

ANAEROBIC/AEROBIC TREATMENT OF HAZARDOUS WASTE LEACHATE

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In the normal operation of a landfill a liquid effluent, leachate, is generated from incorporated liquids mixed with soluble materials disposed within each trench, and rainwater that infiltrates and percolates through these soluble materials. The wastes within a hazardous waste landfill may vary widely from trench to trench thus generating a highly variable composition leachate that is frequently resistant to conventional aerobic biological treatment. Though this hazardous waste leachate has been commonly disposed of by injection on deep disposal wells, the United States Environmental Protection Agency (U.S. EPA) has indicated that this practice may be banned in the near future. In response, Chemical Waste Management, Port Arthur (CWM-PA), has joined with the Gulf Coast Hazardous Substance Research Center (GCHSRC) on a joint project to evaluate anaerobic/aerobic biological treatment of the hazardous waste leachate generated at the Chemical Waste Management, Port Arthur closed landfill. The ongoing anaerobic treatment phase of the project is using a reactor with granular activated carbon (GAC) as a support media. The use of GAC has proven effective in treating synthetic toxic wastes and specific wastes, such as the work of Suidan at the University of Illinois on coal gasification and phenolic wastes. Because the effluent from an anaerobic process is not suited for discharge to a receiving water, an aerobic process, initially using sequencing batch reactors, will be used to provide the final polishing before discharge.

ANAEROBIC DEGRADATION OF PHENOL AND BIOREGENERATION OF GRANULAR ACTIVATED CARBON

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This research evaluates the anaerobic treatment of phenol enhanced by the synergistic effects of granular activated carbon (GAC) on anaerobic microbial

degradation. The bioregeneration of the GAC during the anaerobic degradation of the adsorbed phenol also was assessed. GAC was saturated with radiolabelled phenol at a concentration of 125 mg/L and placed in a glass column. The GAC was seeded with acclimated bacteria and digested sludge. A liquid stream containing non-radiolabelled phenol at the equilibrium concentration was recirculated continuously. Radiolabelled phenol was used to facilitate the development of a mass balance of the phenol and degradation products. Analytical techniques were developed for this study and included: autoradiography of GAC samples, specimen preparation for electron microscopy, and protocols to detect and quantify radiolabelled gases produced in the laboratory-scale anaerobic fluidized bed reactors.

Electron microscopy indicated that the microorganisms were growing both attached to the GAC surface and suspended within the GAC in the form of pellets. The attached bacteria were predominantly of the filamentous and coccus type. Microbial activity, gas production, was noted approximately seven days after inoculating the GAC equilibrated with radiolabelled phenol. Microbial degradation of the adsorbed radiolabelled phenol was verified by the production of radiolabelled methane and radiolabelled carbon dioxide when the column was being continuously fed with nonradiolabelled phenol (Phase I) as well as when no phenol was introduced into the column (Phase II). At 1,200 hours, the calculated bioregeneration rate was at approximately 1 percent of the total adsorbed phenol per day. Efforts are continuing to better quantify bioregeneration rates and correlate bioregeneration with the energy of adsorption of different compounds.

APPLICATION OF MICROWAVE HEATING TECHNIQUES TO THE DETOXIFICATION OF CONTAMINATED SOILS

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A study is being conducted to determine the effectiveness of using microwave energy to heat contaminated soils in order to remove or otherwise destroy toxic compounds that are present in the soil. To increase the effective vapor pressure of the contaminants, which will enhance removal by vaporization, the soil is heated in a vacuum chamber. Heating of solid material in a vacuum chamber is difficult by conventional heating methods since normal convective heating is impossible in the absence of air. This disadvantage is overcome by microwave heating, since microwave energy is transferred to the soil sample equally with or without the presence of air. Contaminates thus removed are absorbed by activated charcoal which can be removed to an offsite commercial

facility for regeneration. The advantage of this method of treatment is that soils can be decontaminated onsite while final hazardous compound destruction is done offsite.

BIODEGRADATION OF MULTICOMPONENT HAZARDOUS SUBSTRATES

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This research evaluated kinetic parameters for a pulse-fed batch reactor that contains a multicomponent substrate media. Glucose, phenol, and pentachlorophenol (PCP) were chosen as the carbon sources because these substrates are very common constituents in industrial waste facilities that have petrochemical waste as the primary influent. A mixture of these three constituents represents a non-inhibitory substrate (glucose), a somewhat inhibitory substrate (phenol), and a very inhibitory substrate (PCP). Two techniques were used to obtain kinetic coefficients. Long-term kinetic studies in the batch reactors were used to evaluate cell growth and substrate utilization which also yielded information on the pollutant's total residence time in the reactor. From these experiments glucose removal is zero-order with respect to substrate concentration whose biodegradation follows typical Monod kinetics. After significant removal of glucose, phenol removal was initiated followed by pentachlorophenol removal. The initial rate method eliminated any possible lag phase that may have occurred in the long-term studies and allowed extrapolation of kinetic coefficients for cell growth and substrate utilization over short duration batch experiments. This method found the maximum specific growth rate (μ_{\max}) for glucose to be 0.45 h^{-1} . Phenol degradation follows Monod kinetics in the non-inhibitory range ($< 80 \text{ mg/l}$) with a μ_{\max} of 0.56 h^{-1} , but PCP is very inhibitory with $\mu_{\max} = 0.03 \text{ h}^{-1}$. When glucose and phenol are present and phenol concentration lies in a non-inhibitory range, Monod kinetics are exhibited. However, when glucose and phenol are present and phenol is in an inhibitory range, substrate inhibition (Haldane) kinetics are observed.

BIOREACTOR DEVELOPMENT FOR THE GROWTH OF THE WHITE ROT FUNGUS *PHANEROCHAETE CHRYSOSPORIUM* AND THE DEGRADATION OF ORGANIC POLLUTANTS

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Phanerochaete chrysosporium is a white rot fungus which can attach and in

some cases, mineralize a wide variety of persistent organic pollutants including polyaromatic hydrocarbons and PCBs. The ability of *P. chrysosporium* to degrade a wide spectrum of compounds is related to the production of ligninases and other extracellular oxidative enzymes. However, these degradative enzymes are not synthesized in conventional large-scale bioreactors, hindering efforts to exploit *P. chrysosporium* for waste treatment. The production of two key enzymes, ligninase and Mn-dependent peroxidase by free and immobilized cells was investigated. Although good production of ligninases was obtained in shake flask cultures, scale-up is hindered by the extreme sensitivity of the cells to liquid shear. Therefore, immobilization was employed to prevent cell damage. Four immobilization methods were used: nylon pads, Ca²⁺ alginate beads, diatomaceous earth, and polyurethane foam. Significant differences in cell growth, and the pattern of enzyme production were observed. When anthracene was used as a model organic pollutant the pattern of enzyme activities paralleled the extent of mineralization.

CHARACTERIZATION OF MUNICIPAL WASTE INCINERATOR FLY-ASH TO IDENTIFY MECHANISM OF DIOXIN FORMATION

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The formation of chlorinated dibenzo-*p*-dioxins in municipal waste incinerator fly-ash may be catalyzed by some component of the fly-ash itself. We have collected over a dozen of fly-ash samples from around the country and are currently performing physical and chemical analyses. The data presented include: pore size distributions by mercury porosimetry; surface areas by nitrogen B.E.T.; electron micrographs; surface chemical analysis by X-ray emission spectra; bulk chemical analysis by atomic absorption; and surface acidity by titration. These characteristics will be correlated with the dioxin content to help identify the catalytically active species.

CHEMICAL OXIDATION OF WOODTREATING WASTE

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The present research concerns the detoxification of pentachlorophenol and

creosote by chemical oxidation using ozone and/or hydrogen peroxide as oxidizing agents. The main goal is to develop an effective scheme for treatment of wood preserving facilities, soils, and ground water contaminated by the hazardous pollutants.

Experiments were conducted in a batch, stirred-tank reactor to determine the feasibility of the oxidation process. In aqueous solutions containing dissolved ozone, the rates of depletion of ozone were nearly identical in the reactor with or without suspended sands. These results indicate that ozone is not reactive with the lean sands. On the other hand, the rate of depletion of ozone was much faster because of additional ozonation reaction if the soils were contaminated with pentachlorophenol. Therefore, the experimental results prove that the contaminated soils are amenable to treatment by the oxidation process.

A stopped-flow spectrophotometer system is being utilized to determine the reaction kinetics and optimum conditions for the oxidation reactions. Products of the reactions will be identified using a gas chromatograph.

DECISION ANALYSIS: PHYSICAL/CHEMICAL TECHNOLOGIES FOR AQUEOUS ORGANIC HAZARDOUS WASTES

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Two treatment technologies for removing volatile organics from water are stripping and carbon adsorption. Since stripping causes air pollution, three treatment schemes were considered in this research: stripping, stripping with gas phase adsorption, and liquid phase adsorption. The research was undertaken to simplify choices among these options.

The specific eight compounds chosen for study included: benzene, chloroform, trichloroethylene, dibromochloropropane, phenol, 1,1-dichloroethane, 1,2-dichloroethane, and methyl tertiary-butyl ether. Mixtures also were considered.

Mathematical models describing the technical behavior of each option were combined with capital and operating costs. A stripping model was written to run on the Macintosh computer. Gas adsorbers to treat stripping tower off-gases were designed in the assumption that equilibrium is achieved (since gas adsorption is rapid). Stripper off-gases were considered to be heated to reduce the humidity. For liquid phase adsorption, a multicomponent plug flow homogeneous surface diffusion model was used to predict the effluent concentration profile.

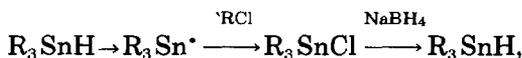
The results show that, when feasible, stripping alone is always the cheapest option; stripping was found to be feasible when the Henry constant exceeded $0.013 \text{ m}^3 \text{ liquid/m}^3 \text{ air}$. An exciting result is the development of a simple guideline for determining when stripping with gas phase adsorption is preferable to liquid phase adsorption. The guideline is based on the ratio of the carbon loading from gas phase adsorption to that from liquid phase adsorption and reflects all the critical design parameters for both options; the stripping factor, Henry's constant, liquid phase influent concentration, adsorption capacities in both phases, and costs.

DESTRUCTION OF CHLORINATED AROMATIC, OLEFINIC, AND ALIPHATIC MOLECULES USING A METAL CATALYZED NaBH_4 REDUCTION WITH PEG/KOH OR TEG/KOH

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The destruction of polychlorobiphenyls (PCBs) in hot KOH/polyethyleneglycol (PEG) media was developed by General Electric and has subsequently been studied at the Cincinnati EPA Laboratories by Kornel et al. Tetraethyleneglycol (TEG)/KOH media have been most recently found advantageous. However, some aliphatic and olefinic chloro compounds are not readily dechlorinated in these systems. In an effort to develop a single dechlorinating (reducing) medium to destroy aromatic, olefinic, and aliphatic chlorocarbons simultaneously, we have begun to investigate NaBH_4 /PEG/KOH and NaBH_4 /TEG/KOH systems. The reducing ability of BH_4^- in these media is complementary to PEG/KOH (or TEG/KOH). Furthermore, the use of trialkyltin hydrides, R_3SnH , as catalysts in the NaBH_4 reduction cycle has been postulated. In the presence of a radical initiator trialkyltin radicals, $\text{R}_3\text{Sn}^\cdot$, are formed which, in turn, abstract chlorine atoms from aliphatic and olefinic carbons to give R_3SnCl . The resulting organic radicals, R^\cdot , react with more R_3SnH to give $\text{RH} + \text{R}_3\text{Sn}^\cdot$. This cycle occurs as a chain process which would stoichiometrically consume R_3SnH as R_3SnCl . However, NaBH_4 reduces R_3SnCl back to R_3SnH *in situ*. Thus, the catalytic cycle involves



where NaBH_4 is stoichiometrically consumed. We have preliminary evidence that NaBH_4 /TEG/KOH is a stronger reducing medium than TEG/KOH, even

when tin hydride is not present. Since NaBH_4 is stable in strongly basic aqueous media, it is hoped that $\text{NaBH}_4/\text{TEG}/\text{KOH}$ aqueous or organic systems can be developed for the destruction of pesticides such as mirex, dieldrin, aldrin, etc. in addition to aromatics such as pentachlorophenol, PCBs, and other materials which might be found in the field. A single reactive solution which works rapidly at fairly low temperatures (below reflux) is one goal of this study.

DESTRUCTION OF TOXIC ORGANIC MATERIALS AND SLUDGES BY SUPERCRITICAL WATER OXIDATION

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The growing quantities of toxic wastewaters and sludges, particularly as guidelines become more stringent, require greater technical attention and more innovative treatment processes. Supercritical water oxidation (SCWO) is a new process that has considerable potential to destroy hazardous organic compounds in wastewaters and convert sludges into harmless ash.

The objective of this research effort was to evaluate, design, construct, and utilize a high-pressure, high-temperature microreactor system capable of conducting batch-type SCWO experiments.

A novel SCWO microreactor system was built to investigate the destruction efficiency for a number of toxic organic compounds, and evaluate the destruction and volume reduction of waste treatment plant sludges. This reactor system is capable of accepting either liquid or sludge samples and operating over a wide range of subcritical and supercritical water conditions (up to 550°C and 6,000 psig or 420 bar). Either oxygen gas or hydrogen peroxide can be used as the oxidant.

Typical compounds tested were *p*-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,4-dinitrotoluene, ethylene glycol, and diethylene glycol. Under the conditions of these tests, removal of 99.999 percent were achieved for 2,4-dichlorophenol and greater than 99.5 percent for other compounds. Efficiency measurements were limited by the resolution of the analytical techniques.

Sludges were readily reduced to ash and the removal of the chemical oxygen demand was subject to temperature and residence time. The transformation of organic material to volatile acids, primarily acetic acid, controlled to total reduction in chemical oxygen demand.

DETOXIFICATION OF POLYHALOAROMATICS VIA FLUOROALKOXYLATION TECHNOLOGY

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The goal of this study is to define the chemical reaction parameters necessary to remove one or more halo groups from polyhaloaromatics using the well-documented fluoroalkoxy substitution reaction whereby halo groups in a polyhaloaromatic are removed and fluoroalkoxy groups are substituted in their place. A series of model polyhaloaromatics are being subjected to the following studies: (1) homogeneous reaction conditions (typical laboratory-scale studies to define the chemical reaction); (2) phase-transfer conditions (heterogeneous mixture under pseudo-environmental conditions); (3) environmental sample conditions (oil-based and/or soil-solid samples); and (4) biological activity studies in order to make toxicity and mutagenicity comparisons between the polyhaloaromatics and the fluoroalkoxy products. Part 1 has been completed for the following model compounds: the 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzenes; the 1,2,3,4- and 1,2,4,5-tetrachlorobenzenes; pentachlorobenzene; hexachlorobenzene; and the dibromo- and difluorobiphenyls. In all cases, reaction parameters have been determined and optimized for converting all of the polychloroaromatic to mixtures of chloro-fluoroalkoxy substituted products. These optimum conditions will be used for the studies in Parts 2 and 3 — i.e., to determine the efficacy of the dechlorination/fluoroalkoxylation reaction of the model polychloroaromatics as pseudo-environmental and environmental samples. Biological activity screens (an *in vitro* human skin cells test and the Ames test) have been developed for use with samples generated from the reaction chemistry studies in Parts 2 and 3.

DEVELOPMENT OF BIOREACTORS FOR THE DESTRUCTION OF CHLORINATED SOLVENTS

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Aerobic bioreactors for the removal of chlorinated solvents in groundwaters are a promising alternative to conventional treatment methods. Chloroform, 1,2-dichloroethane, and trichloroethylene (TCE), for example, are degraded co-metabolically at concentrations of 1 to 1,000 $\mu\text{g/L}$ by certain heterotrophic bacteria, yielding innocuous end products. The optimal reactor design is achieved by proper matching of microorganisms to contaminants, immobiliz-

ing the microorganisms in the reactor, and establishing favorable environmental conditions for maximum degradation rates. Degradation by co-metabolism, in which the organism requires a supplemental growth substrate, necessitates consideration of intermittent versus continuous substrate introduction for maintaining reactor biomass and degradative enzyme activity.

Results and methodology for the screening of numerous culture/substrate combinations are presented as the initial step in the development of a chlorinated solvent bioreactor. Mixed cultures of mono-aromatic degrading bacteria were acclimated with phenol, cresols, and toluene and screened in batch tests for their ability to degrade TCE. These tests were conducted in sealed vials using ^{14}C -radiolabeled TCE and analyzed by liquids scintillation counting. TCE degradation rates and the fractional conversion of TCE carbon to cell mass, carbon dioxide, and undegraded metabolites were measured for the various combinations of organisms and growth substrates.

Preliminary data also will be presented for removal of TCE across a continuous flow column using the most promising organisms. Ultimately, several columns will be in operation to test multiple organism, support media, and reactor configuration combinations. The goal is identification of at least one organism/reactor combination worthy of additional study on the pilot-scale.

DISPOSAL AND DETOXIFICATION OF HALOGENATED TOXICS

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Currently, we are investigating a number of methods for disposal and detoxification of halogenated compounds such as pentachlorophenol (PCP) and polychlorinated biphenyls (PCBs). These include solidification/stabilization (S/S) and electrochemical and photomicroelectrochemical techniques in conjunction with solubilization in organized media such as micellar systems and microemulsions. For PCBs, our main interest is in the PCBs which are present in the oil. PCB-contaminated oil could be used to prepare the oil/water microemulsion in which detoxification can be performed. Also, we are studying extraction of PCBs from oil to micellar solution and other homogeneous solvents. The extracted PCBs can be detoxified by electrochemical and photomicroelectrochemical techniques. We will present results of our work while eval-

uating various techniques that we have investigated. PCP solubilized in micelles and microemulsions and several homogeneous media can be detoxified photomicroelectrochemically.

ELECTROKINETIC DECONTAMINATION OF SOILS

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The purpose of electrokinetic treatment of soils is to aid in the recovery of heavy metals and other chemicals from contaminated soils. The process involves placing electrodes into subsurface wells and passing an electric current through the soil between the electrodes. Water and heavy metals will flow toward the negatively charged electrode, where the chemicals can be collected and removed. The technology is particularly attractive for silt- and clay-rich soils (which are common along the Gulf Coast) because, for such soils, electric currents are far more efficient in driving water and chemical flow than conventional pumping of water from wells.

Several laboratory experiments were performed on samples of kaolinitic soil that were "contaminated" with $\text{Cu}(\text{NO}_3)_2$. Tests were performed over a range in concentration of 0–320 mg/L Cu^{2+} and a voltage of 0–5 V. The amount of copper recovered from the negatively-charged reservoir (cathode) was very low. However, at the completion of the tests, the soil columns were sectioned and a large accumulation of Cu^{2+} was found in the soil adjacent to the cathode reservoir. Copper was transported toward the cathode, but, because of high pH in the soil near the cathode, copper was precipitated and failed to enter the reservoir in significant quantities.

Because there was transport of copper within the soil and significant concentration of copper near the cathode, the process was found to have excellent promise as a remediation technique. Future efforts will be directed toward buffering the pH of the soil in the cathode regions so that heavy metals will flow into the cathode reservoir, where they can be removed.

ENHANCEMENT OF SOLVENT INCINERATION KINETICS

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Incineration is an effective method for destroying certain hazardous wastes. Solvents and other hazardous liquids that are sprayed into an incinerator evap-

orate, mix with air, and then are oxidized. The kinetics of such oxidation reactions are important to the final percent destruction achieved at any given time and temperature in the incinerator.

This research project investigates the effects of certain additives, namely hydrogen peroxide (H_2O_2) and ozone (O_3), on the kinetics of oxidation of certain solvent vapors in the 500 to 700°C range. Experimental equipment has been assembled and operated to test the percent destruction of heptane vapors in an externally heated quartz tube as a function of temperature, residence time, and additive injection rates.

Over the past few months, experimental problems have been overcome, and data are being taken for the heptane-in-air/ H_2O_2 system. Initial results show a marked increase in oxidation of heptane with the presence of less-than-stoichiometric amounts of H_2O_2 . Specifically, based on limited data, heptane destruction (at 550°C and 0.5 seconds) has been observed to increase from near zero (with no H_2O_2) to the 15 to 20 percent range upon addition of H_2O_2 at molar ratios of 1:10 (H_2O_2 /heptane). At 650°C and 0.9 seconds, heptane destruction increases from 28 percent (no H_2O_2) to 50 percent (H_2O_2 :heptane = 1:2.5). Furthermore, several hydrocarbon intermediates are produced as well as significant quantities of carbon monoxide. Kinetic models to describe the system are being developed.

EVALUATION OF NON-TOXIC ORGANIC SOLVENTS IN THE METAL FINISHING INDUSTRY

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The use of various organic solvents for cleaning/degreasing operations in the metal finishing industry is subject to a myriad of environmental regulations which address pretreatment practices, environmental releases, community right-to-know responsibility, and hazardous waste management. The long-term availability of selected chlorofluorocarbons (CFCs) which are widely used for degreasing operations is in jeopardy due to concerns regarding depletion of atmospheric ozone levels. As a result of these factors, there is a widespread interest in identification of substitute compounds for use in metal finishing applications which do not exhibit adverse environmental properties.

The research objectives address evaluation of the potential for formation of toxic by-products upon chlorination of candidate substitute solvents as would be practiced in wastewater disinfection and/or alkaline chlorination for cyanide destruction. The experimental effort also includes limited evaluation of

the biodegradability of the solvents via conduct of biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic halide (TOX).

Criteria for selection of solvents for investigation include: (1) Elimination/minimization of halogen content, (2) Minimization of other listed materials, (3) Existing utilization in the industry for cleaning operations, (4) Acceptable flash point/safety considerations.

The candidate solvents which are expected to be selected for experimental evaluation may include alkaline detergents, non-halogenated organics (e.g., amines, alcohols, surfactants), and petroleum hydrocarbons. Three solvents will be tested with final results anticipated in the summer of 1990.

EXPERIMENTAL DETERMINATIONS OF HAZARDOUS WASTE DEGRADATION REACTIONS DURING DEEP-WELL INJECTION INTO SALINE FORMATIONS OF THE GULF COAST

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Over 8.6 billion gallons (or $3.3 \cdot 10^4 \text{ m}^3$) of liquid hazardous waste are disposed of by deep-well injection each year. About 90 percent of these wastes are injected in the Gulf Coast region at depths of 3,000 to 7,000 ft (900–3100 m). Recent legislation (Federal Register 40 FR 146), however, limits deep-well injection unless the injector demonstrates that there will be no migration of hazardous constituents from the injection zone for as long as the waste remains hazardous. To prove that injected waste does not migrate from the vicinity of the well bore, it must be shown that the fluid, or chemical constituents in the fluid, are immobile or that the hazardous material degrades to a nonhazardous form before the fluid migrates from the area. Sixty to eighty-two wt. percent of the hazardous compounds disposed of annually are organic, and most of these compounds may be able to degrade in the deep surface. If microbes are active at the depths of deep-well injection, as recently suggested by Kreitler and others (1989), biodegradation may transform hazardous waste to nonhazardous materials.

A field test has been proposed to determine the controls and limits on the degradation of commonly injected hazardous organic compounds. Actual field

testing of waste degradation reactions is recommended because thermochemical calculations and laboratory experiments alone cannot adequately predict hazardous waste reactions at subsurface conditions. The exact nature of the proposed field testing depends on the availability of a test well, the type of waste injected, history of injection, and the hydrological setting. These parameters will control the zonation of chemical and biological activity in the injection aquifer around an injection well and, therefore, long-term or short-term backflushing augmented by flow-through testing is necessary to determine reactions other than those that occur in the immediate vicinity of the well bore. Selecting a site with a monitor well is preferred because this setting permits flow-through testing; disposal sites, however, generally lack monitor wells because they increase the possibility of near-surface contamination. The site, to be selected from those owned by interested injectors, will be one that is typical of Gulf Coast injection wells having a sandstone injection interval. Approximately 15 waste disposal wells in Texas are being evaluated to determine their suitability as test wells.

HIGH-PRESSURE SOLVENT EXTRACTION AND CATALYTIC OXIDATION OF HAZARDOUS WASTES FROM AQUEOUS STREAMS

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Our aim is to develop a comprehensive understanding of the supercritical fluid (SCF) extraction of contaminants from aqueous streams, and subsequent catalytic oxidation of the high pressure solvent/contaminant mixture. We want to use this knowledge to aid in the commercialization of SCF-based waste treatment processes. In SCF extraction a solvent gas such as carbon dioxide or propane, at high pressure and moderate temperature, is contacted with the liquid phase. Slight changes in the system temperature or pressure can cause large changes in solvent density and consequently in its ability to dissolve relatively nonvolatile components. Thus, manipulation of system temperature and pressure can be useful in extraction and separation of organic contaminants from aqueous streams. After the contaminants enter the supercritical phase, conventional technology would use distillation to separate the concentrated contaminants from the SCF phase. We are also investigating, as alternative to this distillation step, catalytic oxidation of the high pressure solvent/contaminant mixture. High-pressure air can be added to the SCF-con-

taminant mixture in the desired quantities and conventional mixed-metal oxides can be used as catalysts.

LEAD AND CHROMIUM LEACHING FROM PORTLAND CEMENT — PHYSICAL AND CHEMICAL ASPECTS

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Portland cement samples containing lead and chromium have been investigated in efforts to study the physical and chemical aspects of the toxic metal leaching process. Fourier transform infrared spectroscopy (FTIR) results of leached samples indicate the disappearance of calcium hydroxide, the decrease of carbonate, and changes in the sulfate molecular vibrations. Scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS) reveal the spatial elemental distribution and morphology changes of the leached samples, while mercury intrusion porosimetry reveals the pore size distribution. The chemical interaction of lead and chromium with the cementitious components and the subsequent morphological changes is studied. Also, leaching behavior as described by models using physical chemical effects is compared.

METAL EMISSIONS CONTROL THROUGH HETEROGENEOUS DEPOSITION DURING FLUIDIZED BED INCINERATION

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The U.S. EPA has reported that metals account for almost all of the identified risks from waste incineration systems. However, traditional air pollution control devices (APCDs) are ineffective in collecting submicron size metal particulates. This work involves the development of a fluidized bed technology

for metal emissions control during waste incineration by promoting heterogeneous deposition and reducing homogeneous nucleation whenever metal vapors must condense. Our research has indicated that a fluidized bed incinerator or a fluidized bed waste heat boiler would be the most suitable process unit for promoting metal deposition in a controllable manner on the bed material.

The objective of this work was to study experimentally the characteristics of metal deposition on bed sorbents during fluidized bed incineration of solid wastes contaminated with heavy metals. Experiments were carried out in a 7.62 cm laboratory scale fluidized bed of various sorbents, including limestone, bentonite, aluminium oxide, and sand. Artificial test material contaminated with lead was prepared and incinerated in the bed with each sorbent under different operating conditions. An atomic absorption spectrometer was employed to measure the lead concentration in the original test material and sorbent, the incinerated bottom ash, and the fly ash. The effectiveness of metal capture by each sorbent under specific operating conditions was evaluated based on the material balance principle.

A NEW TECHNIQUE TO DETERMINE EFFECTIVE DIFFUSIVITIES FOR HAZARDOUS IONS SOLIDIFIED IN PORTLAND CEMENT

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Solidification of hazardous waste using portland cement has been and is currently being used in solidification technology, but knowledge of the exact leaching behavior of contaminants is limited. Characterization of the leaching of wastes from the portland cement matrix can be accomplished through a model. Leaching is generally known to be resisted by both chemical and physical mechanisms. The physical mechanism is associated with the structure of the solid matrix and includes such parameters as permeability, tortuosity, and pore dimensions in the matrix.

Modeling the leaching of wastes from the solid matrix predicts transport of contaminants through the slab by Fick's law and diffusion. The problem that has arisen is the need to obtain a diffusivity coefficient. Fick's Law is based on the effective diffusivity which depends only on physical factors such as molecular diffusion and pore structure and must be determined in order to have a valid model.

The new technique is based on the MacMullin number. The MacMullin number relates the free solution effective diffusivity of an ion to the effective diffusivity of that ion in the pore structure of a solid, and is calculated by a

ratio of conductivities. These conductivities are the conductivity of the solid, and the pore water within the solid. The ratio of the conductivities of the pore fluid to the solid yields the MacMullin number. From the MacMullin number, the effective diffusivity through the portland cement matrix of any hazardous ion can be calculated.

THE NOT-IN-MY-BACKYARD SYNDROME AND HAZARDOUS WASTE SITING: AN ANALYSIS OF THE IMPASSE

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A research project initiated in June 1989 entails a two-year study examining the emergence and development of the NIMBY (Not-in-My-Backyard) Syndrome. The study is designed to determine the extent of opposition, the substantive content of the apprehension and fears of citizens, and the parameters of conditions under which the community might accept a reasonable level of risk. The site location is in Dayton, Texas, approximately 45 miles east of Houston where Hunter Environmental Services has proposed construction of an industrial park that includes storage of hazardous wastes in a salt dome. Two locally organized NIMBY groups have formed to oppose the waste facility. The community has entered into negotiations with Hunter through local review committee hearings in order to obtain more information and give the public an opportunity to provide feedback. A research team has been attending local review committee hearings on a weekly basis, taking notes, obtaining copies of the recorded minutes, and interviewing members of the committee and selected city officials. The research team has also attended two public meetings organized by NIMBY groups to mobilize opposition. The committee appears to be split over the proposed facility and both industry and NIMBY groups claim to have public opinion on their side. Like most sites, Dayton is a community experiencing economic decline and the promise of financial boom has been made in exchange for the risks or costs incurred by accepting a hazardous waste facility. In early 1990, the research team will conduct a scientific survey of public attitudes towards the proposed waste site in order to obtain an accurate assessment of public opinion. These data will then be compared with the responses of community leaders (local elite) and NIMBY organizations to evaluate their relative influence in the siting process.

PARTICLE MEDIATED TRANSPORT OF CONTAMINANTS: A RISK ASSESSMENT OF THE NEW BEDFORD HARBOR SUPERFUND SITE

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A three-dimensional particle transport model was developed to assess the particle mediated transport of pollutants within the New Bedford Harbor Superfund Site. A mixed setting column was used to obtain vertical settling rates for cohesive particles under varying salinities, shear rates, particles concentrations, and particle types. The particles used in this column were obtained from three different locations within the New Bedford Superfund Site. A vertical transport model, which included flocculation, was developed and calibrated with this laboratory data. Results show that particles will floc, thus increasing the settling velocity and settling within the harbor. The hydrodynamics of the harbor were determined by extending this model in the horizontal direction to incorporate three dimensions. This involved a finite segment approach for solution which requires the input of advection and dispersion coefficients and segment dimensions, in each of the three dimensions. The model was verified using typical literature values for these coefficients. Calibration of the model used current velocities, tidal currents, river inflows, and wind stress from field observations. All efforts were combined to predict the transport of particles resuspended by proposed dredging operations to remediate the underwater New Bedford Harbor Superfund Site.

PERFORMANCE OF FRACTURED CLAYS AND REPAIR UNDER HAZARDOUS PERMEANTS

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The increasing incidence of failure of existing hazardous waste storage and disposal facilities, due to the failure of primary or secondary clay barriers, has drawn much attention recently. However, very little is known about repairing failed clay barriers *in situ* to satisfy the EPA permeability limit of 10^{-7} cm/s. The hydraulic conductivity of clay is affected by the interactive nature of local defects (desiccation, cracks, fissures, and fractures), chemical wastes, and *in situ* stresses. Improper modeling of clay, *in situ* stresses and boundary conditions in the laboratory tests are totally or partly responsible for the discrep-

ancies in the reported results. Since field tests are expensive, time-consuming, and in many instances impractical, it is essential to develop reliable laboratory permeability tests where the field conditions are closely modelled for the testing clay samples to evaluate the effect of cracks and various repairing techniques to reduce the hydraulic conductivity of permeable clays.

In this laboratory study the interactive nature of cracks and hazardous organic permeants on the hydraulic conductivity of clays was investigated. Kaolinite clay (commercially processed clay) and Beaumont clays were selected for this study with methanol permeant. The interactions between methanol and clays were characterized using index tests and sedimentation analysis. Several methods to simulate cracked clay specimens in the laboratory were investigated. The hydraulic conductivity of clays, compacted at optimum moisture content ($< 3 \times 10^{-8}$ cm/s), was increased above the EPA limit of 10^{-7} cm/s in a controlled manner using syringe needles of various sizes to simulate cracked clay specimens. Relationships between hydraulic conductivity of clays and crack parameters (crack length, size, and density) have been developed. The hydraulic conductivity of the cracked and permeable clays ($> 10^{-7}$ cm/s) was restored to that of the uncracked clay using various grouts such as sodium silicate, cement, lime, and bentonite grouts or mixtures thereof. These findings will improve the current repair practice for leaking clay barriers in waste disposal sites.

REACTOR MODELING AND SIMULATION FOR DEEP WELL OXIDATION OF AQUEOUS HAZARDOUS WASTES

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Deep well oxidation is a novel process that has been developed recently for oxidizing suspended and dissolved organics from aqueous waste streams. This process is expected to be very effective at detoxifying aqueous hazardous streams that are too dilute to incinerate economically, yet too toxic to treat biologically or by other means. The deep well reactor consists of concentric tubes of approximately 5,000 feet (1500 m) suspended in a well encased in earth. In the oxidation process, organics, oxygen, and water are brought together in a mixture at high pressure and elevated temperature. Organic oxidation is initiated spontaneously at these conditions. The heat of combustion is used to heat up the incoming feed to the required temperature and the hydrostatic head provides the required pressure. Under these conditions, organics are destroyed rapidly with efficiencies of 99 percent when residence time is sufficient.

The mathematical models of deep-well reactors consist of coupled hyper-

bolic differential equations (convection–reaction type). The models analyzed account for the kinetics of oxidation, the thermodynamics of the reactions, the heat transfer between the reactor tubes, the heat losses to the surrounding earth, and fluid flow. Detailed analysis of these models has shown that for realistic operating conditions, there exist multiple steady-states (ignition and extinction), isolated branches of steady-states (when residence time is taken as bifurcation variable), and sustained oscillations. It is also found that increasing the heat transfer between the tubes leads to higher steady-state conversions but to extremely long transient times for attaining the steady-state.

REMOVAL OF LEAD FROM SOIL BY VOLATILIZATION IN HYDROGEN

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Of the toxic heavy metals, lead is the most common soil contaminant. Currently, stabilization and landfilling are the methods of choice for dealing with lead-contaminated soils. Unfortunately, these methods are expensive and do not eliminate the eventual leaching into the environment. It would be preferable to extract the lead from the soil and reuse it providing a cost-effective method could be developed. Furthermore, it would produce a large volume of spent acid for further treatment to separate and recover the lead from relatively non-toxic, dissolved materials including aluminium, calcium, magnesium, and iron.

It has been known since the early 1900s that lead forms unstable, volatile lead hydrides such as PbH_4 and $\text{PbH}_{0.2}$. In the late 1950s, analytical chemists showed that lead could be quantitatively recovered from minerals, oxides, dusts, salts, and organic compounds using high temperature distillation in an atmosphere of hydrogen. We have made use of these observations to develop a lead recovery method for contaminated soil.

A laboratory apparatus has been constructed that permits the evaluation of time, temperature, and gas composition on the volatilization of lead from soil samples. The device consists of a tube furnace, a Vycor sample tube, and a magnetically-coupled sample insertion boat. Early results indicate that nearly 100 percent lead removal from soil is possible using the hydrogen volatilization technique. Further work will focus on optimizing time and temperature and on the effects of the form of the lead on the kinetics of volatilization. When these volatilization parameters are defined, the feasibility of lead hydride volatilization as a soil treatment technique or lead analysis will be assessed.

REMOVAL OF ORGANIC VAPORS IN SOIL

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The need to provide treatment for soils contaminated with hazardous materials from accidental spills and land-based handling operations has become increasingly apparent. Many of these hazardous materials contain volatile organic compounds (VOCs) that can sorb to the soil and/or volatilize into the air. To develop adequate treatment and control for volatile air emissions and to predict the fate of chemical constituents in soil, it is necessary to understand the fundamental processes and interactive mechanisms that occur in the unsaturated soil. In addition, such knowledge can be utilized both to provide criteria for designing soil decontamination projects and to evaluate the feasibility of processes such as alternative treatment for industrial vapors and exhaust gases and for soil vapor extraction.

At the present time, it is commonly assumed that volatile compounds in the vapor phase pass unaffected through the soil and enter the atmosphere with no change in mass. This assumption impacts decisions on air emissions, transport and fate of volatile compounds, regulatory limits, one-site controls, and treatment strategies. An evaluation of this assumption and the identification of significant removal mechanisms in unsaturated soil is the focus of this research. The major mechanisms that have been identified are sorption, degradation, and vapor loss.

Data from batch reactors were collected for the vapor phase sorption and degradation of three compounds, benzene, xylene, and trichloroethylene, on an unsaturated soil. These data were used to determine both sorption and degradation coefficients. The coefficients indicate that volatiles are sorbed and removed by degradation as they pass through the soil in the vapor phase. Results indicate the sorption of organic vapors is influenced by soil moisture content/relative humidity and soil organic content. Sorption was found to increase with a decrease in moisture content and increase in the presence of soil organic content.

RESOLVING THE DILEMMAS OF HAZARDOUS WASTE MANAGEMENT: PUBLIC RESISTANCE AND THE RESPONSE OF BUSINESS

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This work focusses on the important practical question: Under what circum-

stances will communities accept hazardous facilities? Most of the answers to this question — both in the academic literature and in applied fields — begin with an implicit economic model. Opposition to hazardous waste facilities, according to this model, is a function of two possible imperfections: poor information about safety or lack of recognition of economic benefits. Yet much of what this literature reveals is that people chronically overestimate the risks associated with treatment facilities (or other low-risk technologies) and that these assessments do not change in the face of increased knowledge, assurances of public monitoring, or economic compensations.

The seeming intransigence of public disapproval, well-documented in the relevant literature from political science, economics, and public policy, has led us beyond the economic model to an investigation of the cultural model of public opposition. Continued opposition, according to the cultural theory, depends on the success of certain adversarial elite groups (environmental organizations and the media, for example) in mobilizing latent public distrust of business and government. Thus, public acceptance depends on the ability of business leaders and scientific experts to demonstrate the viability of treatment techniques in a way that addresses the cultural problem directly. The state-wide survey of public attitudes that is being administered attempts to get at the cultural roots of opposition and acceptance.

SITE REMEDIATION OF CONTAMINATED WETLANDS: CHEMICAL CHARACTERIZATION, BIOTREATMENT, WASTE MINIMIZATION, AND RAPID TOXICITY ASSAY DEVELOPMENT

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National attention has focussed on the need for feasible technologies to permit on-site remediation of hazardous waste sites. To address this need, we are developing a biodegradation-based hazardous waste site remediation system in which an innovative analytical technology, thermal chromatography-mass spectrometry (TC-MS), in concert with short term genotoxicity and teratogenicity assays is being used to monitor the progress of degradation of the

wastes. The Pab Oil site, located near Abbeville, LA, has been chosen as the hazardous waste site for the study. This site was originally established to recycle oil from oil-based muds generated from numerous sources. A series of remediation tests using liquids/solids contact (LSC) reactors were conducted on produced water sludges similar to those at the Pab Oil site. Total organic carbon was reduced from 9,800 mg/kg dry weight to 321 mg/kg dry weight after 14 days in the reactors. Residuals are undergoing further remediation in a modified land farm approach. TC-MS analysis showed significant reductions of both aliphatic and asphaltine fractions. A new reactor for the suspension of up to 40 percent solids in an aqueous slurry, which is present at this site, has been designed to improve remediation kinetics and minimize upsets. Preliminary studies using polymer chelation of metals from standing water from the Pab Oil site, has shown that 74 to 97 percent of arsenic, chromium, nickel, and zinc were removed in a fixed bed reactor. Six microbial strains, including two isolated during a recent cruise in the Gulf of Mexico where deep ocean petroleum seep communities in the Green Canyon were explored, show great promise for anaerobic degradation of polyaromatic hydrocarbons/petroleum mixtures. Four toxicity assays have been validated to monitor the toxicity of the oil wastes during the bioremediation process.

SOLIDIFICATION/STABILIZATION OF ORGANIC WASTE USING CEMENTITIOUS AND POLYMERIC MATERIALS

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Methods of handling organic wastes more safely and decreasing the degree of hazard of disposed organic wastes are becoming critical elements in any hazardous waste management planning. The primary concern of the current solidification/stabilization technology, using cement and pozzolanic systems, is the interfering effect of organic contaminants which affect setting, chemical stability, and sometimes destroy the cement after setting. Due to the lack of understanding of treating organic wastes and anticipating problems from using the currently available treatment, regulators have used limitations on the amount of organics treatable, which range from 1 percent to 20 percent. Hence,

alternative materials for solidification/stabilization of non-volatile organic hazardous wastes (liquids and semi-solids) must be developed to meet the current demand in organic waste management. Polymers, which have been used successfully in nuclear waste disposal and in special industrial waste treatments, also have the potential for being used with organic wastes.

The initial objective of this study was to investigate the potential of polyester polymer to solidify/stabilize non-volatile organic hazardous wastes and compare the performance to cement. Phenol was selected to represent the organic contaminant because of its wide industrial use, toxicity, boiling point, and difficulty in treating with currently available methods. The interactions between phenol and polyester and phenol and cement were studied in a fundamental way from the time of mixing to final solidification. The study included leachate tests, mechanical property tests, and microstructural analysis using the scanning electron microscopy. Morphological studies show that even low concentrations of phenol (0.5% by weight) can cause a number of large pores with blister type appearance which will substantially increase the porosity of cement and make it susceptible to increased leaching. Test results show that polyester polymer can be used for effectively solidifying/stabilizing phenolic waste very rapidly.

STATE-OF-THE-ART STUDY OF HOSPITAL WASTE HANDLING

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This report is a study of the current technology used to manage infectious and hazardous wastes in hospitals. The interest in infectious waste is directly related to concern about AIDS and the news coverage of medical wastes found on East Coast beaches during the last few summers. The news media equated medical waste to hospital infectious waste. Analysis of beach debris shows the medical content at less than 0.2 percent and not of the type used in hospitals.

Three waste categories can be discerned: medical, hospital, and infectious. Hospital waste is any waste from a hospital (85 percent is equivalent to waste from a hotel). Medical waste relates to medical treatment and may or may not be infectious. Hospitals are only one of many generators of infectious waste. Most states have some minimum (but perhaps vague) definition of infectious waste. Each hospital has a committee that may have more stringent rules.

Infectious waste is either incinerated or it is sterilized and landfilled (a few states permit landfilling without pretreatment). Most hospital based waste incinerators are adequate to dispose of syringe needles and body parts. Chlor-

inated plastics require state-of-the-art commercial incinerators that can remove the hydrochloric acid, dioxins, and furans from the stack gas. Current technology is adequate, though expensive.

Hazardous waste generation in the medical operation of the hospital is small. Chemotherapy waste is mostly gloves and gowns and if not properly sorted can represent a large volume. A potential problem is the discharge of small concentrations of formaldehyde into the sewer.

THREE-DIMENSIONAL MODELING OF AQUIFER CONTAMINANT TRANSPORT

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The objective of this proposed research investigation has been to develop an accurate, robust, and cost-effective three-dimensional numerical model for the simulation of groundwater contamination and mitigation techniques. A two dimensional test version of the model based on an operator splitting formulation has been completed. This prototype model divides the problem into the solution of the pressure field using a finite element based model and a solution for transported species using a finite difference approach. It is anticipated that this approach to the numerical solution will result in significant improvements in model accuracy and parallel computational efficiency. A three-dimensional colorgraphics package has been developed to allow visualization of complex flow fields. Finally, aquifer contamination data with three-dimensional character have been made available to the project from the Borden Air Force Base Landfill Site (Canada) and the Conroe, Texas, United Creosoting Superfund Site. Future work will focus on the continued development of the three-dimensional model, development of colorgraphics visualization capabilities, and application of this model to real field data.

TRANSIENT SOURCE GAUSSIAN PLUME MODEL

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A model has been developed to predict the subsurface fate and transport of groundwater pollutants. This model uses an analytical solution of the two-dimensional advection–dispersion equation in which the source concentration

history serves as a boundary condition. The source is modelled as a transverse Gaussian-shaped profile and can be variable through time. The model includes advection, longitudinal and transverse dispersion, first order decay, and retardation through linear sorption. The solution has been incorporated into a FORTRAN computer program in which the concentration at any location in the aquifer can be determined for any given time. Specific applications include exposure and risk assessment for non-point, time variable sources such as landfills or a free phase hydrocarbon lens.

TREATMENT OF CHLORO-HYDROCARBON CONTAMINATED GROUND WATER BY AIR STRIPPING

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Air stripping was performed by using a 5 ft by 4 inches I.D. plexiglas column packed with 12.5 mm Raschig ceramic rings. The contaminated ground water was simulated by using local residential well water spiked with six chemicals: trichloroethylene (TCE), dichloromethane (DCM), 1,2-dichloroethylene (DCE), 1,2-dichloroethane (DCA), chlorobenzene (CB), and 2-dichloroethyl ether (DCEE). Concentrations of these chemicals in water were detected by using a purge and trap concentrator (PAT) connecting to a capillary gas chromatograph with an electron-capture detector (GC-ECD).

Experimental results indicated that all the six chemicals could be removed easily from the ground water by air stripping except DCEE. In order to remove DCEE efficiently, a high air/water loading ratio has to be utilized. At this high air flow rate the cooling effect due to the vaporization of water was found to be significant. It has been observed that temperature drop between the inlet and outlet water could be as high as 10°C.

Overall mass transfer coefficients of volatile chemicals calculated from experimental data were found in good agreement with those predicted from Onda's correlation. In general, water flow rate affects the value of overall mass transfer coefficient more than the other factors. However, for the low-volatile chemicals such as DCEE, the air flow effect was found to be significant. This indicated that the air stripping of DCEE may be controlled by gas-phase resistance. The error source of overall mass transfer coefficient estimated for a low-volatile organic was investigated and an improved method was developed.

WASTE MINIMIZATION BY PROCESS MODIFICATION

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Waste minimization by modification of reaction parameters is defined as changing the selectivity of the reaction so undesirable reactions which produce waste products are minimized while desirable reactions produce the desirable products. This research involves development of examples of waste minimization by process modifications which can be used as guidelines for minimization of waste generation.

Allyl chloride synthesis is used as an example. The parameters that are studied in the evaluation of the minimization of waste products are: reaction model, reactor type, feed temperature and composition, and thermodynamic mode of operation of the reactor. For the two-reaction model (neglecting third reaction), the best selectivity and yield are obtained in the adiabatic continuous flow stirred tank reactor with a feed ratio of propylene/chlorine (C_3H_6/Cl_2) of 6 and a reactor temperature of 800° F. For the three-reaction model, the best selectivity and yield are obtained in the non-adiabatic with a C_3H_6/Cl_2 of 6 and a temperature of 674° F. The third reaction which may have been negligible before consideration of waste minimization makes the results totally different. Side reactions which may have been neglected and assumed insignificant in the past will become a significant part of future kinetics studies.

Waste minimization by chemical reaction parameters has significant potential for identifying changes which will reduce by-products. Each process will need to be evaluated separately, however, case studies will provide insight and guidelines for similar processes and aid the educational process. Studies of waste minimization for the total process including recycle reactors, separations process recycling, and waste treatment will be needed if not required, for future capital investment decisions.

SOIL/AIR FLUXES OF HAZARDOUS SUBSTANCES AT TREATMENT, STORAGE, AND DISPOSAL FACILITIES: MODELS AND MEASUREMENTS

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This project has been directed at understanding and quantifying the trans-

port of volatile organic compounds (VOCs) in soils and subsequent emissions to the atmosphere from treatment, storage, and disposal facilities (TSDFs). The first phase of the research involved the development of a computer model providing dynamic simulation of gas phase contaminants in spatially and temporally varying environments. The model used diffusion and advection only as transport mechanisms and was validated with experimental data. The second phase involved the design and implementation of a flux sampler. The sampler used an activated carbon sorbent housed in an insulated weather-proof case. This device should provide a cost effective technique for quantifying soil fluxes. The sampler has succeeded in detecting trace levels of hydrocarbons in a 5-year-old landfill. The results of this sampler will later be compared to a flux isolation chamber. The third phase of the project is the use of ambient measurements of VOCs in conjunction with meteorological and modelling information to determine area source emission factors. The analytical method used is the cryogenic preconcentration of a whole air sample, and gas chromatography and mass selective detection (GC/MS) for quantification of selected VOCs. This method has a sensitivity of detection in the part per billion (ppb) range. Field studies for this phase are planned for this year.

THE FEASIBILITY OF *IN SITU* TREATMENT OF SOIL TO PROMOTE DESORPTION OF HAZARDOUS WASTES, THUS PERMITTING CAPTURE AND TREATMENT

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Hazardous wastes are frequently immobilized on soil particles by adsorption. Final destruction of these wastes is limited, because they are not available for treatment. If some technique could be found to desorb these materials from the soil surface, then they would be mobilized, and could be intercepted, captured, and treated. Treatment alternatives could be either biodegradation or chemical oxidation. Neither of these processes would be effective on adsorbed organics, thus, some method of liberating the organics bound to the soil must be found.

This project is investigating altering, *in situ*, either the surface chemistry of the soil particle or the nature of the sorbed organic compounds, such that the organic compounds will be desorbed and then be ready for transport and treatment. Three approaches will be investigated to alter the soil-sorbate bond: (1) the addition of an oxidant to make the sorbate more oxygenated (more polar), (2) the addition of lime as a source of calcium and hydroxide ions to alter the surface properties of the soil, and (3) the addition of surfactants to competitively displace the sorbate. This will lead to follow-up studies to demonstrate

the optimum treatment method for the "freed" organics, biodegradation or advanced oxidation being two possibilities. Initially these studies will be carried out in laboratory-scale flexible-wall permeameters.

HYDROGEN PEROXIDE AND VISIBLE-ULTRAVIOLET IRRADIATION FOR THE OXIDATION OF ORGANIC ENVIRONMENTAL CONTAMINANTS

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Groundwater contamination by synthetic organic compounds has become a major water quality concern nationwide, and will most likely continue to be so for some time in the future.

Hydrogen peroxide/visible-ultraviolet irradiation for oxidation of organic environmental contaminants is a promising treatment technology. This research established that six of the test compounds (trichloroethylene; benzene; 1,4-dichlorobenzene; 1,1-dichloroethene; 1,1,1-trichloroethane; and 1,1,2,2-tetrachloroethylene), at both high (multiple mg/L) and low (less than 1 mg/L) concentrations, were successfully treated by mineralization to carbon dioxide and water under reasonable operating conditions.

The effect of several process parameters such as pH, alkalinity, initial concentration of organics, initial concentration of hydrogen peroxide, and UV intensity, were investigated. In addition, although actual identification of intermediate compounds was not performed, gas chromatographic tracings suggested that oxidation of certain parent compounds resulted in the transient appearance of intermediate products.

A PROJECT MANAGEMENT INFORMATION SYSTEM (PMIS)

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The Director of the Hazardous Substance Research Center is concerned with coordinating research activities between participating universities, federal and state government officials, industrial researchers, and a variety of other personnel in this effort. In this capacity, he is involved in the review, coordination,

and acceptance of many research proposals. He must track the proposals and their associated budget requests from the time they are submitted until their approval or rejection. Once a project is approved, the funding requirements for it must be balanced between available state and federal appropriations.

In order to effectively and efficiently manage this effort, a Project Management Information System (PMIS) was developed. The PMIS was designed to be "user friendly" and modular, so that changes or modifications could be easily made. The dBase III Plus programming language was used and proved to be very effective. The PMIS was developed in about six months. Several major modifications and enhancements have been made to the system. Additionally, the data base has grown quite large and the system is somewhat slower than expected. Work is underway to improve the speed and reduce user response time.

CHOOSING LANDFILL SITES: STABLE ISOTOPE ANALYSIS OF GROUND WATER AS AN EVALUATION TOOL

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Leakage of wastes from landfill to the shallow groundwater system is a problem of ever increasing concern to society. Determining the rate of percolation of rainfall into shallow groundwater systems is therefore of basic importance. A study of oxygen isotope ratios, a natural tracer, in rain waters and shallow ground waters collected at the University of Houston Coastal Center in Galveston County, has been in progress to evaluate such groundwater percolation. This location is adjacent to an existing and actively operated landfill.

Isotopic spikes caused by natural atmospheric phenomena have been found in a collection of rainfall samples dating back to January 1985. Ground waters from shallow wells completed in November of 1988, are being monitored for these isotope spikes. Although no spikes found in the rainfall have yet been identified in the wells since monitoring began in February of 1989, it is anticipated that continued monitoring will eventually detect these spikes. Comparison of the spikes in the rainfall and the shallow ground waters will then allow percolation rates to be determined. Future studies will include measurements of tritium in both rainfall and ground waters to better evaluate groundwater percolation. Tritium is a radioactive component of rain that can be analyzed to date ground waters.

AN EXPERIMENTAL STUDY OF TREATED WASTE/SOIL INTERACTIONS AND THE LONG-TERM FATE OF HEAVY METALS IN THE VADOSE ZONE

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The attenuation of metal elements by soils is being studied by interacting packed soil columns and treated waste solutions in a dynamic flow-through apparatus. The long-term mobility of attenuated metals in soil will be modeled by distilled water leaching of soil columns that have been previously saturated with metals in the attenuation experiments.

Bulk samples of Shatta silty loam soil from the A1 and B horizons and samples of Smithdale sandy loam soil from the A1 and B horizons have been characterized for use in this study. These soils were collected to provide samples with contrasting textures/permeabilities and different organic carbon contents. Soils from the A1 horizons (samples SH-1 and SM-1) have slightly higher pH values (4.22 and 4.35, respectively), higher organic carbon contents (0.47 and 1.06 weight percent, respectively) and lower sulfur contents (0.0090 and 0.0091 weight percent, respectively) than soil samples (SH-2 and SM-2) from the B horizon (pH 4.08 and 4.17; total organic carbon 0.14 and 0.07 weight percent; total sulfur 0.0132 and 0.0121 weight percent). A 20-liter sample of treated municipal waste has been analyzed and is being used in the initial column loading experiments. Although the treated waste solution is low in most transition metals, it provides a relatively simple aqueous matrix (pH 7.5) in which to study the attenuation of low levels of Sr, Ba, Mn, Fe, and Zn by soils.

The first column loading experiment using Shatta silty loam sample SH-1 and the treated municipal waste solution is presented, conducted at ambient temperature and pressure, using a fluid flow rate of 0.05 ml/min. Treated waste solution pH values dropped sharply upon initial interaction with the soil column, and the pH of the effluent solutions climbed slowly through the remainder of the experiment. The pH drop is the result of the buffer capacity of humic substances present in the soil, and the steady climb in pH is one indicator of the extent of equilibration between the treated waste solution and the soil column. Metal concentrations in the effluent solutions have been analyzed by inductively coupled plasma emission spectroscopy. Plots of element concentration versus time give information on the partitioning of metal elements on the soil column, and on the rates of metal adsorption processes. Scanning electron microscopy is being used to collect X-ray generated element maps of vertical and horizontal sections of the soil column. These maps help discern fluid flow patterns through the soil column, and where metals are being preferentially adsorbed.

HYDROMETALLURGICAL TREATMENT OF HAZARDOUS WASTE FOR SIMULTANEOUS DETOXIFICATION AND METAL RECOVERY

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Industries which produce materials classified as hazardous wastes have been faced with seriously reduced productivity in part due to increased costs associated with waste disposal. The bulk of this material is currently disposed of in hazardous waste landfills, which is not only expensive, but carries with it the risk of future liabilities. This research program addresses an alternative process for detoxification of metal-containing hazardous waste and for metal recovery. Two types of waste have been investigated, waste sand from a non-ferrous foundry and fly-ash from a municipal incinerator. The process is aimed at recovering Cu, Pb, and Zn from the waste sand, and Zn, Cd, and Pb from the fly-ash. For either material the process involved is a two step hydrometallurgical process: (1) chemical dissolution (leaching) of the metal values from hazardous waste, and (2) recovery of the dissolved metals from the aqueous leaching solution by cementation. For the first step several leaching schemes have been investigated, e.g., chloride solutions, acetic acid solutions, and sulfuric acid. The effects of particle size, temperature, and acid concentration have been determined. The best overall extraction is obtained in hydrochloric acid solutions which yield generally rapid extraction of Zn, Pb, and Cd from the waste. In the case of copper recovery from foundry sand, an oxidizing agent is necessary for a reasonable extraction rate, since a significant portion of the Cu is present in metallic form. The success of the leaching procedure in removing toxic elements is currently being tested by subjecting leaching residues to the TCLP test. For the second step, i.e., recovery, experiments thus far conducted show that Cu, Pb, and Cd can be successfully precipitated from the leaching solutions to levels below 0.01 g/l by using Zn dust of an appropriate size. In summary, the potential of a hydrometallurgical process for recovery of metal values from waste materials appears to be promising. Future experiments will address the recovery of zinc by electrolysis.

SUPERCRITICAL EXTRACTION OF ORGANICS FROM WATER AND SOIL

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Organic contaminants in the environment, in water and soil, are gaining increasing attention because of the desire to increase the environmental quality. Various techniques are available for remediation of contaminated water and soil; supercritical extraction is an alternative to existing technologies. We have measured the thermodynamic parameters for supercritical extraction of single components and mixtures from water and developed the thermodynamic models for prediction. Similarly we have determined the parameters that control extraction of organics from solid-matrix soil by using static and dynamic techniques. The data presented will include the effects of co-contaminants, as well as co-solvents (entrainers). In all cases the supercritical fluid used was CO₂.

SELECTIVE RECOVERY OF METALS FROM WASTE WATER STREAMS

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Industrial wastewater contains high concentrations of metals such as copper, chromium, nickel, and zinc. It is desirable to recover each metal separately to allow recycling of metals and to satisfy waste minimization requirements. Metals can be selectively removed from aqueous solutions by chelation, since chelation of individual metals is controlled by pH. Research was undertaken to determine the parameters of the extraction of copper, chromium, nickel, and zinc with two chelating agents, dithizone and Aliquat 336. The chelating reaction must be performed in a pH-buffered solution to maintain a constant pH. The percentage extraction of copper, nickel, and zinc with dithizone was measured at several pH values. At pH 1 copper was completely extracted and zinc was slightly extracted. Copper and zinc were completely extracted at pH 5. Nickel was completely extracted in the pH 7-8 range. The average apparent first-order reaction rate constant of the nickel-dithizone reaction was $3.22 \times 10^{-7} \text{ min}^{-1}$, while that of the zinc-dithizone reaction was $1.92 \times 10^{-2} \text{ min}^{-1}$. The results of this research will be utilized to design a process to selectively recover metals from wastewater.
