluid flow, or induce migration of solid phase particles. However, EK's abilities in all of these areas are reasonably subtle. Electroosmosis (EO), for example, is not capable of replacing pumps under most conditions. Electromigration (EM) or Electrophoresis (EP) are not effective over long distances and Electrolysis (ET) can be a very expensive method of generating acid. One must be selective in identifying opportunities where EK has compelling advantages over competing remediation technologies. One of these opportunities appears to be in the application to aggregate remediation where mass transport rates are constrained by slow intra-aggregate mass transfer.

Aggregate remediation refers to remediation of soils where contamination is sequestered deep within aggregate volume rather than being concentrated on the surface. This is often one of the characteristics of "old contamination" soils (e.g. Brownfield soils) where the soil contamination (Cr, Pb, Cd) has had decades to migrate deep within the solid phase. Thus, when contamination is striped from the aggregate surface by conventional remediation processes, not all of the contaminant burden is removed and given time, the sequestered contamination can recontaminate the soil surface. EM offers the possibility of enhancing the transfer of contaminants from deep within the aggregate matrix to the mobile liquid interface.

To determine if EM can significantly enhance aggregate remediation, one must be able to predict the rates at which aggregate will release sequestered contamination to an aggressive solution in the presence and absence of an applied DC field. For this to be realistic, the prediction should account for the physical and chemical complexity of a real soil. However, the model must not be so complex that it cannot be run using information that is unlikely to be available.

The model presented here is based on the total mass remediated from a soil made up of "M" aggregate compositions of density ρ_m and "N" size fractions of dia. d_n ($W_{m,n}$ mass fractions).

$$M^R(t) = \sum_{m=1}^{M} \sum_{n=1}^{N} \left(\frac{W_{m,n} S_{m,n}(x_i,0)}{\rho_m} - \frac{6 W_{m,n}}{\pi \rho_m d_n^3} \int_{x_i} S_{m,n}(x_i,t)\,dx_i \right)$$

The sequestered contamination burden $S_{m,n}(x_i,t)$ within a particle of size "n" of composition "m" subjected to a DC voltage field $\Psi(x_i)$ is given by solving the following where D^* and E^* are the effective (intra-aggregate) diffusion and ion mobility coefficients.

$$\frac{\partial S_{m,n}(x_i,t)}{\partial t} = D^* \frac{\partial^2 S_{m,n}(x_i,t)}{\partial x_i^2} - E^* \frac{\partial \psi(x_i)}{\partial x_i} \frac{\partial S_{m,n}(x_i,t)}{\partial x_i} \; ; \forall x_i = 1,3; (x_i \geq 0) \in 4\sum_{i=1}^{3} x_i^2 \leq {d_n}^2$$

Although this may look foreboding, it will be illustrated that with appropriate coordinate system orientation and non-dimensional analyses one can reduce this to a set of numerical solutions that allow one to evaluate the potential improvements in removal efficiency when EM is applied.

THE USE OF REGENERATIVE ACTIVATED CARBON FILTRATION FOR WATER TREATMENT

By: Oliver Johnson
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Custom Engineered Systems (CES) Inc. has developed a new water filtration system based on the use of regenerative activated carbon. Activated carbon is a very effective water-purifying agent, but is expensive to replace. CES regenerative filters will provide a revolutionary solution to this problem.

The regenerative filter was created to offset the expense of unloading and shipping spent granular activated carbon back to suppliers for reactivation. Regenerative filter units are loaded with a special blend of granular activated carbon, which will adsorb hazardous organic compounds, chlorine and heavy metals from water. The regenerative filter unit is designed to be regenerated in place and can be configured as modular banks to meet any desired flow rate from 20 to 32,000 gallons per minute.

Regenerative filters can remove both organic and heavy metal contaminants like lead, mercury, cadmium, iron, selenium, aluminum, zinc, arsenic, pesticides, herbicides, PCBs, silver, cobalt, sulfites, chromium, detergents, soaps, fuels, oils, algae, and radioisotopes. During regeneration, trapped organic pollutants are catalytically oxidized into harmless gases and water. Metallic and mineral pollutants are removed using a proprietary charge reversal process. Each filter case can be regenerated in four to six hours.

Activated carbon is usually reactivated using large, high temperature tumble furnaces. In many cases, the reactivated carbon does not retain its original capacity. The CES process will return granular activated carbon to virtually its original capacity an indefinite number of times without changing its virgin pore structure. It can also selectively desorb certain molecules while retaining others. This capability is important in special circumstances, for example: when target effluents are radioactive or loaded with mercury or cyanides.

An afterburner cycle loop is used to catalytically decompose any organic vapor coming off the carbon during regeneration. Hazardous volatile metals and other inorganics are condensed, captured and contained in secure disposal vessels or as a thin film on a disposable liner if desired.

Abstract

THE MECHANICAL SOLUTION TO THE HOG WASTE WATER PROBLEM

By: Oliver Johnson, Custom Engineered Systems - Atlanta, GA

Background:

Animal waste is a growing problem in America. Although the health risks to humans have not been consistently empirically validated nor the ecological threat soundly measured, the absence of alarming hard data should not cause us to abandon conventional wisdom.

A fully grown hog is an eating machine that produces about three gallons of waste per day. This waste is flushed into a lagoon using lagoon water to do the flushing. Over a short period of time, the concentration of ammonia and nitrates becomes so high it will kill most plants and animals. The law requires that land be set aside for growing grass or some other animal feed source using the disease-ridden lagoon water as irrigation. Cows graze on the grass. The problem arises when humans eat the cows which have eaten contaminated grass, and the contamination has gone undetected.

There is another problem with hog lagoons. Since grass will not grow in the winter, getting rid of the excess lagoon water become problematic. During heavy rains, hog farmers get very nervous because they know it is only a matter of time before their lagoons fill and overflow into a stream which feeds into some river. When this occurs, disease spreads down the river through millions of gallons of water which support river fish, which is consumed by humans.

Solutions:

1. Custom Engineered Systems has invented a water purification system capable of processing over a million gallons of hog lagoon water per day, turning it into potable drinking water in just a few minutes. The system disinfects, removes nitrates and 3,000 other pollutants, including heavy metals.

2. Create a water cleaning technology which is economical and compact enough to transport to each farm.

3. Offer a Lagoon cleaning service which can remove pollutants from the bottom and body of water.

NUMERICAL SOLUTION OF LINEAR AND NONLINEAR EQUATIONS IN GROUNDWATER FLOW MODELING

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Numerical methods for temporal integration of large nonlinear problems in groundwater flow must take into account rapid changes in the solution, non-smooth nonlinearities, ill-conditioned Jacobians, and large problem size. Combinations of these effects can cause conventional nonlinear solvers to either fail or return incorrect results. In this talk we will show how numerical methods for nonlinear equations can be adapted to these problems and how the linear equation for the Newton step can be solved efficiently.

This work is being done in collaboration with S. E. Howington, J. H. Schmidt, and A. Stagg from the US Army Waterways Experiment Station, M. D. Tocci from Worcester Polytechnic Institute, and C. T. Miller, G. A. Williams, and C. E. Kees from the University of North Carolina.

KINETIC AND IN SITU FTIR STUDIES OF THE CATALYTIC OXIDATION OF 1,2-DICHLOROBENZENE OVER VANADIA-BASED CATALYSTS

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Flue gas of municipal and medical waste incinerators contains small quantities of polychlorinated dioxins (PCDDs) and furans (PCDFs). The emissions of these highly toxic compounds are closely monitored and regulated. Incinerator units are frequently fitted with V_2O_5/TiO_2 catalysts, which represent state-of-the-art technology for the control of NOx emissions. Field measurements have indicated that these catalysts are also active for the catalytic oxidation of dioxins and furans.

In this work, we have performed detailed kinetic and in situ FTIR studies of the catalytic oxidation of *o*-dichlorobenzene (*o*-DCB) over V_2O_5-based catalysts. This work represents part of our continuing efforts to understand the fundamental chemistry of the oxidation of dioxins over vanadia-based catalysts. *O*-DCB was chosen as the model compound for the more toxic dioxin, due to their structural similarity.

Vanadia was found to be the active site for *o*-DCB oxidation. The turnover frequency was not affected by the vanadia loading in the range studied. The activity however, was affected by the nature of support. The reaction was found to be first order in *o*-DCB and zero order in oxygen under excess oxygen conditions. Finally, a 15% loss in activity was observed after 80 hours on stream in the case of the V_2O_5/Al_2O_3 catalyst.

The in situ FTIR studies on V_2O_5/Al_2O_3 indicated the formation of several adsorbed species on the catalyst surface. The presence of partial oxidation products namely phenolate, maleate and carboxylates was identified. On the contrary, no surface species containing C-Cl bonds were detected suggesting that Cl abstraction is the first step in the activation of *o*-DCB. Furthermore, IR peaks characteristic of ring vibrations were observed suggesting that the aromatic ring remains intact during *o*-DCB adsorption. All these species with the exception of the maleates react with gas phase O_2 at temperatures above 623 K.

Accelerated Solvent Extraction and Gas Chromatography/Mass Spectrometry for Determination of Polycyclic Aromatic Hydrocarbons in Smoked Food Samples

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Polycyclic aromatic hydrocarbons (PAHs) are a major class of environmentally hazardous organic compounds due to their known or suspected carcinogenicity. PAHs are ubiquitous in the environment, largely due to the extensive use of fossil fuels. In addition to a wide distribution of PAHs in air particulate and soil, PAHs are also introduced into waters and marine sediments by storm runoff, factory discharge, and petroleum spills. PAH contamination in foods and the effects on human health have been the subject of major concern. Several sources are responsible for the occurrence of PAHs in foodstuffs: processing of food including smoking and cooking, natural sources, and environmental contamination. Determination of PAHs in biological samples such as foods has traditionally relied on prolonged extraction and clean-up procedures such as Soxhlet extraction and saponification extraction. These procedures are time-consuming and require large quantities of organic solvents which are usually toxic and are expensive to dispose. The continued investigation into alternative methods that are more efficient and generate little additional laboratory wastes has lead to the introduction of supercritical fluid extraction (SFE) and more recently, accelerated solvent extraction (ASE). ASE enhances extraction efficiency by operating automatically at elevated pressure and temperature using small volumes of traditional organic solvents. ASE recoveries of PAHs from several types of environmental samples such as sewage sludge and marine particulate matter have been reported to be comparable with or better than conventional extraction methods. This paper applies ASE to the extraction of PAHs from smoked food samples. Gas chromatography-mass spectrometry was employed to quantify the extracted PAHs. A post-extraction clean up method was also developed to remove high lipid contents present in the ASE extracts. PAH recoveries in the accelerated solvent extraction was investigated followed by determination of PAHs in selected smoked food samples. For recovery studies, fish tissues and fresh ground pork were homogenized and fortified with standard solutions containing 16 PAHs. Aliquots of the spiked samples were then extracted by ASE, and the extracts were treated with sulfuric acid to remove coextracted impurities (lipids) and passed through a florisil column. Using gas chromatography-mass spectrometry as quantitation method, the extraction recoveries of ASE method were found to be comparable with or better than traditional methods. The extraction and quantitation method was then applied to the determination of PAHs in two smoked pork samples and a smoked salmon sample obtained from a local supermarket. Up to 7 PAHs were found to be present at concentrations ranging from 2 to 20 ng per gram wet sample.

HYDRODEHALOGENATION OF 2- AND 3-CARBON HALOGENATED ORGANIC GROUNDWATER CONTAMINANTS USING A PALLADIUM CATALYST AND HYDROGEN GAS

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One percent (w/w) Pd-on-Al_2O_3 and metallic Pd catalysts along with hydrogen gas rapidly hydrodehalogenate commonly found 2 and 3-carbon halogenated groundwater contaminants and result in little or no production of halogenated intermediate compounds. Half life's of 4-6 min were observed for tetrachloroethylene (PCE), trichloroethylene (TCE), cis-, trans-, 1,1-dichlorethylene (DCE), carbon tetrachloride (CT), and 1,2-dibromo-3-chloropropane (DBCP) at ambient temperature and pressure with a catalyst concentration of 0.22g/L. TCE transforms quantitatively (96.9%) to ethane without formation of any detectable chlorinated intermediate compounds using Pd-on-Al_2O_3. With metallic Pd, transient chlorinated intermediates are detected, accounting for 3-4% of the initial TCE at their maximum. This implies a direct conversion of TCE to ethane at the Pd surface, without significant desorption of intermediate compounds. Carbon tetrachloride transforms to methane and ethane, but ethylene, propane, and propylene were also detected. Chloroform is a reactive intermediate and accounts for 20-23% of the initial carbon tetrachloride at its maximum. The formation of C2 and C3 products implies a free radical mechanism. Kinetic models and pathways for TCE, carbon tetrachloride, and chloroform transformation are presented.

TECHNOLOGY INNOVATIONS FOR ENVIRONMENTAL RESTORATION

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At the Savannah River Site (SRS) Environmental Restoration Division (ERD), utilizing technology innovations to accelerate remediation activities while reducing project costs and waste volumes is a high priority. SRS-ER is continually challenged to meet the Accelerated Cleanup Plan requirements to reduce risk, accelerate schedules, and enhance efficiencies by the year 2006. The working target for technology based savings at SRS-ER is currently $300 million over the next twenty years.

Technology innovations such as the Cone Penetrometer Gamma Probe, Fenton's Chemistry, and the GeoSiphon, among others, will allow SRS-ER to achieve the Accelerated Cleanup Plan goals. The Cone Penetrometer Gamma Probe is an in situ site characterization tool that utilizes "direct push technology" to allow for real-time identification of radionuclides in soil and elimination of wastes associated with conventional drilling techniques. In situ chemical oxidation (Fenton's Chemistry) employs injection wells to treat soil and groundwater contaminated by volatile organic compounds (VOCs) and dense non-aqueous phase liquids (DNAPL) by using hydrogen peroxide and other oxidizing agents to convert various organic contaminants into harmless, natural compounds. Another innovative application is the GeoSiphon Cell, which uses granular cast iron in a reductive application on solvents to produce less harmful products such as methane, ethane, ethene, and chloride ions.

These and other SRS technology innovations reduce risk and cost by eliminating or reducing project waste while accelerating remediation schedules.

IN-SITU THERMAL DESORPTION FOR RAPID SOURCE REMOVAL OF CONTAMINATED SOILS

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TerraTherm Environmental Services, Inc. is a wholly owned subsidiary of Shell Technology Ventures, Inc. and was created to develop Shell Oil Company's patented thermal technology systems. TerraTherm provides a unique In Situ Thermal Desorption (ISTD) process designed to remediate a broad range of surficial and deep zones of soil contamination.

The ISTD technology applies heat and vacuum simultaneously to subsurface soils and is remarkably versatile and effective: it can remediate virtually all organic contaminants, including hydrocarbons, manufactured gas plant waste (coal tar), chlorinated solvents, PCBs, pesticides, and dioxins. Unlike fluid injection processes, ISTD is applicable to tight soils, clay layers, or in heterogeneous soils with wide variations in permeability and water content. Because the soil is not disturbed, there is minimal exposure to workers and the public.

With the ISTD process, heat is applied to the soil using thermal conduction only. For ISTD-Thermal Wells, an array of heater/vacuum wells is placed vertically in the ground in triangular patterns. The wells are equipped with high-temperature electric heaters (1700 deg F) and connected to a vacuum blower. As heat is applied and soil temperatures rise, the vaporized products are drawn into the wells by the applied vacuum and are mostly destroyed in situ at the heater well. Produced vapors are treated in a flameless thermal oxidizer and a final carbon bed polishing to remove residual contaminants that have not been destroyed *in-situ*.

The ISTD process is a clean, odorless system that is fast and low-cost. It can be used under roads, foundations and other fixed structures. If required, the thermal wells can be slanted or drilled horizontally. The operations are low profile, quiet, and cause little disruption of adjoining neighborhoods. The ISTD process possesses high removal efficiency because the narrow range of soil thermal conductivity provides excellent sweep efficiency and because its high operating temperature assures complete displacement efficiency of contaminants in the gas phase.

A case study will be reviewed that describes the flexibility and efficiency of this portable technology, and the ability of ISTD to operate under harsh weather conditions as well as in soils containing back-fill debris and tight clay.

THE ISOLATION AND CHARACTERIZATION OF PROPYLENE AND TRIETHYLENE DEGRADING BACTERIA

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Propylene glycol is a major ingredient in airplane wing deicers, which are applied to reduce ice formation during winter months. Triethylene glycol is an anti-corrosion additive used in most deicing fluids. Due to the extended and severe winter months airports in northern climates have accumulated large quantities of these chemicals which are stored in large tank until the spring. Alaskan soil contaminated with these chemicals and samples from North Carolina A&T Hog Lagoon were collected and used as a source of propylene and triethylene- degrading bacteria. Alaskan soil was used in order to isolate bacteria with a high tolerance for high concentrations of deicing agents, and to compare with bacteria not exposed to the chemicals and found in a temperate zone.

We have isolated seven strains of propylene glycol- degrading bacteria and seven strains of triethylene glycol- degrading bacteria. All of the propylene glycol- degrading bacteria were Gram positive bacilli, except for (OR-2AA wd), which was Gram negative. The growth media for the propylene glycol-degrading bacteria had to be supplemented with Peptone Yeast Extract in order to initiate growth. The triethylene glycol- degrading bacteria were gram negative bacilli except for specimen designated as: Sample B (wf), HTEGM(wl), and HTEGM(wt), which were Gram positive bacilli. The growth media for the triethylene glycol -degrading bacteria was supplemented with glucose in order to stimulate growth on triethylene glycol.

This indicates that biodegradation of propylene and triethylene glycol wastemay be treated by proper supplemention of the medium with a primary carbon source.

Mycological Potential for Trichloroethylene Remediation

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Trichloroethylene (TCE) is an aliphatic compound that is widely used as a solvent and degreasing agent. It is also considered a carcinogen that can remain in the natural environment for extensive periods of time. The purpose of this study was to develop an alternative method for remediating TCE by using lignin-degrading fungi. By their non-specific nature, fungi (primarily basidiomycetes or white-rot fungi) are not restricted by the boundaries of most bacteria. The extracelluar systems of these fungi enable them to tolerate higher concentrations of toxic pollutants. Bacteria have primarily done the remediation of this compound. Specifically, strains of methanotropic and psuedomonas species. Meaning these bacteria require an outside source of energy and carbon such as toluene, phenol, or ammonia before breakdown of the desired compound. These substrates required by these bacteria are not environmentally friendly compounds. Therefore, exploring, the use of fungi that have been found to degrade a range of complex contaminates is a positive alternative. The fungal species examined in this study degraded a variety of pollutants by both oxidative and reductive mechanisms. Three specific white-rot fungi were evaluated: Phanerochaete chrysosporium, Trametes versicolor, and Irpex lacteus. The effectiveness of fungal degradation at optimal conditions was determined by Respirometric Analysis in liquid cultures spiked with TCE.

The analysis of O_2 consumption of the fungi revealed TCE had an impact on growth. Degradation of 44% to 35% occurred when 100 ppm and 50 ppm of TCE was applied. An 8 day degradation study was conducted in micrososms by using P. chrysosporium in liquid growth media. In 8 days 59% of TCE was degraded by the fungi.

The partition coefficients (K*p*) for TCE in liquid to soil phases were determined by equilibrium studies resulting from sorption activity. Sorption activity was studied using a sandy clay loam soil and a loam sand amended with a high organic soil. The sorption (soil: sandy and clay loam) can influence TCE retention and volatilization and bioavailability. The K*p* values showed that TCE had a higher affinity for soils with a high organic carbon content. Continuos sorption was observed in the organic carbon amended loamy sand, where as the sandy clay loam quickly reached the equilibrium. This data will be useful in future studies of TCE remediation in soils by White-Rot fungi.

MODELING OF THE EFFECT OF THERMAL IN SITU TECHNOLOGIES ON THE DYNAMICS OF SUBSURFACE MICROORGANISMS

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Soil heating technologies are increasingly being used for the in situ remediation of contaminated subsurface sites with difficult contaminant profiles and site characteristics. These technologies show promise for contaminated soils that have large fractions of dense non-aqueous phase liquids (DNAPL). In the resistive heating technology electrodes are placed in the contaminated site and the voltage increases the subsurface temperature to nearly 100°C to solubilize and oxidize the target contaminants. Typically resistive heating technologies maintain high subsurface temperature for months even after the pollutant removal process is completed. The microbial ecology associated with extensive subsurface heating that results from such heating technologies along with the repopulation of the soils after a heating event is not well understood.

Performing meaningful studies of the effect of heating technologies on the dynamics and activity of soil microorganisms at either lab or pilot scale requires knowledge about the spatial and temporal temperature profiles in the system along with the transport profiles of water and the contaminants. To achieve this our aim is to model a similar scenario using mathematical equations and proper boundary conditions. A computational fluid dynamics (CFD) algorithm is solved to establish temperature and moisture profiles in soil and the cool down period linked with the repopulation of the microbes. The results of this solution are compared to experimental results from a 2-dimensional lab-scale soil resistive heating setup.

Developing A User-Centered Database System for Assessment and Evaluation of Environmental Restoration Technologies

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ABSTRACT

A technology resource review showed that many commercial database systems have been developed which provide valid information on most of the known technologies. A further review of these database systems, also revealed the need for a more comprehensive system that could work as a one-stop restoration "solution shop" for most users. Such a database system is structured to provide any necessary information in the form desired by users whose interests are to find technology solutions to specific problems. A database structure that is user-oriented and solution-driven must, therefore, consider data elements that would assist or lead users to effective solution options, while at the same time providing them information to meaningfully assess and evaluate alternate solutions, given site-specific constraints. A review of the essential design elements for a user-centered and solution-driven database system will be presented.

Development of a Relational Database for Remediation Technologies

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This paper discusses the development of a relational database for environmental technologies used for remediation. In the development, the ability of the information provided by the database to provide assessment information is designed for. A relational database management software which could be used in two major operating systems was chosen. The selection of this particular software for the project will be briefly presented.

To facilitate the access of information from the database the following categories were considered in its design: Media (where contamination is to be remediated); Contaminant Groups (of contaminant to be removed or reduced); and the technologies were grouped into a manageable size. The design of the database system so that the technologies could be assessed in such a way as to guide the user in decision making is presented.

Development of PC-Workstation Cluster for Groundwater Modeling

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This paper describes the development of a workstation/PC cluster for groundwater modeling using MSTS. In the development, a network of computers is used to set-up a system which facilitates data input, simulation execution and visualization, and assessment of simulation results.

MSTS is capable of solving fully coupled equations for conservation of water and air mass, conservation of energy, and conservation of dilute species mass in variably saturated geologic media hence it has a wider applicability. MSTS uses an integrated finite-difference numerical scheme in addition to a Newton-Raphson iteration scheme to solve the coupled equations for water conservation, air conservation, and energy conservation. The fourth governing (set of) equation (dilute species solute mass conservation) is solved sequentially to the coupled governing equations with a direct integrated finite-difference scheme. MSTS is also available free of charge from Pacific Northwest Laboratory funded by the US department of Energy.

Dose Dependent Study of Ethoxyresorufin O-Deethylase (EROD) Activity in Channel Catfish Exposed to River Extracts as a Biomarker of Contamination

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The responses of various xenobiotic-metabolizing enzymes in fish models are rapidly evolving as important biomarker for monitoring unacceptable levels of environmental contaminants. Ethoxyresorufin o-deethylase, a specific cytochrome P450-dependent monooxygenase, is often used as an indicator of polycyclic aromatic hydrocarbon pollution. Ethoxyresorufin o-deethylase is sensitive to inhibition by organophosphates. EROD is located predominantly in the liver. Chemicals other than carbamates and organophosphates that are environmental contaminants can also affect the activity of EROD.

Fish exposed to dichlorvos (DDVP) showed considerable inhibition of brain and liver enzyme activity. The degree of enzyme inhibition was reported to follow a positive correlation with the insecticide concentration and time of exposure. Brain exhibited a higher degree of enzyme inhibition as compared to the liver in Acetylcholinesterase.

The purpose of this study is to investigate the effects of various river sediment extracts on brain, liver, and muscle EROD activity in catfish.

A PRACTICAL APPROACH TO BIOREMEDIATING RESIDENTIAL FUEL OIL SPILLS

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Spills from residential aboveground heating oil tanks (ASTs) can pose unique clean-up problems. Because residential ASTs are usually located adjacent to the house, spills from these tanks can result in a discharge of oil adjacent to and under the building foundation and/or under the building in the crawl space. The presence of heating oil in the surface soils in the crawl space of a house results in unpleasant odors in the living space as well as possible hazardous conditions, both from a health and from a safety standpoint. Remediation of these soils by conventional methods such as excavation are not feasible because of logistically and structural considerations.

Through the application of a bacteria innoclum and nutrients, three such sites in the Piedmont geographical area of North Carolina were remediated to below State cleanup standards. Surface spills ranging 50 to 150 gallons of #2 fuel oil were successfully remediated in six to 12 months for costs averaging between $5,000 and $10,000. The bioremediation systems consisted of an easy to assemble, 0.050 inch slotted Sch. 40 PVC pipe, distribution system manifolded together to single standpipe. At the onset of treatment, bacteria innoclum was generally applied weekly for one month. The number of subsequent treatments was dependent on the aerial extent of the contamination and the initial level of contamination, but never more often than monthly. Follow-up sampling showed that initial Total Petroleum Hydrocarbon levels as high as 3,700 ppm were reduced to below 40 ppm and concentrations as high as 33,000 were reduced to 5,200 ppm before treatment was stopped.

BIOREMEDIATION AND MICROBIAL ECOLOGY

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Although, the microbial ecology of contaminated sites is receiving increased attention, much remains to be done. Fundamental questions such as what are appropriate sample sizes, what is the heterogeneity, what is the diversity, how does the diversity change with contamination, water content, and sediment structure are only now being addressed. Until very recently, these questions could only be addressed using culture techniques. For example, to examine the relative role of lithology and contamination in controlling microbial populations at contaminated sites we have compared patterns of bacterial abundance in close interval sampling (with hundreds of samples) at contaminated and uncontaminated sites. CFU analyses and ^{14}C activity assays have indicated that, in many cases, 1 g sample sizes give equivalent data to sample sizes of 0.1 to 100 g. It appears that the factors controlling subsurface microbial heterogeneity at contaminated and uncontaminated sites of similar geology and geochemistry are very much alike. At both the Dover contaminated sites and at similar uncontaminated sites, Oyster, Va. and Abbott's Pit, Md., sampled as part of the DOE Subsurface Science Program, we have found that in the absence of lithological changes CFU, and total biomass as indicated by lipids, tends to decrease logarithmically from highs at the surface. Geostatistics and constraints analyses applied to the same data have given interpretable results on the scale of heterogeneity (e.g., about 1 m) and the factors controlling the bacterial populations (e.g., water content and phosphorus) in subsurface sediments. Also, at both Dover and Abbott's Pit, an increase in CFU at depth was associated with an increase in grain size. However, culture techniques may miss the majority of the in situ microbial populations. Modern molecular techniques are now allowing us to address these questions more effectively but these techniques are time consuming. They are also difficult to apply to the number of samples that are required to address many of the important questions. However, techniques will be refined and automation will become more common. Thus, the molecular techniques will be able to be combined with standard and novel statistical approaches to address the fundamental questions of microbial ecology at contaminated sites and efficient implementation of bioremediation.

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[1] Oak Ridge National Laboratory is managed by Lockheed Martin Energy Research, for the U.S. Department of Energy under contract DE-AC05-96OR22464.

INNOVATIVE TOOLS TO ASSESS MICROBIAL COMMUNITIES DURING BIOREMEDIATION

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Artificial neural networks (ANNs) were evaluated for assessing changes in microbial communities during bioremediation as evidenced by phospholipid profiles. The ANNs are being applied in an effort to use the microbial membrane lipid profiles data to better define microbial functional groups, metabolic processes, community composition, and potential efficiency of bioremediation. ANNs do not require mechanistic assumptions and are able to analyze non-linear relationships. Different types of ANNs (feed forward and autoassociative) are chosen to reflect the particular purpose of data analysis - inference, description of chemical profiling, or description of association between profile and arbitrary target parameters. Pattern recognition, using associative ANN analyses, was tested with lipid signatures from soil microcosms with and without added heavy metals. In different analysis, lipid signature profile data (up to 86 peaks) were reduced to two sets of variables, 11 and 43, by elimination of rare values and by aggregating peaks. These reduced data sets were used as the input and output nodes in an autoassociatve ANN. The autoassociative ANN architectures were optimized for the number of nodes in the mapping, factor, and demapping layers. Using the optimized architectures, results show ANN methods routinely account for over 90% of variance, comparing favorably with multivariate statistical methods such as factor analysis and multilinear regression. The ANNs documented microbial community shifts with respect to incubation time and metal concentration. In conjunction with the lipid profiles, geochemical parameters, microbial activities, and DNA probe data could be included in the ANN analyses. This should enhance site assessment of microbial community structure and the prediction of the efficacy of treatment as modifying pollutant bioavailability or adding enriched/engineered cultures to the soil remediates metals. The success of this approach is expected to be of particular relevance to monitor and control natural and accelerated bioremediation.

[2]Oak Ridge National Laboratory is managed by Lockheed Martin Energy Research, for the U.S. Department of Energy under contract DE-AC05-96OR22464.

HYDROTREATMENT OF SULFUR-CONTAINING ORGANICS USING HIGH SURFACE AREA MOLYBDENUM NITRIDE CATALYSTS

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Abstract

Since the first reported synthesis of high surface area molybdenum nitride by Volpe and Boudart, high surface area interstitial transition-metal compounds produced by means of temperature programmed reduction (TPR) have found applications as unsupported catalysts in hydrogenation/dehydrogenation reactions, ammonia synthesis/decomposition reactions, isomerization reactions and model petroleum hydrotreatment reactions and also as electrode materials in electrochemical systems.

High surface area molybdenum nitride powder, macrocrystals and nanoparticles and molybdenum metal were synthesized using temperature programmed reduction of molybdenum oxide powder and crystals with reactant feed gases consisting of ammonia and nitrogen/ hydrogen mixtures. The product metal nitrides were passivated in air before characterization. The molybdenum nitride products were characterized using BET surface area analysis, X-ray diffractometry, thermal gravimetric analysis, scanning and transmission electron microscopy and scanning tunneling microscopy. The molybdenum nitride materials were also examined as unsupported catalysts for the hydrodesulfurization (HDS) of thiophene.

Each form of the high surface area molydenum nitride was observed to possess significantly higher activities than common industrial Co-Mo hydrotreatment catalysts for the HDS of thiophene. While in many cases significant increases in catalyst surface area have been demonstrated to improve activity, for molybdenum nitride crystals this result was not observed. In fact, relatively lower surface area molybdenum nitride crystal catalysts (SSA = 44 m^2/g) have been reported by this group to have a greater specific activity than that of the higher surface area molybdenum nitride powder catalysts (SSA = 150 m^2/g) for the hydrodesulfurization of thiophene. The reactivity of the molybdenum-based catalysts for the thiophene desulfurization reaction will be compared with structural characterization data and evaluated with regards to material properties and catalytic performance.

BAROMETRIC PUMPING FOR CHARACTERIZATION AND REMEDIATION

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Passive soil vapor extraction (barometric pumping) has been used as a rapid, interim remediation strategy at a waste site contaminated with chlorinated solvents. Cone penetrometer-installed wells have removed more than 50 pounds of solvent in the first year of operation. The cone penetrometer was used to both characterize the site and install 2"- diameter, vadose zone remediation wells fitted with check valves to enhance the passive removal rate of vapor phase contaminants. The complete vadose zone characterization and remediation system installation at the 3-acre waste site was completed in three weeks.

At the Savannah River Site (SRS), significant fluxes of contaminants out of vadose zone wells have been observed in response to atmospheric pressure drops. The airflow in and out of barometric pumped wells is a result of the difference in pressure between the formation at the screened zone of the well and the atmosphere at the surface. Earlier work confirmed that atmospheric pressure is transmitted through the subsurface but that this energy is damped and delayed when it encounters zones of lower permeability. The delay and attenuation of the pressure signal in the subsurface with respect to the surface pressure produces a pressure differential between the two zones when they are directly connected as by an open well. Airflow through the well is sustained during the period that the surface pressure is different than the pressure in the subsurface zone accessed by the well. If volatile contaminants are present near the well, gas phase contaminants will be removed during periods of flow out of the well and surface air will be injected during periods of flow into the well.

A comprehensive, rapid characterization program was performed at a site with chlorinated solvent contamination in which 26 cone penetrometer test (CPT) pushes were made to collect depth-discrete soil gas information (in addition to standard CPT logs) and directly install 2" diameter, vadose zone extraction wells. The screen intervals were selected in the field based on the CPT data. The wells were fitted with Baroball® valves to begin contaminant extraction by passive soil vapor extraction immediately after installation. Later upgrades to an active extraction system could be made as appropriate in the future. The entire characterization and remediation system installation was completed in three weeks for less than $60K.

In addition to inexpensive remediation applications, estimates of residual contaminant mass and removal rates in the zone of influence of a barometric pumping well can be determined using measured concentration and flow data and multiphase modeling techniques.

POLLUTION PREVENTION BASED ON THE ISO 14000 ENVIRONMENTAL MANAGEMENT STANDARDS

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The ISO 14000 series of standards provides specifications for an Environmental Management System (EMS) as well as guidelines for developing an EMS, environmental labels, environmental auditing, environmental performance evaluation, and life-cycle environmental assessment. The standards were developed by Technical Committee 207 of the International Organization for Standardization and the first two standards (ISO 14001 and 14004) were published in 1996. This paper will briefly discuss the elements of ISO 14001 and will describe how this standard provides direction for industry to initiate and maintain pollution prevention programs.

An EMS based on ISO 14001 permits the management of any organization to exercise control over the impact it's business processes have over the environment. In particular, an EMS motivates the development of a structured approach to setting environmental objectives, finding ways to achieve these objectives, and finally, demonstrating the accomplishment of the objectives. An EMS standard such as ISO 14001 does not specify the minimum levels of environmental performance; instead, it provides a managerial framework for a strategic approach to environmental concerns. More importantly, an EMS does not diminish or replace the need to adhere to environmental regulation; it simply provides a mechanism by which such regulation can be complied with in a proactive manner.

The requirements of ISO 14001 that underscore pollution prevention include the following. First, the standard provides a common language for pollution prevention programs worldwide, for instance, terms such as environment, environmental aspect and impact, environmental management and environmental performance are defined. Second, the standard requires the establishment of a company-wide environmental policy that commits to pollution prevention. Third, organizations are expected to identify environmental impacts of their activities along with the significance of each impact. Finally, there is a requirement to set objectives for pollution control, select appropriate technologies and strategies for pollution abatement, measure the extent to which pollution control strategies have succeeded, monitor degree of compliance to environmental regulations, and document the explicit role of top management in ensuring the effectiveness of the pollution prevention programs.

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EFFECTIVE PROPERTIES OF HETEROGENEOUS ISOTROPIC AQUITARDS

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ABSTRACT

We have developed relations that allow the analysis of saturated steady-state flow through heterogeneous statistically isotropic aquitards. This is done through the concept of the effective hydraulic conductivity of a homogeneous aquitard that is equivalent hydraulically to the original heterogeneous system. By equivalent hydraulic behavior we mean here that the homogeneous aquitard reproduces both the average flux and gradient of the original heterogeneous aquitard.

We consider saturated flow in three-dimensional leaky heterogeneous and statistically isotropic aquitards of finite and uniform thickness L and of infinite horizontal extent. Constant-head conditions apply on the top and bottom of the aquitard. The hydraulic conductivity field $K(\mathbf{x})$ of the aquitard is considered to be lognormally distributed and the spatial autocovariance of this field (taken to be of exponential form) depends only on the separation vector but not on the specific locations of the measurements.

We have performed Monte Carlo simulations to investigate the effect of different ratios of thickness L of aquitard to heterogeneity scale λ and of the variance, σ_Y^2, of $Y(x)=\ln K(x)$. The heterogeneous $Y(x)$-fields were generated with the Turning Bands and the Sequential Gaussian methods. The steady-state, three-dimensional saturated flow equation was solved numerically with a block-centered, seven-point finite difference scheme utilizing a line successive over-relaxation technique. We have found that, for each ratio L/λ and variance of Y, 250 realizations are needed for a good reproduction of the statistics of the hydraulic conductivity field.

We have found that for small ratios of L/λ the arithmetic mean of hydraulic conductivities serves as a good approximation to equivalent homogeneous aquitards. For large ratios ($L/\lambda>4$) the hydraulic behavior of a heterogeneous aquitard can be approximated by that of a homogeneous aquitard with conductivity $K_e = K_g \exp(\sigma_Y^2/6)$, where K_g is the geometric mean of the hydraulic conductivity values. For finite ratios L/λ and for variances of $Y(x)$ up to 7 the effective conductivity is described by the expression $K_e = K_g \exp[\sigma_Y^2(0.5-D)]$, where D is a dimensionless integral, developed in 1996 by Paleologos, Neuman and Tartakovsky for bounded, heterogeneous media.

NONDISPERSIVE LIQUID-LIQUID EXTRACTION OF CADMIUM, COBALT, COPPER AND ZINC BY DEHPA AND STRIPPING WITH EDTA

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Development of technologies for the selective removal of dilute heavy metal contaminants from wastewater continues to be a major challenge. In this study, a liquid-liquid extraction (LLE) procedure was used to study the amount of cadmium, cobalt, copper, and zinc that could be simultaneously extracted from aqueous solution with DEHPA (di(2-ethylhexyl) phosphoric acid). The back-extraction of these metals with EDTA (ethylenediaminetetraacetic acid) was also studied.

Using 0.3 M DEHPA in n-heptane, 25 ppm concentrations of cadmium, cobalt, copper, and zinc were simultaneously extracted at equilibrium. The effect of interference on extraction from the other metal ions was studied. At equilibrium a 0.003 M EDTA solution at pH's of 1.6 to 1.8 was able to back-extract 83%, 70%, 88%, and 54% of cadmium, cobalt, copper, and zinc, respectively. The non-equilibrium extraction and back-extraction behavior was studied using polysulfone hollow fiber membrane modules operated at 100% recycle. The contaminated aqueous feed solution and EDTA solution were passed through the tubeside while DEHPA was passed through the shellside. Under optimum flow rates, 77%, 63%, 93%, and 56% of cadmium, cobalt, copper, and zinc were back-extracted from DEHPA, respectively.

D&D QUANTITY TAKEOFF AND COST MODEL FOR ENVIRONMENTAL REMEDIATION PROJECT

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After the end of the World War II, the United States recognized a need for new facilities to produce uranium metal and other radioactive materials in support of defense activities. Following the recommendation of the Atomic Energy Commission (AEC), a selected number of sites were chosen to embark on Uranium metal production.

Uranium-metal production reached a peak during the height of the cold war in the 1950s and 1960s. However, during the late 1970s, funding was reduced. As a result, supporting activities were reduced as well. By late 1980s, the Department of Energy (DOE) decided to change its mission from Uranium production to environmental restoration. As a result, DOE announced its plan to close some of its production sites, and embark on comprehensive cleanup. One of such production sites is located in Fernald, Ohio.

Decontamination and dismantling activities are currently being undertaken at Fernald site. The scope of work involves approximately 22 complexes as identified in the CRU3 PSR. Included in the scope of work are over 200 buildings consisting of wood, transite, masonry, and pre-engineered buildings. An overall budget of $95 million was planned for the entire Fernald site cleanup.

Accurate budgeting is crucial to the successful completion of any project. Although budgets for most projects are often based on detailed cost estimates, the actual project cost is not definitive until the final completion of the project. This final cost estimate then becomes the basis for evaluating the productivity and cost performance of similar future projects.

This presentation would focus on the development of a cost model for D&D work at Fernald site, using plant 7 as a framework. Three basic fundamental parameters of scope, cost, and schedule were used. The result showed that this model could serve as a basis for estimating, scheduling and budgeting future D&D work. At a level of detail known as the "project", the cost per cubic foot of D&D buildings can be tracked and an average or mean cost can be developed. Also, the model could be used in other DOE cleanup programs to improve cost performance with the ultimate goal of lowering remediation cost.

ESTIMATION OF BIODEGRADATION RATES FOR NATURAL ATTENUATION AT HAZARDOUS WASTE SITES

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Over the past decade, natural attenuation has been accepted as a remediation alternative for contaminated sites. Natural attenuation relies on advection, dispersion, sorption, biotic and abiotic reactions that contribute to decrease both contaminant concentrations and plume size. Numerous studies presented in the general literature have shown that the key mechanism affecting the rate and extent of migration of a contaminant plume is biodegradation since it is the only process that accounts for mass reduction. This paper attempts to address the importance of biodegradation for fuel and chlorinated solvent plumes and to present a comprehensive review of rates of biodegradation obtained from field and laboratory studies. Data from approximately 150 studies are statistically analyzed to determine ranges of biodegradation rates for various contaminants under different redox conditions and to find a probabilistic distribution that fits the observed values. For instance, a review of more than 100 studies has shown first order biodegradation rates of BTEX up to 4.8 day^{-1} under aerobic conditions and up to 4.3 day^{-1} under anaerobic conditions. On the other hand, data from over 50 studies with chlorinated solvents show that the less chlorinated compounds biodegrade with rates lower than 1.96 day^{-1} under aerobic conditions and that highly chlorinated compounds biodegrade with rates up to 1.8 day^{-1} under anoxic environments. The values presented in this study serve as a point of reference to determine the most favorable pathways for biodegradation of BTEX and chlorinated solvent compounds, as well as to have a preliminary approximation of rates of attenuation at sites contaminated with these compounds.

"The Role of Innovative Technology in Achieving DOE's Cleanup Goals"

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Cleanup of the radioactive, chemical, and other hazardous waste left after 50 years of U.S. production of nuclear weapons is the largest environmental management program in the world. Only in the last five years has the Department of Energy (DOE) made substantial progress in systematically defining the technical scope, schedules, life-cycle costs of meeting this challenge, and creating a step-by-step work plan to complete the 353 projects currently comprising the cleanup program.

The Department of Energy, its stakeholders and regulators, Tribal Nations, the Congress, and the American people want to accelerate and finish the job of cleaning up DOE's sites. At the same time, we all continue to share the goal of placing the safety of our workers, our communities, and the environment first among all other priorities.

Innovative technology deployment will play an important role in DOE's ability to meet its cleanup challenges within the budget constraints facing the Environmental Management Program. This paper provides an overview of DOE's Accelerating Cleanup/Paths to Closure document with an emphasis on the role of innovative technology to accelerate cleanup while driving down lifecycle costs.

SELECTIVE CATALYTIC REDUCTION OF NO AND N2O BY PROPYLENE IN EXCESS OXYGEN

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Abstract

The selective catalytic reduction (SCR) of nitrogen oxides (NO_x) by hydrocarbons is an environmental catalytic technology that has recently been proposed because of its advantages over the current NO_x emission control technologies, such as the selective catalytic reduction of NO_x by ammonia (NH_3-SCR) and three way catalysts (TWC). At present, some of the more promising catalysts for commercial development are noble metal-based catalysts, namely platinum and rhodium-based catalysts, and iron-based catalysts, because of their demonstrated hydrocarbon-SCR activity and resistance to the effects of H_2O and SO_2, which are common industrial and automobile components in potential flue gas streams.

Pt-based catalysts are currently the most active of all tested noble metal-based catalysts for the selective catalytic reduction of NO by propylene. This group has reported that Pt-based catalysts show a strong influence of metal loading level and support type on the maximum NO reduction, N_2 selectivity, and C_3H_6 lightoff temperature. Platinum-based catalysts have been reported by this group to exhibit two distinct kinetic regions at temperatures before and after the maximum temperature of nitric oxide reduction and to show a strong correlation between the propylene lightoff temperature and the maximum NO reduction. We have also reported that N_2O is a primary product of reaction over supported platinum catalysts, and that several Pt-based catalysts are inactive for the selective catalytic reduction of N_2O by propylene. Although nitrous oxide is not currently regulated, it is a suspected greenhouse gas.

In this work, several platinum and rhodium-based catalysts supported on alumina (Al_2O_3), silica (SiO_2),and titania (TiO_2) were characterized using BET surface area analysis, hydrogen chemisorption, inductively coupled plasma-optical emission spectroscopy, scanning electron microscopy and kinetic characterization. The effects of catalyst properties such as metal type, loading, and support type, on activity for the selective catalytic reduction of NO and N_2O by propylene will be discussed.

Electrokinetically Enhanced Reduction of Cr(VI) in Porous Media

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Heavy metals in soil and groundwater supplies present an on-going threat to the environment. These metals or contaminants may affect humans and adversely affect the soil and groundwater supplies; thereby, threatening the survival of a variety of plants and animals. Current research suggest that the in-situ stabilization of some heavy metals may be a more viable treatment alternative to many commonly practiced above-ground technologies.

This study has focused on the enhanced electrochemical stabilization or containment of hexavalent chromium in porous media. Electrochemical containment is considered an alternative to treatment to processes which may require additional ex-situ technology to extract heavy metals from contaminated soils. The fundamental processes required for the reduction of hexavalent chromium, Cr(VI), to trivalent chromium, Cr(III), by the introduction of ferrous iron, Fe(II), through the electrokinetic process has been studied. Fe(II) was allowed to migrate electrokinetically into the contaminated samples; thereby, interacting with and reducing Cr(VI) to its less toxic and less mobile species of Cr(III). Once reduced, Cr(III) is expected to become readily adsorbed onto the soil matrix. The retention of Cr(III) within the porous medium provides an intermediary treatment phase for the remediation of chromium. The three types of porous media used during this study included kaolinite-clay, non-reactive glass beads, and a laboratory-prepared "field-simulated" specimen.

Using the results obtained from the Cr(VI) reduction study, a model to estimate the final concentrations and form of the reduced chromium species will be proposed. The proposed method will employ the fundamentals of the Nernst equation by taking into account the relationship between the concentrations of the oxidized and the reduced species, varying soil potentials, and some properties of the contaminated porous medium. Use of this method is expected to assist in the approximation some experimental parameters, including:

- The concentration of Fe(II) to electrochemically reduce Cr(VI) to Cr(III);
- The rate of application required to introduce Fe(II) into soil medium; and
- The duration for the complete reduction of Cr(VI) and the adsorption of Cr(III) to occur.

The results obtained suggest that Cr(VI) can effectively be reduced to Cr(III) in soils via electrokinetic applications. Within the range of this study, a reasonable estimate for the concentration of Cr(III) is obtained as a function of varying soil potentials. Overall, the results obtained suggest that containment may be a promising in-situ alternative for the treatment of heavy metals.

NEW PCB REGULATIONS CUT ON-SITE CLEAN-UP COSTS

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The US EPA has finalized new regulations for Polychlorinated Biphenyl (PCB) disposal under 40 CFR 750 and 761, published in the June 29, 1998 Federal Register. These regulations allow an option for "Self-Implementing On-Site Cleanup and Disposal of PCB Remediation Waste". Under this new regulation, the first option for site cleanup allows "Any person cleaning up bulk PCB remediation waste on-site or using a soil washing process may do so without EPA approval..." subject to certain terms and conditions.

The new regulations cut the cost of implementation of mobile on-site soil washing technology, allowing site owners to more effectively clean their sites. Terra-Kleen, the only soil washing technology with a nationwide commercial operating permit issued by US EPA for on-site PCB processing, provided a working model for EPA's rule change.

Terra-Kleen will discuss the new regulations along with a presentation of two case studies; 1) the recent site clean-up 10,000 tons of PCB and Trichloroethlylene contaminated soil at Cape Canaveral Air Force Station, and 2) the treatment of PCB contaminated low-level radioactive wastes at Fernald, Ohio.

COMPARATIVE EFFECTS OF PH ON MACROPHYTE GROWTH SUCCESS IN A RESTORED WETLAND

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Water chemistry variables, particularly pH, play a key role in controlling plant growth in aquatic ecosystems. In establishing successful phytoremediation programs, plant primary production and growth cost-minimization are important project goals. Information basic to achieving these goals includes not only determining how well a plant species can degrade or concentrate a contaminant, but also whether the plant will thrive under the environmental conditions at a site.

This project is addressing aquatic plant growth potential in a restored wetland, Lost Lake, at the Savannah River Site. Prior to restoration this wetland received contaminant inflow including heavy metals, uranium, TCE, and other solvents. Following cleanup, aquatic species were transplanted, however sharp differences existed between plant growth success in the restored wetland versus similar wetland plant community control sites. A major water chemistry difference between the restored and control sites was pH. Since many of the plant species in these Carolina bay wetlands are considered to be acidophilic, the basic pH ranges detected in Lost Lake (>9.0 at some stations) may be affecting aquatic plant regrowth. However, other factors including substrate, hydroperiod, and potential contaminant inflow could also play a role.

To investigate the role of pH in controlling aquatic plant community success, microcosms were established in Lost Lake with different pH and substrate treatments. Healthy plants, *Brasenia schreberi*, from a control site, Flamingo bay, were transplanted into the different pH treatments and controls. Ambient Lost Lake water was used in each microcosm and its pH was adjusted using sodium hydroxide and / or sulfuric acid. *B. schreberi* was selected as the test species not primarily with respect to its potential as a phytoremediation species, but rather due to its relative abundance differences between the two bays. The primary objective was to better isolate the effects of pH as a controlling variable for aquatic macrophyte regrowth in a previously impacted wetland. Implications concerning potential use of aquatic plants in phytoremediation and their growth success in similar habitats could then better be assessed.

Program: Getting Undergraduate Students Interested in Science, Engineering and Math

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The LIFE Scholars Program started at Xavier University in 1993 through funding from the Department of Energy. LIFE is an acronym for Living Intelligently to Foster Earthcare. The goal of the program is to encourage students to pursue environmental careers and to become environmental stewards in whatever career they choose. Students are selected on the basis of their academic performance and interest in the environment and are not restricted to any major. In addition to structured mentoring, students are exposed to research projects as early as their freshman year and work closely with a faculty mentor. Field trips and seminars designed to heighten their interest also enhance the undergraduate experience of these scholars. Scheduled activities on campus provide a venue for highlighting scholarsí achievements. A summary of the program to date will be presented, as will various research projects in which these scholars are involved.

VOLATILE LOSSES AND GLOBAL(?) REDISTRIBUTION OF PCBS DURING SOIL REMEDIATION

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Recent research by the Environmental Research Center and the University at Albany School of Public Health indicates PCBs readily volatilize during evaporative losses of water. These findings suggest significant quantities of organic contaminants may be released to the atmosphere during remedial measures involving excavation, dredging, dewatering and drying of contaminated solids.

Laboratory experiments conducted by the Environmental Research Center on PCB-contaminated sediments collected from New York Superfund sites and air dried indicate 14-23% of the total PCB concentration can be lost through volatilization at ambient temperatures and relative humidity. Rewetting the dried sediment resulted in an additional 7.5% loss. Volatile losses of PCBs as high as 74-76% occurred in sediment samples suspended in water which were allowed to evaporate over a 7 day period. The lower and ortho chlorinated congeners volatilized preferentially and the loss was directly correlated to the evaporative loss of water.

These results have implications on the handling and remediation of PCB-contaminated sediments with specific emphasis on the evaporative loss of water. Volatile losses from activities involving dredging, dewatering and other remedial technologies (low temperature thermal desorption, aerobic biodegradation, lime solidification, biopiles and others) may result in the global redistribution of PCBs and other organic contaminants.

DEGRADATION OF PCBS, AND OTHER CHLORINATED AND NON-CHLORINATED CONTAMINANTS BY ELECTROCHEMICAL PEROXIDATION

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Laboratory and pilot-scale testing of the Electrochemical Peroxidation Process (ECP) have been carried out by the Environmental Research Center on various aqueous systems and slurries contaminated with polychlorinated biphenyls (PCBs), and other chlorinated and non-chlorinated contaminants. The aqueous systems and slurries tested included water and slurries from a subsurface storage tank (SST) at a New York State Superfund Site contaminated with chlorinated solvents and PCBs, groundwater and sediment contaminated with gasoline, and groundwater contaminated with chlorinated solvents. The water from the SST was also subjected to pilot-scale testing involving about 200 liters of liquid.

The ECP process utilizes a small electric current to enhance Fenton's Reagent reactions. Sacrificial steel electrodes serve as the iron source and the current allows recycling of dissolved iron by electrochemical reduction.

Laboratory testing of ECP on 500 mls of the SST water and slurry containing a small amount (<1%) of organic sludge resulted in PCB reductions of 97.2 and 68.2%, respectively. Solvent degradation of the SST contents yielded greater than 94% degradation for chloroethane, dichloromethane, 1,1-dichloroethane, 1,1,1-trichloroethane, and acetone in both water and slurry. Pilot tests conducted on 200 liters of SST water resulted in 87.9 and 85.2% degradation of PCBs in duplicate treatments.

Laboratory testing of ECP on groundwater and sediment contaminated by gasoline from the Onondaga Nation located near Syracuse, N.Y., resulted in the reduction of MTBE, benzene, ethylbenzene, toluene and total xylenes to non-detect levels after two treatments.

Concentrations of trichloroethene (TCE), perchloroethene (PCE), and 1,1,2,2 tetrachloroethane (TCEA) in contaminated groundwater from the Massachusetts Military Reservation were reduced by 95%, 97.9%, and 65.3%, respectively. Other groundwater from the Reservation treated by ECP showed a 95-98.1% reduction in ethylene dibromide (EDB) and 100% degradation of benzene and xylene.

Future work will focus on pilot scale applications. A continuous flow ECP treatment system has been designed and constructed to treat contaminated liquids, and an in-situ ECP system has been designed.

NON-THERMAL PLASMA DISCHARGE FOR EFFECTIVE NOX REMOVAL

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The threat posed to the environment by NOx is serious and far-reaching. The compound most often directly released, nitric oxide or NO, is detrimental to plants and animals and when bombarded by UV radiation reacts with oxygen to form the components of photochemical smog. In the United States alone, millions of metric tons of NO are released into the atmosphere each year. Most of the NO emissions are from stationary sources such as coal fired power plants. Exhaust from diesel driven equipment at military installations makes up a significant portion of NO emissions and munitions disposal techniques currently being considered by the Air Force will further contribute to the mounting NOx problem.

Since NO is formed in the combustion process from both nitrogen in the air (thermal NOx) and nitrogen bound in the fuel (fuel NOx), many control processes have focused on modifying the combustion process. Techniques such as staged combustion and gas recirculation have been somewhat effective; however, because they usually reduce combustion efficiency and do not adequately reduce the NO concentration, post combustion removal processes are currently being considered. The most widely used post combustion treatment is selective catalytic reduction or SCR. The performance of SCR devices is often limited due to the presence of particulate matter in the gas stream that contaminates the catalyst. Other methods such as selective non-catalytic reduction, SNCR, and electron beam injection are equally limited due to the high temperatures required for SNCR (900 to 1100 C) and the high cost of electron beam injection.

In this paper the experimental results of NOx removal using non-thermal plasma discharge as a post-combustion NO removal technology are presented. With this technique an electric field is utilized to produce high energy electrons in the gas stream while leaving the bulk temperature of the gas unchanged. The high energy electrons serve to generate reactive species such as O, OH, and HO2 that remove the NO through subsequent reactions. The specific device utilized in the experiments is a double dielectric barrier discharge (DDBD), meaning the discharge is sustained between two dielectric surfaces that are backed by conductors. An ac voltage is applied between the electrodes resulting in a series of short duration microdischarges that process the gas. Within the microdischarges the ratio of the electric field (E) to the number density of the gas (N) is rather large, producing electron energies well suited for excitation and dissociation of molecular gases.