

In situ remediation through contaminant mobilization by vacuum stripping combined with biodegradation*

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Abstract – Project number 041TAM0203

This project focuses on a *in situ* remediation technique for contaminated soil. The technique combines vacuum stripping for mobilization of the contaminants together with biodegradation in a reactor at the site. The project comprises two major tasks: studies on adsorption of contaminants and studies on biodegradation of contaminants.

The engineering data needed for vacuum stripping, include the adsorption rate and equilibrium parameters, and are not readily available. The first objective of this project concentrates on the determination of adsorption equilibrium and rate parameters for a variety of contaminants on soil and soil constituents. It is shown that soil moisture has a significant effect on these parameters, the nature of which is yet to be determined. Thus our second objective is to quantify the effect of soil moisture and determine the mechanism by which it affects contaminant adsorption/desorption and transport. This project will provide the necessary data base needed for the design of vacuum stripping processes for *in situ* remediation. In addition the data will be extremely useful in relating soil-gas analysis to the extent of soil contamination and for modeling of subsurface contaminant dispersion.

The second task of this project is to understand the fundamentals of the biodegradation of complex chemical mixtures using acclimated mixed microbial cultures. These studies will approach the degradation of selected environmentally significant chemicals from several directions. Specific growth responses and kinetic parameters will be evaluated for mixed microbial cultures from an activated sludge facility acclimated to phenol in a batch-fed apparatus at inhibitory concentrations. These studies will evaluate starvation effects and initial substrate to biomass concentration. A feasibility evaluation will be conducted for TEE degradation introduced via a gas stream with propane and air to the propanotroph, *Mycobacterium spp.*, grown under pseudo-continuous

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batch-fed conditions. From this study we will determine growth kinetics, loading rates and degradation efficiencies. Simultaneous studies will be conducted to determine the degradation kinetics of multiple substrate combinations of phenol, 2,4-dichlorophenol (DCP) and pentachlorophenol (PCP) fed to acclimated mixed microbial cultures in completely mixed reactors with recycle. To link the air stripping studies to the biodegradation work, we will conduct a series of experiments to quantify the transport of phenol from a soil column to the aqueous phase with and without microorganisms present. Mathematical models will be developed for all phases of this research to evaluate mechanisms of degradation and facilitate interpretation of the results.

Remediation of contaminated soils, sediments, and/or sludges by supercritical fluid extraction combined with adsorption

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Abstract – Project number 100TAM0087

In this project, we are proposing to develop at laboratory scale a novel process which can be used for remediation of soils, sediments and/or sludges contaminated with organic pollutants (e.g. pesticides, herbicides, polyaromatic hydrocarbons, solvents, PCBs, phenols). In this process, the organics are continuously extracted using supercritical carbon dioxide (SCCO₂) and then deposited on activated carbon. Since activated carbon has high affinity for organics and the soil contamination is in ppm levels, larger volumes of soil can be treated using small volumes of activated carbon which can either be regenerated or incinerated for complete destruction of organics. The existence of a similar process on an industrial scale for decaffienation of coffee beans, based on the same principles, provides proof on the technical and economical feasibility of the proposed process.

The work comprises design and construction of the process on a laboratory scale and initial feasibility studies by determination of adsorption isotherms, kinetic and hydrodynamic parameters, extent of decontamination of soil samples, optimum operating conditions, cycle times and the loading capacity of

adsorbents. The experiments will initially be conducted with artificial soil mixtures (0% and 2% organic content) contaminated with known amounts of model organics. The organics will be phenol, pentachlorophenol, a PCB and anthracene. As soil constituents sand, silt, clay (montmorillonite and bentonite), dolomite and soil humic material will be employed. Synthetic soil will be mixtures of these soil constituents at various proportions.

Soil remediation and waste oil treatment by agglomeration with coal

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Abstract – project number 100UAL0075

Recovery, transportation, and processing of petroleum and other hydrocarbon fuels generate soil and water contaminated with oil, tar, and other heavy organics. This project will treat oily soil and oily waste water with fine coal. The bridging liquid (oil) will be supplied by the contaminated soil or water. The agglomerated fine coal and contaminant oil will be floated and removed, leaving an oil free water or soil.

The coals processing industry first used oil agglomeration to commercially clean and recover coal in 1922 in Alexandria, Virginia. Agglomeration never enjoyed popularity due to the prohibitively high cost of oil. Due to the demand for higher quality coal, there is renewed interest in this technique because of it's ability to clean fine coal. Very simply, agglomeration works by sticking the finely ground organic coal particles together with the oil in a dilute coal-water slurry after intense mixing. The agglomerates (organic+oil) float to the top and are skimmed off, while the organic free ash sinks and is rejected.

To date, our studies have shown recoveries of combustibles (organics) to be as high as 96.2 percent. Our laboratory has been working on oil agglomeration since 1989 and has received continuous funding from the Alabama Department of Economic and Community Affairs (ADECA) and the School of Mines and Energy Development (SOMED). Our work has focused on recovery of waste coal from impoundment ponds, coal washing plant reject streams and from in-plant fine coal that is not recovered by present day coal preparation plants.

This ongoing work has also investigated low-cost oils for recovery of coal.

The work will also investigate the fate of metals from used lubricating oils in the agglomeration process. There is a potential that waste coal and used oil can be combined to form a clean fuel by rejecting metals with the ash.

Deep well oxidation of aqueous hazardous wastes in supercritical water: modeling and experimental studies

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Abstract – Project number 100UHH3007

The development of supercritical oxidation technology is still in its infancy. The scientific principles needed for the safe design and scale-up of the supercritical water oxidation reactors have not been studied and well understood. In addition, very little experimental data is available on the kinetic and thermodynamic behavior of important hazardous substances in supercritical water. Thus, a major goal of our research is to understand through a combined program of modeling and experimental efforts, the physical and chemical processes that dictate the behavior of supercritical water oxidation reactors. These fundamental principles will then be applied for the safe design scale-up and control of various supercritical combustion systems.

The goal of the proposed theoretical studies is to extend our work on the modeling of the subcritical reactor to supercritical conditions. We plan to develop mathematical models of the supercritical deep well oxidation reactor that will incorporate the experimentally determined kinetics of oxidation of various organic and inorganic compounds that may be present in the waste, the thermodynamics of the reactions as well as the phase behavior, the heat transfer between the reactor tubes, the heat losses to the surrounding earth, the fluid flow and the change of physical properties with temperature and pressure. These models will be used to simulate the steady-state and dynamic behavior of the deep well oxidation process and for predicting the destruction efficiencies of the various organic compounds, temperature and pressure profiles in the reactor up and down tubes, in the casing annulus, and in the earth around the reactor well assembly, as a function of position and time.

Chemical characterization of pore water of a solidified hazardous waste

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Abstract – Project number 10TAM3142

The goal of solidification/stabilization is to limit the ability of disposed hazardous wastes to migrate in the environment via leaching mechanisms. The pore water components of a solidified waste constitute the leachable fraction of the waste form. Chemical characterization of the pore water will provide information about the fraction of the waste available for leaching. In this study, synthetic portland cement-based waste forms were prepared by varying heavy metal concentration at constant water cement ratio and varying water cement ratio at constant heavy metal concentration. Pore water was expressed and analyzed for heavy metals, major cations, major anions and alkalinity. Analytical results were used to calculate the fraction of the original contaminant mass present in the pore water. The results varied with original contaminant concentration and alkalinity. Minimum pore water concentrations of each heavy metal showed a significant decrease from the original concentrations. The results can also be used to calibrate a chemical equilibrium model for use in conjunction with a leach model.

Using a modified TCLP to determine the leaching characteristics of stabilized/solidified wastes

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Abstract – Project number 100TAM3142

Solidification and stabilization using portland cement is an established procedure in the management of hazardous wastes. The technology is relatively

simple, cheap, and highly reliable in prohibiting the migration of the hazardous contaminants into the groundwater.

The success of this technology is measured by the amount of contaminants retained in the solidified matrix system. The most prominent procedures to measure the amount that can leach out of the solidified waste were developed by the EPA: the Extraction Procedure (EP) and, its successor, the Toxicity Characteristics Leaching Procedure (TCLP).

However, because of the lack of control on the shape and dimensions of the tested samples, as well as the pH at which the test takes place, the TCLP can be further improved by keeping the pH at a constant value and using samples with fixed dimensions. This will allow most of the leachate to leach out of the matrix at controlled conditions. Thus, the characteristics of the leaching process can be measured more accurately.

The proposed procedure, the Constant pH leaching Test (CPLT), is a modification of the TCLP. It is designed to measure the leaching rates of a fixed-dimension sample at a constant pH.

A mathematical model to predict the leaching of hazardous inorganic wastes from solidified/stabilized waste forms

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Abstract – Project number 100TAM3142

Solidification/Stabilization (S/S) technology is an important best demonstrated available technology (BDAT) for treating hazardous wastes. The method focuses on trapping the waste in a confined area and preventing it from disrupting the environment in the future. This is achieved through various mechanisms which solidify the waste by removing free water, decreasing the surface area to minimize loss of waste, limiting solubility and therefore mobility of the contaminants, converting the waste to less toxic form, reducing partic-

ulate or organic air emissions, and improving handling characteristics of the waste. Immobilization of the wastes is achieved with binders which can be inorganics, organics or a mixture. They need to be selected judiciously to obtain the desired solid waste characteristics. Inorganic binders are used in this research project and are predominantly portland cement with varying combinations of additives. Effectiveness of the S/S process can be established by different leaching and physical tests like the TCLP, EP, equilibrium batch, and sequential. However, the results from these tests are specific to the solidified/stabilized waste being tested and give little indication of the long-term behavior of the wastes. Leach models are an effective means for predicting leaching of the contaminants, describing the immobilization and binding mechanisms, predicting performance of the waste in the TCLP test, and aiding in the understanding of S/S.

A mathematical model has been developed to predict leaching of contaminants from solidified/stabilized waste forms. It assumes local chemical equilibrium, Fickian diffusion as the only means of transport of the mobile contaminants, and homogeneous distribution of the waste at the start of the leaching period. Other assumptions include: rectangular geometry of the waste form, conditions at the solid bath interface being similar to those in the bath, and no sorption phenomena. The model is set-up for an infinite bath (no change in component concentrations in the bath) and can be easily modified for finite bath conditions. These assumptions are used in solving the mass balance equations. The equations are developed in terms of the total concentration of contaminants and their mobile fraction. As non-linear, multicomponent interactions are being considered, a modified Crank-Nicholson technique is developed to solve the stiff set of equations. The solid is divided into nodes of decreasing size from the center to the interface because the leaching rate is not the same throughout the solid. Each node is treated as a homogeneous unit. Thus, accuracy in the computations increases as the nodal size is reduced. The chemical interactions occurring in the solid are solved by the chemical speciation model, SOLTEQ (modified form of MINTEQ version 3.1 developed by EPA). SOLTEQ computes the mobile phase concentration of each contaminant a node at a time starting from the node closest to the interface. To prevent superfluous computations and lower the execution time, SOLTEQ is called for the interfacial node onwards, until the node at which a minimum prescribed component concentration change has occurred compared to the previous time step. Mobile component concentrations at nodes beyond this one are assumed to remain unchanged. To reduce oscillations in the numerical solution technique, small time steps are required. An adaptive time step approach is employed which computes the maximum time step possible while remaining within a user specified error criteria. To increase accuracy, the error criteria can be made more stringent and/or the number of nodes in the solid can be raised which would reduce the individual node sizes. However, both of these lead to an increase in

execution time and the latter could cause memory space problems in the computing facility being used. Enhanced accuracy without increasing the total number of nodes is achieved by increasing the number of nodes only in the portion of the solid which requires SOLTEQ computations. The number of nodes in the portion which is not undergoing any significant chemical changes is made use of to achieve the above. The model makes use of the extensive database of MINTEQ modified to SOLTEQ requirements. Therefore, it is capable of modeling waste forms containing a vast array of inorganics.

The model has been tested for a four component system containing Ca^{2+} , Pb^{2+} , H^+ , and Ac^- . The results of the model have been found to agree with in 2% of the analytical solution.

Development of a rapid technique for measurement of effective diffusivity of contaminants in solidified hazardous wastes

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Abstract – Project number 100TAM3142

Solidification/Stabilization (S/S) is an effective treatment process in hazardous waste management. As with any technology, it is necessary to be able to predict the performance of the S/S end-products. To do this, an understanding of the binding and leaching mechanisms involved in solidified hazardous wastes is needed. The effectiveness of this process is determined by the degree to which contaminants will leach from the waste end-product.

The physical and chemical factors that determine this leaching rate need to be evaluated separately, and then described. Using a mechanistic model approach, the observed diffusivity can be related to a physical factor (effective diffusivity coefficient) and to a chemical factor. To describe the effective diffusivity the MacMullin number approach is used. The MacMullin number can be defined as the ratio of molecular diffusivity times porosity divided by a tortuosity factor. The MacMullin number can then be shown to be equal to the tortuosity factor divided by the porosity.

An electrical conductivity approach is used to measure the MacMullin num-

ber. Substantially all of the conductivity of the bulk solid is due to the conductivity of the pore water. The conductance of the solid therefore, is the conductivity of the pore water times the cross-sectional area of the pores. From this a relationship between the ration of pore water conductivity to solid conductivity and the MacMullin number can be established.

The proposed procedure involves the development of a rapid technique for measurement of the effective diffusivity of contaminants in solidified hazardous wastes. Thus there now is a way to independently, separate from any leach test, measure in a matter of minutes the effective diffusivity of a material through the pores. This is the basis of the physical characterization of the solid being tested.

The use of in-vessel composting as a treatment technology for hazardous waste minimization

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Abstract – Project number 100UTA0065

Increasingly stringent governmental regulations regulating the land disposal of hazardous wastes have created a need to develop new technologies for waste stream treatment to minimize the concentrations of hazardous constituents prior to disposal. Concurrently, advances in composting of municipal sewage sludge have resulted in the development of the in-vessel composting technology. The proposed study will investigate the use of in-vessel composting for the treatment of hazardous waste. Information is available from past studies on the optimum operating conditions for in-vessel composting (type of bulking agent, C:N:P ration, moisture content, and oxygen supply). Other researchers have documented the biodegradability of many of the hazardous organic components of oily and other wastes. What is missing is clear documentation of the fate of these waste components as the waste is treated by in-vessel composting.

The present study is designed to provide a comprehensive database on the fate of selected volatile organic compounds as a hazardous waste stream undergoes in-vessel composting. During the first year we have developed, constructed, and tested our laboratory composters which will be used in the re-

mainder of this study. Preliminary experiments using motor oil are being run to test the sampling and analytical techniques after which experiments will be run in which API separator sludge will be composted. A mass balance of selected organic constituents will be maintained to document the quantities which are degraded, volatilized, or remain after treatment. In the second and third years the experiments will be repeated for waste streams contaminated with pesticide (100 mg kg⁻¹ Endrin on adsorbent as from a spill cleanup), PNAs (100 mg kg⁻¹ dimethylnaphthalene in API waste), and 100 mg kg⁻¹ pentachlorophenol (PCP) in a pond sediment/sludge.

Successful completion of this study will provide data which can be used by the petroleum industry, those faced with cleaning up Superfund sites, and others to design and operate in-vessel composting systems for hazardous waste treatment.

Field study of mineral precipitation associated with biodegradation

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Abstract – Project number 100UHH0111

Although biodegradation is the most effective method for subsurface transformation of hazardous organic compounds, the inorganic and organic chemical changes associated with this activity have not been well documented. In this study we propose to conduct a field experiment in which an organic solution is injected into a shallow aquifer. After a quiescent period adequate to permit microbial degradation to proceed, a nearby well that is in hydraulic communication will be pumped. Samples will be collected from the pumped well and analyzed for all major and minor organic compounds and for gases that may have been produced by the microbial activity. In addition, microbial populations will be characterized. Data from these chemical and microbial analyses will be used to document degradation processes, chemical changes resulting from microbial activity, and mineral precipitation or dissolution reactions. The thermochemical reaction progress code EQ3/6 will be used to quantify the mineral-waste reactions that have taken place, and to study the chemical controls on the degradation process.

Solidification of salts of As, Cr and Pb using cement and various additives

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Abstract – Project number 100LSU3015

Solidification/stabilization (S/S) is a valuable technology for the treatment of certain waste streams; e.g., metal plating wastes, incinerator ashes, etc., and has great potential for use in treatment of contaminated soils arising out of historical malpractice or inadvertent spills. While the technology is relatively cheap to apply, significant questions remain about the range of its applicability. The first broad aim of the present project is to survey solidification/stabilization binding agents and additives with respect to their abilities to immobilize As, Cr and Pb, three species which are known to give problems in S/S practice. These wastes are being studied individually as well as in combinations with themselves and with water-soluble organics, particularly the very common phenolic wastes. The most basic information being obtained is metal concentration in TCLP leachates from solidified samples prepared with cementitious and pozzolanic binders and a variety of additives.

The second goal of the project is to understand the interactions between waste and matrix with the eventual intention of predicting performance and designing effective mixes. That work employs sophisticated characterization techniques, including solid-state nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared spectroscopy, and is being carried out in collaboration with the group at Lamar University.

Results to date include the following:

- Type 1 portland cement (OPC) has broad effectiveness for immobilizing metal ions, and certain deficiencies of OPC can be corrected using additives.
- Matrix changes that take place over long periods of time (1 year or more curing time) have serious consequences for the prediction of leachability. For instance, almost all of our metal waste samples, regardless of binder, show increased leachability after one year compared with after 28 days.

- Particularly large matrix composition changes take place in cement-fly-ash mixtures after long times of cure (> 1 y), and the changes are catalyzed by arsenic salts.
 - Alterations in the matrix due to one metal, such as Cr(III), result in enhanced leachability of a second metal, such as arsenic.
 - Leaching with a pH 5 buffer produces a predictable effect of degradation of the cement matrix, while TCLP leaching produces a very variable effect on the matrix depending upon which metal has been solidified and also the age of the sample being leached.
 - Phenolic wastes are present in either an ionized or non-ionized form, and sometimes both, depending upon the specific phenol, other wastes present, and curing time. Up to 28 days, the phenol, in whatever form, is largely dissolved in pore waters and not present as a solid Ca salt.
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Advanced oxidation for the simultaneous removal of NO_x and SO_2 from flue gas in a multi-phase system

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Abstract – Project number 100LUB0083

Nitrogenous oxides (NO_x) and SO_2 emission control is needed for incinerators, industrial furnaces, and boilers to comply with the Clean Air Act Amendment of 1990 and state regulations. In many areas of the USA, NO_x emission control is a more effective alternative than VOC emission control for curbing urban ozone. The preliminary results from our laboratory using a bubbling reactor show that the rate of ozonation for NO is increased by a factor of 10 with UV photolysis. The O_3/NO ratio is 0.5 which is half of the stoichiometric ratio required in a gas phase reaction. Work is under way to set up a new bubble reactor in order to run UV-assisted ozonation for NO/NO_2 system with longer contact time under different pH and temperature conditions and to test synergistic effect of NO_x and SO_2 removal.

Biosurfactant enhanced bioremediation of hazardous substances

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Abstract – Project number 100UAL0069

The purpose of this project is to study the influence of biodegradable surfactants on the rate of petroleum hydrocarbon waste internalization in bacteria and mineralization in aqueous environments. Biodegradation of hazardous hydrocarbons is being evaluated as a function of surfactant type and concentration, hydrocarbon loading rate, contaminant hydrophobicity, nutrient concentration, dissolved oxygen concentration and temperature. For the currently funded portion of this research program, multiple sealed model bioreactors have been employed to examine hydrocarbon contaminant phase partitioning and microbial cell mineralization in the absence or presence of varying concentrations of biodegradable surfactants.

The multiphase study employed in the research program utilizes bioreactor systems having several levels of complexity with respect to the number of phases, microbes and test hydrocarbons present. The early project phases have been devoted to study of simple pure compound and commercial consortia or single microbial species in aqueous phase bioreactor systems. These systems model aquatic or soil bulk water phase biodegradation environments. Bioreactor studies have demonstrated the action of surfactants to enhance hydrophobic contaminant mineralization by soil microbiota. Surface desorption, aqueous dispersion and enhanced hydrocarbons uptake by microbes can be facilitated by system amendment with biodegradable surfactants, either synthetic or biosynthetic.

Project year 1 has focused on extensively testing several biodegradable surfactant products for their ability to accelerate mineralization of test compounds in aqueous solution. The test surfactants include mixed rhamnolipids, which are biosynthesized surfactants produced by a *Pseudomonas* species, and Inipol EAP-22, the oleophilic fertilizer tested by the U.S. EPA in beach bioremediation of the Valdez oil spill in Prince William Sound, Alaska. Both products have been shown to accelerate the biodegradation of aliphatic hydrocarbons by both microbial consortium and pure bacterial strains in a concentration dependent manner similar to that observed for other synthetic surfactants ex-

aminated (Bioversal and Biosolve). With the exception of one known case, aliphatic substrates are chromosome-encoded; when specific metabolic pathways were not induced, the primary enhancement effects observed were attributable to decreased degradation lag phase with respect to non-amended controls.

Other surfactant enhanced biodegradation experiments have targeted selected hydrophobic aromatic pollutants. Dispersion and accelerated cell barrier transport effects promoted the degradation of benzene, toluene, *p*-cresol and naphthalene by pure *Pseudomonas* microbial strains. The oxidation of the later three compounds was carried out by specific *Pseudomonas* strains known to contain plasmids which encode metabolic pathways responsible for the primary metabolism of these aromatic compounds. Mineralization of *p*-cresol, benzene and toluene was considerably accelerated by Biosolve, Inipol EAP-22 and rhamnolipids when the catabolic plasmid enzymes were induced. Enhancement was attributed to (1) reduction in degradation lag phases (in most cases), and (2) increased rate and extent of mineralization. The mineralization rate of naphthalene increased only slightly. The possibility that the *Pseudomonas* spp. responsible for naphthalene degradation produces cell wall biosurfactants is a point of current investigation.

All surfactant preparations utilized, including Inipol EAP-22, were shown to substantially lower surface tension of the aqueous systems tested. Although the level of the rate enhancement was specific for individual surfactant, compound and microbe combinations tested, the maximum rate acceleration per preparation was achieved when the concentration exceeded the critical micellar concentration (cmc) of the surfactant of interest for all combinations tested. Increasing the surfactant concentration beyond the cmc had little additional effect on rate enhancement. This observation supports a micellar-mediated aqueous phase dispersion and transport model.

Feasibility of recovering metals from soil, ash, and sludges using anhydrous ammonia

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Abstract – Project number 100UHH3165

We propose to continue the development of an anhydrous ammonia extraction process for the removal of toxic metals from soils using ammonia alone or

in combination with enhancing ligands such as acetate or EDTA. In the commercial process that we envision, finely divided soil containing toxic metals ranging from 0.1% to 50% will be extracted in a closed system at ambient temperature at the saturation pressure of ammonia - 110 psig. The metals extracted under these conditions will be collected for reuse in a separator where the ammonia will be flashed off prior to recompression and recycling.

Experimental results obtained during the last six months indicate that cadmium, mercury, copper, and zinc can be extracted from contaminated soil using anhydrous ammonia alone. Lead can be removed using anhydrous ammonia in conjunction with extraction-enhancing anionic ligands such as acetate and EDTA.

Extensive screening tests were performed at a slightly elevated temperature of 43°C and 250 psig using a pressurized stainless steel Soxhlet extractor to rapidly evaluate the anhydrous ammonia extraction concept. A typical test involved soil spiking and aging prior to Soxhlet extraction for 2-hours with 30 extraction/siphon cycles. When extracting soils that were soaked with metal nitrate solutions prior to drying and aging, the metal removals were 73% for copper and cadmium, 64% for zinc, and 26% for mercury when the metal-nitrate spiking concentrations ranged from 20,000 to 50,000 mg/kg. Only 8% lead removal was observed using ammonia under these conditions. Furthermore, poor extraction efficiency was uniformly observed for all metals when extracting soil samples with spiking concentration below 2,000 mg/kg.

When enhancing ligands were added prior to ammonia extraction, lead removals greatly improved. For example, 95% removal was achieved from $\text{Pb}(\text{NO}_3)_2$ -spiked soil previously soaked in disodium EDTA solution and dried prior to extraction. When using dry-mixed enhancing ligands such as powdered sodium acetate or disodium EDTA, 75% to 87% lead removal was achieved on PbSO_4^- , PbCO_3^- , PbO - or Pb° -spiked soil samples during ammonia extraction. Similar extraction results were obtained for lead-contaminated Superfund soil treated with solution-mixed or dry-mixed enhancing ligands prior to ammonia extraction.

A commercially available Supercritical Fluid Extraction (SCE) Screening System has been purchased and used under subcritical conditions (110 psig, 23°C) to further evaluate the anhydrous ammonia extraction concept. The limited SCE experimental results obtained to date are confirming the Soxhlet extraction data for copper removal from $\text{Cu}(\text{NO}_3)_2$ -spiked soil. Eventually the SCE will be modified to incorporate a mechanically-stirred extraction reactor in place of the fixed-bed extractor now in use. The modified SCE will more closely simulate the extraction mixing conditions in a full-scale soil extractor. The general objectives of the continuing research are to (1) determine the effects of soil parameters such as size and composition on the rate and extent of metal - cadmium, copper, or mercury - extraction by pure ammonia in a stirred reactor, and (2) to determine the effects of the form - oxide, carbonate, sulfate or nitrate - of metal on the rate and extent of extraction.

Feasibility of removing lead and other toxic metals from contaminated soil by volatilization in nitrogen

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Abstract – Project number 100UHH2092

We propose to continue the development of an inert-atmosphere thermal process for the removal of lead from soil, particularly at battery waste sites and lead reclaiming operations. In the commercial soil treatment process that we envision, finely divided, surface soil containing up to 30 wt% lead will be heated above 850°C in an inert atmosphere furnace such as a rotary kiln purged with nitrogen. Lead volatilized under these conditions will be collected in a scrubber containing pure-lead-metal pellets which will grow in size as lead vapor condenses on them.

Bench-scale tests completed during the last year have proven that lead in essentially any form can be removed from contaminated soil with greater than 90% efficiency by heating in reducing (hydrogen) or inert (nitrogen) atmospheres. For example, heating a Texas Superfund soil from a lead-acid battery waste site for 20 minutes in nitrogen at 900°C reduced the lead content from 8,220 mg/kg to less than 560 mg/kg, i.e. a 93.2% removal. Similar percent lead removal was achieved using hydrogen while only 73% removal was attained in air under the same conditions.

The lead volatilized from soil in these tests appeared to condense on the cool surfaces of the clear vycor glass heating tube near its exit. No attempt was made in these tests to quantitatively measure the lead recovered because the apparatus was not designed to do so. The continuation work will address the recovery issue by continuing the study of lead collection on small glass beads in a modified apparatus using pure lead compounds and lead spiked soils. The effects of purge gas oxygen content, soil particle size, and soil clay and organic content will also be studied. One goal of the continuing research is to establish the design parameters for a larger bench-scale apparatus which will be used to determine the quantity and quality of lead recovered from 100-fold larger (50 g) samples.

Development of new environmental analytical methods with high performance planar liquid chromatography

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Abstract – Project number 100LUB0091

Many environmentally important chemical substances are not amenable to analysis by convenient methods such as gas chromatography (GC). Carbamate pesticides, for example, are not stable at the high temperatures that exist in the injection port of a GC. Compounds such as these are often analyzed by high pressure liquid chromatography (HPLC). HPLC, however, is an expensive and very time consuming technique, and requires a highly skilled technician in order to obtain reliable measurements. High Performance Planar Liquid Chromatography (HPPLC) provides a potentially excellent alternative to HPLC. HPPLC has sensitivity comparable to HPLC, but samples can be analyzed in a fraction of the time and for a fraction of the cost of HPLC. If funded, we intend to develop analytical methods using HPPLC for the analysis of environmentally important chemical substances. Under the direction of Dr. Rudolf Kaiser, a pioneer in the field of HPPLC, we plan to utilize equipment already in his possession to develop these new methodologies for the rapid, inexpensive, and reliable measurement of selected hazardous substances. In addition we plan to utilize a fast atom bombardment (FAB) mass spectrometer to investigate the process of HPPLC at the molecular level to make optimal use of the technique for donated to the Environmental Chemistry Laboratory will be used to investigate decomposition, adsorption-desorption, and diffusion phenomena which are the key phenomena of the HPPLC process. The FAB will also serve as an extremely sensitive detector for HPPLC, especially important in the detection of compounds which do not absorb or emit light. The successful development of HPPLC methodology in this project will result in faster and more economical hazardous substance analyses.

Binding chemistry and leaching mechanisms in solidified hazardous wastes

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Abstract – Project number 100LUB3142

This continuation proposal requests funding to further examine the binding chemistry and leaching mechanisms of priority metal pollutants and selected organic hazardous substances with cement and other pozzolanic materials. It can be divided into three main tasks: (a) to determine the nature of the bound states, (b) to determine the mechanism of leaching, and (c) to develop concepts and models that will improve the stabilization/solidification process. The present proposal includes plans to extend this work to mixed metals and to mixed metals and organics to explore the possible synergistic effects in these more complicated systems. Considerable progress is continuing to be made as to the chemical nature of the fixation of Pb, Cr, Ba, Zn, Cd and Hg in the cement solidification medium. These metals strongly affect the hydration chemistry of the cement. Models for these effects have been developed. This work is also leading to a better understanding of the leaching mechanisms. The chemical changes induced by leaching are being explored by surface analysis of XPS, ISS, AES and RBS and bulk techniques of XRD, SEM-EDS, and optical spectroscopies. Leaching substantially removes surface and subsurface calcium. In addition, the material structure as to pore volume, pore area, bulk density and pore diameter are being probed before and after metal doping and before and after leaching with mercury porosimetry. These results that show the original trimodal pore distribution (i.e., three size regions) of the cement is substantially altered by the presence of the metal and the leaching process.

Enhancement of the kinetics of incineration of dilute hazardous organic vapors – phase III

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Abstract – Project number 100UCF3149

The destruction of dilute hazardous organic compounds (HOC) in air often is accomplished by oxidation in an incinerator. Many organic pollutants have been combusted at temperatures from 1200 to 2200 °F. High temperatures are needed for the high efficiency (99.99%) destruction of odors, paint solvents, chlorinated hydrocarbons and other hazardous organics. Addition of a material that enhances the kinetics of the oxidation reactions in the post-flame zone could result in lower temperatures and more complete destruction of all HOCs of industrial significance. Experiments are being conducted on the enhanced destruction of HOCs by hydrogen peroxide in an externally heated, plug flow quartz tube reactor, and state-of-the-art analytical equipment.

Development of screening tools to estimate the performance of free product recovery

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Abstract – Project number 100TAM0093

The success of recovery of the hydrocarbon spill depends on the accurate placement of the recovery well at the spill site. This research obtains analytical expressions for the recovery of a light immiscible fluid on the groundwater table

following an oil spill. Using conservation of mass principles of the oil phase, incorporating boundary conditions and averaging the vertical direction, a governing equation in terms of the oil thickness is derived. By combining the governing equation, boundary conditions and an initial profile, the gasoline thickness at any radial distance from the oil source and at any time can be calculated. The resulting equation is solved analytically by imposing a variety of boundary conditions for a multi-level, two pump recovery technique.

Electrokinetic detoxification of soil

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Abstract – Project number 100UTA3158

For the past two years, we have been studying electrokinetic decontamination of soil. We have been able to move metals in soils and electric currents but have found that several complicating factors can “make or break” electrokinetic treatment of contaminated soil. The intent of our research is to characterize the complex system of soils treated electrokinetically and to identify an optimal technique.

The single most critical factor in removal of metals from contaminated soil with electrokinetic treatment has been found to be pH. In low pH environments, most metals tend to be quite mobile. However, in high pH environments, most metals adsorb and precipitate to solid surfaces and are extremely difficult to remove from the soil. During electrokinetic treatment, the pH of the soil solution near the anode is low, and near the cathode it is high. With time, the acid front generated near the anode may migrate through the soil and “flush out” the sorbed metal accumulated near the cathode. However, this migration of the acid front depends significantly on the flow rate, boundary fluxes, and internal buffering of the soil solution. For instance, the tendency of alumina to be dissolved from the soil at low pH appears to determine the lower limit of pH in the soil and, ultimately, the migration of the acid front toward the cathode. Thus, we have found that electrokinetic treatment may or may not work, depending largely upon the complex relations that control pH.

We have developed a multicomponent transport model that will predict the changes in pH and associated migration of inorganic chemicals in soil during electrokinetic treatment. Model results have been compared to measured be-

havior. The model has shown the same trends as the experiments: the pH gradients that develop in the soil dominate contaminant transport during electrokinetic treatment.

An experimental study of treated waste/soil interactions and the long term fate of heavy metals in the vadose zone

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Abstract – Project number 100UAL3004

Knowledge of soil-heavy metal sorption-desorption processes is incomplete and experimentally obtained data for heavy metal behavior in soil often fails to accurately predict the behavior of these toxic contaminants in natural systems. We believe that this failure is due in part to the complexity of vadose zone processes, but also to the fact that much of the heavy metal-soil interaction data was collected using overly simplified experimental systems. In addition, the fate of heavy metal elements attenuated by soil during recharge conditions has not been adequately examined, particularly for acid rainwater leaching conditions. In this GCHSRC-funded project, the attenuation and mobility of heavy metal micropollutants in soils is being studied in column flow-through experiments. Treated municipal waste effluent has been reacted with two sandy loam and two silty loam soil samples to study soil-waste interactions characteristic of this waste matrix in the absence of high concentrations of heavy metals. These experiments have been performed in duplicate with very good reproducibility. The mobility of soil-attenuated metals has been studied by subjecting one of the reacted columns for each soil sample to aggressive leaching conditions using a synthetic acid rain solution. These experiments have characterized the interactions occurring between the treated municipal waste effluent and the four soil samples, and examined the response of the reacted soil columns to acid rainwater leaching conditions. In the second half of the project, treated municipal waste effluent spiked with heavy metal elements (Ba, Cd, Cr, Cu, Zn, Mo, Pb) will be reacted with each of the soil samples in column flow-through experiments. One set of reacted soil columns will be leached with the synthetic acid rainwater solution to determine the mobility of soil-attenuated heavy metals. Through the use of a complex waste matrix,

these experiments will increase our knowledge of heavy metal attenuation mechanisms in soil, and will provide basic data needed to more accurately model the behavior of heavy metals in the vadose zone. The data obtained in this study will have application to land disposal of treated waste, the accidental discharge of waste materials containing heavy metals, and the establishment of soil heavy metal accumulation regulation criteria.

Application of microwave heating techniques to the detoxification of contaminated soils

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Abstract – Project number 100MSU3107

Investigations have continued to determine the effectiveness of microwave heating techniques to remove the volatile compounds of benzene and xylene from contaminated sand and clay soils. Studies indicate that 99.99% Destruction and Removal Efficiency (DRE) can be obtained when 3% water is added to the soil and the system is operated under vacuum conditions. Additionally, it was found that clay soils were much more amenable to treatment by this method than sandy soils.

The work was expanded to study the removal of semi-volatile compounds such as those found in oil refinery API separator sludges (APISS). Phenanthrene was used as the base representative was used as the base representative semi-volatile compound found in a typical APISS. Near 100% DRE was obtained when synthetic sludge was treated in a modified microwave apparatus with carbon black added to the mixture.

Additional work has been done using soils contaminated with pentachlorophenol (PCP). To date, the results with PCP have been poor (60%)-DRE. However, results from the work with the APISS highlights the necessity of adding an additional liquid in order that co-volatilization might take place. Since the normal boiling point (NBP of PCP is 340°C, water with its NBP of 100°C is not able to act as an effective carrier. The phenanthrene studies indicate that the addition of a light oil may be necessary for complete removal of PCP.

Equipment which has been purchased during the course of this research now includes a 1.5 kW Gerling Laboratories microwave power supply and research center. Funds from both GCHSRC and Mississippi were used for this latest acquisition.

Biodegradation of PCBs by the white rot fungus *Phanerochaete chrysosporium*

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Abstract – Project number 100UTA3168

White rot fungi are able to attack and degrade a wide variety of recalcitrant organic pollutants including polyaromatic hydrocarbons and chlorinated compounds. However, the unique degradative potential of these organisms has not yet been exploited for commercial waste treatment processes. *Phanerochaete chrysosporium*, the best studied white rot fungus, synthesizes a variety of oxidizing enzymes, such as ligninases and Mn-dependent peroxidases, that catalyze the initial rate limiting step in the degradation of recalcitrant compounds. While the production of these enzymes is essential for biodegradation, it occurs only when the mycelia are grown under very specific conditions that cannot be easily reproduced in bioreactors. We have examined the production of ligninases in batch cultures of *P. chrysosporium*. High levels of enzymes were obtained reproducibly using mycelia grown at 33 °C in optimized growth medium. The effects of concentration and degree of chlorination on biodegradation of biphenyl and PCBs is being investigated. The compounds degraded include biphenyl, 2-chlorobiphenyl, and 2,2',4,4'-tetrachlorobiphenyl at concentrations up to 500 to 1000 nmoles. Using uniformly ¹⁴C labeled biphenyl, we have shown that as much as 20% of the initial amounts can be mineralized to ¹⁴CO₂, and another 60% converted to water soluble by-products. These studies have demonstrated that *P. chrysosporium* holds great promise for future waste treatment applications. Currently, the use of calcium alginate immobilized cells is being studied for scale up to laboratory scale bioreactors.

Destruction of toxic organic materials and sludges by supercritical water oxidation

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Abstract – Project number 100UTA3155

Super Critical Water Oxidation (SCWO) has demonstrated its capability to treat toxic organic compounds. However, the data base that incorporates the destruction performance on a wide variety of compounds does not exist. Since design data are critical to the development of the SCWO process, it is very important to develop batch and continuous-flow apparatus capable of providing the information. In addition, solving engineering problems such as charring, encrustation, and corrosion is also critical to the overall success of SCWO process. Therefore, the objectives of this continuing project are to: (a) obtain supercritical water oxidation data on a wide variety of toxic organic compounds such as heptachlor, γ -BHC, anthracene, 1,2,4-trichlorobenzene, and dimethyl phthalate; and (b) evaluate pyrolysis, hydrolysis, charring, and oxidation for biological sludge.

The two unique batch-microreactor systems that have been developed in the previous period will be used to accomplish the research objectives. One (UT Mark I) will be used to collect destruction data and the other (UT Mark II) will be used to investigate hydrolysis and charring phenomena with/without oxygen.

Chemical degradation of unsaturated priority pollutants by oxidation with aqueous sodium perborate

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Abstract – Project number 100LUB3140

Oxidative degradation has long been an important procedure used both by nature (i.e., various living organisms) and by man (e.g., waste treatment fa-

cilities) to treat and/or effect the decomposition of many substances which pose a significant risk to human health or to the environment. Unfortunately, some of the most common oxidizing agents used by man (e.g., chlorine, hypochlorites and related substances) produce undesirable by-products such as chlorinated hydrocarbons. In addition, such agents are, of course, not effective against certain classes of priority pollutants such as the unsaturated chlorinated hydrocarbons. Thus, the development of safe, inexpensive and efficient alternative oxidative degradation agents and procedures remain a challenge. A material which holds great potential as such an agent is sodium perborate. It is a cheap non-toxic, large scale industrial chemical that serves as a ready source of the "active oxygen" required for oxidative processes. For example, it is used as an oxidative degradation agent in a variety of human, oral hygiene products (e.g., antiseptics, mouthwashes and toothpastes) and has even replaced chlorine as the agent of choice used in fiber bleaching. The objective of the studies outlined in this proposal is to determine if sodium perborate can be used to effect a chemical, oxidative degradation of a variety of EPA priority pollutants which are members of the unsaturated chlorinated hydrocarbon class. Specifically, the ability of sodium perborate to degrade the chloroethylenes, styrene, heptachlor, chlordane, pentachlorophenol, polychlorobiphenyls (PCBs) and other similar priority pollutants will be investigated. The chemical methodology to be used will be based on several previously reported successful studies of sodium perborate's ability to act as an oxidative, degradation agent - i.e., our report of the degradation of 1-methylstyrene, a compound related to the priority pollutants listed above, and the reports by other workers on the oxidation of sulfides, anilines, phenols and ketones. The proposed methodology of the former report, which involves reaction in a water environment at temperatures of 25-50°C., is a model of simplicity and efficiency. This method will be applied to the priority pollutants listed above with the aim of optimizing the characterization of the degradation products and the concentration, pH and time parameters required for the degradation process. These studies are the initial phase of what is envisioned as a long-term project aimed at eventually developing degradation processes for virtually every class of priority pollutants.

The clam *Rangia cuneata* as a standard biomonitor of hazardous substances in gulf coast and southern atlantic estuaries and inland waters

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Abstract – Project number 100MSU3144

The emphasis on hazardous substances, and knowledge that very low concentrations of some substances can cause adverse effects due to bio-accumulation, has caused an increased interest in biomonitoring. The ability of bivalve mollusks to accumulate some toxic materials is well documented. The U.S. Mussel Watch Program uses *Mytilus edulis* as a standard biomonitor species in cold temperate waters along the Pacific and Northern Atlantic coast. No single species is used as a biomonitor along the Gulf Coast and Southern Atlantic estuaries and inland waters. This project is investigating the use of the clam, *Rangia cuneata*, as a standard biomonitor for hazardous substances for southern Atlantic and Gulf Coast estuaries and inland waters.

Accumulation of the metals cadmium, copper, chromium, and lead are being studied under laboratory and field conditions. Bio-accumulation rates and concentrations of the metals in *Rangia* tissues and in the media are being determined in the laboratory for determination of bioconcentration factors (BCF). Specimens from a control population are being placed below industrial effluents that receives some of the metals. After 5, 10, 20, and 40 day exposure periods clams are removed and water, sediments, and clam tissues are analyzed for metal concentrations. Metal concentrations and accumulation rates from the laboratory and field exposures will be compared. Results from laboratory tests on exposure to copper resulted in BCF ratios between 41 and 149, with a correlation coefficient of 0.82. Exposures to chromium resulted in BCF ratios between 12 and 534, with a correlation coefficient of 0.92. Laboratory exposures to cadmium and lead are currently being conducted. Field exposures have been conducted at two sites in the Neches River estuary and the metal analyses have been completed from one site. These data revealed low concentrations of metals in the water, very high concentrations in the sediments, and intermediate concentrations in *Rangia* tissues. No linear relationship was found to exist between exposure time and concentration for any of the metals.

Academic partnerships for minority participation in environmental education, environmental careers, and the EPA Superfund program

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Abstract – Project number 1050UCF0062

Using the Environmental Protection Agency's Intergovernmental Personnel Act, the EPA will cooperate with a majority institution, the University of Central Florida, to develop a Florida statewide pilot program with historically black colleges and universities with emphasis on: (1) the prevention of pollution through increased environmental education awareness, (2) informing, stimulating, and preparing minorities for increasing environmental career opportunities, and (3) mentorship programs for minority faculty in Superfund research projects to help solve environmental pollution problems. This pilot program also will study increased statewide networking with respect to EPA Superfund-industry-university-elementary and secondary education linkages for future activities.

Metal capture and partitioning during fluidized bed incineration of solid wastes

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Abstract – Project number 100LUB3114

The U.S. EPA has reported that metals account for almost all of the identified risks from waste incineration systems. However, current incineration technology does not control metal emissions effectively. The proposed project is to develop an alternative control technology for heavy metal emissions via the capture of metals during fluidized bed incineration. The objectives of the project are to demonstrate the technology and to investigate the characteristics

of the metal capture process. Experiments have been carried out in a 7.62 cm laboratory-scale fluidized bed of various sorbents, including limestone, bentonite, aluminum oxide and sand. Artificial test materials contaminated with lead nitrate and lead chloride were utilized. The results from the first two years of investigation have demonstrated that the proposed technology is highly practical. The capture efficiency has been observed to range from 19 to 96% depending on operating conditions. In this continuation application for the third year, two phases of investigation are proposed. Phase I is to continue the current experimental investigation to quantitatively and systematically characterize the metal capture process with emphasis on wastes contaminated with mixed metals. Phase II is to construct and test a novel two-stage fluidized bed incinerator which has a great potential to further enhance the metal capture process.

Waste minimization by process modification

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Abstract – Project number 100LUB3139

This research involves a continuation of development of examples of waste minimization by process modifications including reaction and separation parameters. Such examples can be used as guidelines for process and environmental engineers to minimize waste generation.

In the first phase of the research, waste minimization by process modification was investigated for the production of allyl chloride. The investigation focused on modification of reaction and separation parameters to minimize the generation of 1,2-DCP (1,2-dichloropropane) by-product while maintaining the production of allyl chloride (3-chloro-1-propene) product. For the two-reaction model, specific condition (temperature, propylene/chlorine mole ratio, residence time, pressure, distillate/feed mole ratio, reflux ratio, etc.) were specified for minimum generation of 1,2-DCP by-product.

In the present study of waste minimization by process modification is being conducted for the production of acrylonitrile. Acrylonitrile (propanenitrile) is one of the largest volume chemicals produced in the U.S. It is used in acrylic fibers, copolymers, nitrile rubber and many other applications. It is produced by gas-phase catalytic air oxidation of propylene and ammonia. Several by-products are generated in the process.

The present study will focus on minimization of generation of the by-products by conducting the following primary activities:

- (1) Develop an analysis of the effect of modification of reaction parameters on the waste minimization for the process.
 - (2) Develop an analysis of the effect of modification of separation parameters on the waste minimization for the process.
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An electronic bulletin board system for the Gulf Coast Environmental Library

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Abstract – Project number 031CWP0190

Disposal of the ever-increasing amounts of hazardous substances is a critical concern in our society. Vast amounts of resources are necessary to conduct research into the most efficient and effective means to treat these wastes. Officials of the Federal Government, State Governments, and in Industry are involved in the planning, allocation of resources and exchanging technical information to combat this problem.

An important element in this process is the rapid transfer and exchange of information concerning new technology, existing and proposed research efforts, current literature, and scientific conference information exchange. Sharing of data and information among agencies can reduce cost and eliminate unnecessary redundancy. Storage of this information in a central repository for expeditious retrieval and transmittal can result in timely decisions in situations dealing with hazardous materials and substances.

The Gulf Coast Environmental Library is designed to assist and share this current, state-of-the-art information and/or technology with requesting researchers, scientists, government officials, and individuals.

High-pressure solvent extraction and catalytic oxidation of hazardous wastes from aqueous streams

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Abstract – Project number 100LSU3101

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.

We are investigating a new treatment process for contaminated streams – the application of non-toxic SCF (high pressure, moderate temperature) solvents to effect contaminant extraction. In particular, advantage can be taken of the unique properties which exist when a solvent becomes supercritical. In supercritical fluid (SCF) extraction, a solvent gas such as carbon dioxide, at high pressure and moderate temperature, is contacted with a solid or liquid phase. Slight changes in the system temperature or pressure can cause large changes in solvent density and consequently in its ability to solubilize relatively nonvolatile components. Thus, manipulation of system temperature and pressure can be useful in extraction and separation of organic contaminants. We are examining both CO₂ and propane as candidate SCF solvents, with a current focus on cleanup of priority pollutants from contaminated streams. Results for the removal of benzene, *m*-cresol, *p*-chlorophenol and phenol from water have been reported. To help demonstrate the utility of SCF technology, we have also reported on our cleanup studies of industrial waste streams.

Removal of toxic heavy metal ions from industrial effluent by membrane separation technology

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Abstract – Project number 100TAM2036

Waste streams of toxic and hazardous substances usually are dilute solutions. Removal of hazardous substances from effluent by conventional methods (liquid-liquid extractions, flocculations, adsorptive separations and distillation) often are not economical due to the large volumes that need to be handled. Even if the treatment is based on oxidation or reducing agents in mole-to-mole basis, reductions in volume can drastically reduce capital costs of waste treatment facilities. Many treatments are energy intensive or produce secondary waste materials that can create environmental problems.

The proposed research will combine advantages of both aqueous Micellar Enhanced Ultrafiltration (MEUF) and ultrafiltration/reverse osmosis to develop a non-aqueous MEUF technique to separate organics and dissolved metal complexes in waste waters, oils and solvents from metal finishing industries by using biodegradable natural surfactants such as phospholipids. The retentate from this process containing concentrated hazardous and toxic organics and heavy metals attached to surfactant or phospholipids could be treated economically due to its low volume by various processes including electrochemical, chemical, thermal and physical methods.

The first phase of the project that was funded last year includes the study of the binding of pollutant and five dissolved metals (Cd, Cu, Pb, Ni, and Zn) to phospholipids (micellas) using ultrafiltration (diafiltration) method to obtain binding parameters to prepare binding curves showing the molar binding ratio vs. the free dissolved toxic metal complexes/organics concentration to determine the number of binding sites available within the micelle structure and intrinsic association constants. In addition, the stability of the membranes was determined by examining UF membranes (ceramic, metallic and polymer) before and after separation trials to evaluate effects of solvents on membrane structure, using scanning electron microscopy as needed.

The proposed second phase will evaluate the commercial membranes identified during the first phase of the project in pilot scale and determine permea-

tion rates at various system pressures, operating temperatures, and critical micella concentrations and to correlate data with removal of toxic substances. Effects of surfactant concentration and permeate/feed concentration ratio, critical micella concentration (CMC) and on permeate flux, membrane pore size and selectivity will be determined. Also, opportunities for separating phospholipids from the pollutants by chemical methods for reuse and easy disposal will be examined. As time permits, in-field applicability of the process with samples of electron-plating wastes will be determined and finally a feasibility report on construction of small a portable non-aqueous MEUF system will be prepared.

Detoxification of pentachlorophenol and cresols in woodtreating waste

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Abstract – Project number 100MSU3104

The present research concerns the detoxification of woodtreating wastes containing pentachlorophenol and/or cresols by chemical oxidation. A stopped-flow spectrophotometer system and several stirred-tank reactors were applied to study kinetics of the oxidation reactions. Treatment of the pollutants by hydrogen peroxide may not be feasible because of slow rates of oxidation. The ozonation process can be an effective mean for the detoxification; the half-life of the pollutants in the ozonation reactions is only a few milliseconds. The kinetics of reaction is second order overall with first order in the concentrations of the dissolved ozone and pollutant. For complete conversion of one mole of a cresol isomer, three moles of ozone are required. On the other hand, the stoichiometric ratio is five moles of ozone per mole of pentachlorophenol.

In distilled water at 25°C, the second order rate constant for the pentachlorophenol-ozone reaction is 4,860,000 L/mol s. For the ozonation of cresols, the rate constants are 32,240, 60,870 and 45,460 L/mol s, respectively, for *o*-, *m*- and *p*-cresol at the same condition. In the temperature range of 10 to 40°C investigated in this work, the ozonation rate of *m*-cresol is faster than that of the other isomers. The experimental results indicated that the ozonation rate of a pollutant increases with the temperature and pH value of an aqueous solution.

Characteristics of MSW incinerator fly ash promoting the formation of polychlorinated dioxins

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Abstract – Project number 100UAL3106

Polychlorinated dioxins are known to be formed on municipal waste incinerator fly ash by catalytic activity of the fly ash itself. However, it is unknown what characteristics of the fly ash are responsible for the dioxin formation. The study is aimed at correlating specific fly ash characteristics to dioxin content of fly ash samples from various MSW incinerators across the United States. Several elemental species exhibited positive correlatability to dioxin formation. Laboratory experiments were performed to confirm the reactivity of several of the noted elemental species.

Systematic approach for the selection of the least-cost treatment technology for aqueous organic hazardous wastes

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Abstract – Project number 100UTA0098

Decisions concerning the technologies to be used to treat waters contaminated by hazardous organic chemicals are complex. The complexity stems from the mixture of chemicals in contaminated waters, the range of concentrations encountered, the variety of available treatment technologies, the maze of reg-

ulatory constraints, and the multitude of process configurations that give technically feasible solutions. Faced with this complexity, designers aim for a reasonable design, but not necessarily a least-cost design. The proposed research is designed with two objectives:

- (1) to create a unified decision tool, a computer-based system, that will allow designers to investigate systematically a wide variety of technically-feasible solutions and arrive at the least cost option, and
- (2) to increase our understanding of one treatment option, simultaneous biodegradation and liquid-phase adsorption.

The two objectives are linked because understanding of the biodegradation/adsorption technology is poor and designers ignore the biodegradation that can occur in an activated carbon adsorption bed. This omission leads to choosing an entirely different technology. The results of our previous research indicate that, when technically feasible, air stripping with off-gas adsorption is cheaper than liquid phase adsorption. For liquid phase adsorption to be a reasonable option, understanding the biodegradation/adsorption process is critical.

The accomplishment of both objectives requires a large amount of computer work; the second also necessitates laboratory experimentation. To accomplish the first objective, the framework for the computer-based system for the decision analysis and optimization will be created first, using expert system software and several programs to guide the user. Then, simulation models for each treatment process will be written (or improved), and set into the unified framework. Six treatment processes are to be included: air stripping, air stripping with gas phase adsorption, liquid phase adsorption, combined biodegradation and adsorption, steam stripping, and biodegradation. Finally, results of many hypothetical cases will be analyzed and the results synthesized into general guidelines; these guidelines will be incorporated back into the expert system framework in the final package. For the second objective, a rapid screening model for the applicability of biodegradation/adsorption systems will be developed first. A refinement of an existing detailed model will then be undertaken. As noted above, these models will be inserted into the unified decision analysis framework established in accomplishing the first objective. Finally, laboratory experimentation will be undertaken to verify the biodegradation/adsorption models.

Treatment of chloro-hydrocarbon contaminated ground water by bio-degradation

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Abstract – Project number 100LUB3136

Air stripping of trichloroethylene, dichloromethane, 1,2-dichloroethylene, 1,2-dichloroethane, chlorobenzene, and 2-chloroethyl ether from groundwater has been demonstrated in a pilot scale packing column unit with a granular activated carbon (GAC) adsorber in the air stream. This study has shown that these compounds can be stripped but that the removal efficiency of 2-dichloroethyl ether (DCEE) needs to be improved. This can be accomplished by using a stripping system of multiple columns in series instead of one single stripping column.

Although air stripping is cost effective, it is still a separation method which leaves a hazardous residue. This residue must be collected from the air stream and treated to reduce its toxicity before it can be safely sent to final disposal.

The previous work on this project has established basic data on the air stripping approach coupled with collection on carbon for biological treatment. It is now proposed to examine the direct treatment of the original waste by an anaerobic aerobic treatment train to provide data to permit evaluation of the comparative advantages of the two approaches.

The biodegradation method proposed here will degrade the chloro-hydrocarbons to methane, carbon dioxide and water or at minimum to an effluent suitable for discharge under an NPDES (National Pollutant Discharge Elimination System) permit.

The objectives of this research proposal are:

- (1) To develop a microbial community acclimated to the following chloro-hydrocarbons :
 - 1,2-dichloroethane,
 - 1,1,2-trichloroethane,
 - 1,1,2,2-tetrachloroethane, and
 - 2-chloroethyl ether
- (2) To design and demonstrate a continuous flow bioreactor to treat the chloro-hydrocarbon contaminated ground water.

Optimum operating conditions such as temperature, pH value, hydraulic retention time and fluidized velocity in the reactor will be examined. Important parameters such as biodegradation rate constant, microbes yield coefficient, and endogenous rate constant will be estimated.

Analysis of post-combustion products from waste derived fuel by FTIR spectroscopy

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Abstract – Project number 100MSU0137

Many cement manufacturers now employ waste-derived fuel as an energy source. The use of this fuel either alone or in combination with coal is attractive as fuel costs are reduced and large quantities of waste are used in energy recovery. Some studies of the environmental impact of cement clinker formation using supplemental fuel have been reported. In most cases, the quantitative determination of the products of incomplete combustion and gases like CO, NO_x and SO₂ has been accomplished by sampling followed by gas chromatography with or without a mass spectrometer. In this work we are evaluating the use of a Fourier Transform Infrared (FTIR) spectroscopy as an on-line, near-real-time diagnostic instrument for the analysis of products of incomplete combustion, particulates and combustion gases. Optics development, laboratory experiments and initial studies on DIAL's existing 500 kW oil-fired test facility will be discussed. Laboratory work has centered on the quantitative analysis of CO, CO₂ and Freon 22 (chlorodifluoromethane, a species which does not contribute to depletion of the ozone layer). Additionally, qualitative scattering measurements are reported for SiO₂ particles. The test facility experiments have been aimed at the determination of CO and CO₂ concentrations. Such data provides a measure of the stoichiometry (fuel-to-air ratio) of the combustion process. At present, no limiting factors have been observed in using the FTIR spectrometer as an on-line diagnostic instrument.

Fate of volatile organics in soil

Raymond Loehr

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Abstract – Project number 100UTA3006

This research: (a) is providing fundamental data on removal of volatile organics in soil, (b) is identifying the significant mechanisms causing such re-

moval, (c) will improve existing unsaturated soil contaminant transport models to reflect volatile organic removal processes, and (d) will provide unsaturated soil model output estimating air emissions and leachate concentrations when vapor removal in the soil is accounted for properly. This knowledge will benefit both industries and regulatory agencies as decisions are made about the use of soil as a waste management alternative, particularly for disposal of hazardous wastes and for contaminated soil bioremediation.

The research has several phases. Batch laboratory studies are underway to evaluate the sorption, degradation and gaseous losses using radio-labeled and other volatile organics. The kinetic coefficients from these studies will be utilized in an unsaturated zone contaminant transport model (RITZ-UT) to quantify the effect of volatile organic removal in the soil on volatile emissions from the soil.

To date, extensive protocol development has been completed, sorption data have been collected, and degradation rates have been determined. Batch sorption studies have been conducted in unsaturated soil with benzene, trichloroethylene (TCE) and *o*-xylene. Results indicate VOCs are attenuated as they pass through the soil in the vapor phase.

Laboratory degradation studies have been conducted with the same three compounds and with radio-labeled benzene. The results indicate that degradation of benzene and *o*-xylene does occur and that the degradation rates increase rapidly as the volatile compounds sorb and the bacteria in the unsaturated soil become acclimated to the compounds.

The sorption coefficients and degradation rates have begun to be used with the unsaturated zone contaminant transport model noted earlier. This component of the research will have increased activity during the rest of 1990 and in 1991.

The initial studies have been conducted with single compounds. However, rarely are there only single compounds in unsaturated contaminated soils. Therefore, laboratory sorption and degradation studies with mixtures of volatile compounds are beginning. The resultant kinetic constraints also will be used with the unsaturated zone contaminant transport model.

Hazardous waste site cleanup design: Pump-and-treat systems

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Abstract – Project number 110UTA0172

Remediating sites where hazardous substances have contaminated groundwater is an urgent and important task for environmental regulators, responsible parties, and consultants. In a pump-and-treat system, contaminated groundwater is pumped from the aquifer to the surface where it is transported, usually via pipeline, to a groundwater treatment system. The treatment system removes contaminants using a combination of wastewater treatment processes. Once the water has been treated it is either reinjected into the aquifer or discharged to a surface water body. Currently, pump-and-treat systems are designed in a piece-meal fashion. First, a pumping well field is configured to approximately contain and remove a contaminant plume which exists in an aquifer, then a groundwater treatment system is designed to remove enough of the contaminants to meet required effluent standards for reinjection or discharge. Treatment systems used to remove contaminants from the extracted groundwater are designed independently of the extraction and reinjection well fields. However, these systems are intimately related to each other in that the flow rate of the extraction wells and the contaminant concentrations in the aquifer affect the treatment process design, scale and size, and, in addition, the removal efficiencies of the unit processes of the treatment system affect the concentration and flow rate of the reinjected or discharged effluent.

A new pump-and-treat system design methodology is needed which integrates both well field and treatment process design to provide an overall optimal system design. In addition to this integrated design methodology, a technique is needed to assess the reliability of remedial designs in light of the uncertainty present in the aquifer property estimates used in the design process. This reliability analysis will help to estimate the likelihood that the remedial actions will actually achieve cleanup goals in a reasonable length of time.

This research will develop a rational methodology for integrating the optimal design of pumping well fields, groundwater treatment systems, and injection well fields. A second objective is to identify and evaluate the potential effects of deviations from the presumed subsurface conditions (i.e., aquifer property heterogeneity) used in the design of pump-and-treat remediation. The objectives will be accomplished in two steps, first a mathematical optim-

ization model will be developed and used to determine the optimal configuration and operation of the pumping well field and groundwater treatment system, then a sensitivity analysis of the resulting design will be conducted to determine the effects on system performance of the heterogeneity or spatial variability inherent in the aquifer properties that the design is dependent upon. This optimization-sensitivity analysis approach will lead to increased cost-effectiveness of cleanup designs and improved estimates of the reliability of the remedial designs and the time required to achieve cleanup.

Technical feasibility and cost effectiveness of the co-disposal of spent organic solvents and municipal sludges using anaerobic digestion

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Abstract – Project number 100UTA0073

Organic solvents used in the electronic industry and other manufacturing facilities in urban-industrial complexes require disposal with minimal impact on human health and the environment. In some cases the solvents can be reprocessed and reused; however, some organic residue remains. In many situations the spent solvents are incinerated with or without the need for auxiliary fuel to sustain combustion. However, public resistance to land disposal or incineration of spent solvents has limited the available sites in Texas for the disposal of spent solvents. One alternative technology is the co-disposal of spent solvents with municipal wastewater sludges using anaerobic digestion. The technical feasibility and the cost effectiveness of this type of co-disposal system has not been established. However, perceived advantages include co-disposal of spent solvents (hazardous wastes) and sludges; elimination or at least reducing hauling cost and energy used in transporting the solvents great distances to disposal sites, conversion of the solvents biologically to methane gas and the recovery of methane gas for other municipal uses, elimination of the need for auxiliary fuel required to incinerate some solvents, and elimination of the potential air pollution resulting from improper incineration of the spent solvents.

The objectives of this proposed engineering investigation are the evaluation of effectiveness of co-disposal of spent organic solvents and municipal sludges by anaerobic digestion; evaluation of the effects of organic solvents on the performance of the anaerobic digestion process; and establishment of the solvent loadings at which efficient co-disposal is energy efficient, cost effective, and with minimal environmental impact.

Laboratory and bench-scale anaerobic digestion systems will be operated. Solvents used will be selected from acetone, benzene, cyclohexane, ethylbenzene, toluene, xylene, furfural, carbon tetrachloride, naphthalene, 2-butanone, nitrobenzene, phenol, chlorobenzene, di- and tri-chloroethane, methylene chloride, chloroform and butyl benzyl phthalate, among others. Continuously fed anaerobic digestion systems will be operated under quasi steady-state conditions to establish engineering design data.

The chemistry of stabilized Cr^{3+} , Hg^{2+} and Pb^{2+} ions in cement

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Abstract – Project number 100TAM0067

X-Ray Photoelectron Spectroscopy (XPS) is applied in the elucidation of the chemistry of Cr^{3+} , Hg^{2+} and Pb^{2+} ions stabilized in portland cement. Cement samples tested were aged over periods of approximately twenty eight days, six months and two years. No significant differences in the chemical speciation of the metal ions were observed. There is an observed increase of surface carbonate content in the doped cement over the undoped cement during the earlier periods of aging. In the latter period of aging, the carbonate content of the undoped cement approximates that of the doped cement. There is evidence of Cr^{3+} ion incorporation in the bulk cement grains. Small area analysis of Hg^{2+} doped cement, shows that there are areas of mercury deposits, some of which are lacking in silicon.

Chemical binding and leaching mechanisms of solidified hazardous substances

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Abstract – Project number 100LUB3160

Solidification/stabilization (S/S) frequently employs cement and related silicate materials to treat liquid or sludge forms of hazardous materials to produce solids which are suitable for safe land disposal. Key issues in assessing the effectiveness of the treatment concern the durability of the solid produced and its resistance to leaching under various conditions. Important concerns in S/S studies therefore include characterization of the interactions of binding agents with the hazardous material and the effects of leaching solutions on the solidified matrix. Because ground water is usually acidic and since cementitious matrices are adversely affected by acidic aqueous solutions, it is important to define the effects associated with acid leaching. Our recent efforts using spectroscopic techniques (Fourier transform infrared and ^{29}Si solid-state nuclear magnetic resonance) have enabled us to more clearly understand the leaching process. Briefly, we have shown that silicate polymerization is slightly enhanced with lead doping and retarded in the presence of zinc. Leaching studies reveal that silicate polymerization occurs when the samples are exposed to acidic leaching conditions. The degree of cross-linking is directly proportional to the acidity of the leaching solution, being pronounced when pH five buffers are employed. The percentage of solidified metal leached during a buffer extraction is extremely high compared to the TCLP protocol. These results are important in helping to devise guidelines for S/S technologies and environmental protection. In addition to achieving a more fundamental understanding of the chemistry and leaching mechanisms of solidified hazardous systems, we have found that certain additives (phosphates, sulfates, sulfides, arsenites) greatly enhance stabilization of toxic metals when subjected to repeated batch leaching treatments. At the present time, efforts are being directed to studying mixed waste systems containing two or more priority pollutant metals and one or more organic contaminants. In addition, successful solidification of an industrial sludge from a munitions plant containing lead, cadmium and zinc has been achieved.

In a separately funded but related project, interactions of toxic metals, arsenates and organics on montmorillonite interlayer silicate surfaces are being pursued. Initial results indicate promising applications in the field of S/S.

Also during the past summer, we performed lead analysis on a soil sample

taken from a Texas superfund site. Four different extraction methods were used for comparison purposes. Methods studied involved extraction with (1) hydrochloric acid, (2) nitric acid, (3) nitric and hydrochloric acid and (4) nitric acid with hydrogen peroxide. It was obvious from our results that the highly oxidizing mixture of (4) was most efficient in removing lead from contaminated soils.

Our goals for the near future are to complete ongoing studies of the mixed metal systems (lead, chromium, cadmium) with chemical binders and additives (phosphates, sulfates, sulfides, latex) and to investigate mixed waste systems containing both metals and organics. The techniques to be employed include Fourier transform infrared spectroscopy, ^{29}Si and ^{27}Al solid-state nuclear magnetic resonance, leaching studies, flame and graphite furnace atomic absorption analysis and thermal methods. Results of our studies will lead to a better understanding of the effectiveness and chemical behavior of specific binding agents, the mechanisms of acidic leaching processes and the usefulness of cement based materials and montmorillonite clays in solidifying hazardous organics.

Destruction of chlorinated aromatic olefinic and aliphatic aliphatic molecules using hydride reducing agents together with glycol ether/KOH nucleophilic displacements

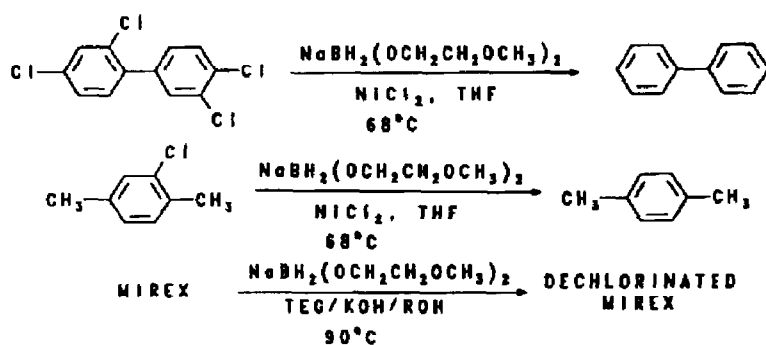
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Abstract - Project number 100MSU3144

The goal of this research is to develop a single decontaminating solution which can dehalogenate all common pesticides, herbicides, chlorinated solvents, PCB's, etc. Hydridepromoted poly(ethylene glycol) PEG/KOH or tetraethylene glycol TEG/KOH dechlorinations of aromatic, aliphatic and olefinic chlorocarbons were conducted at mild conditions. The use of NaBH_4 , $\text{NaBH}(\text{OR})_3$ and $\text{NaBH}_2(\text{OR})_2$, alone, or with TEG/KOH began in July 1989 with GCHSRC support. Destruction of PCBs using PEG-KOH (PEG=poly(ethylene glycol), pioneered by General Electric Co., converts highly chlorinated aromatic compounds to arylpolyglycols and phenolic compounds but high temperatures were required. We have discovered that $\text{NaBH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ in THF will dehalogenate PCBs. This reaction is greatly accelerated upon adding NiCl_2 to the solution at 68°C . Apparently,

Ni(O) or nickel boride intermediates promote dehalogenation. Thus, Arochlor 1016 is quantitatively converted to biphenyl in a few hours at 68°C using excess hydride and NiCl₂. Model compounds 2-chloro-*p*-xylene and 4-chlorobiphenyl were readily reduced to *p*-xylene and biphenyl, respectively. Many hazardous wastes have aliphatic or olefinic C-Cl bonds not readily destroyed by PEG/KOH. They are, however, dehalogenated by the hydride reagents coupled with PEG (or TEG) plus KOH. Mirex (a very stable aliphatic chlorinated pesticide) is destroyed at <90°C in NaBH₄/TEG/KOH/CH₃OCH₂CH₂OH. The catalytic effects of tin hydrides and transition metals was studied. A key finding was the high activity without the need of catalysts for aliphatic systems. The role of *in situ* conversion of BH₄⁻ to BH₂⁻ and the increased dehalogenating power of such reagents is being explored. Some example reactions are given in the scheme depicted below.



Scheme 1. Destruction path of several hazardous chlorinated compounds.

Hydrogen peroxide/ultraviolet irradiation process for treatment of leachates and contaminated groundwater

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Abstract – Project number 100UHH3132

Organic contamination of groundwaters from improper disposal of wastes and hazardous waste sites is a national problem. The problem manifests itself

both in production of highly contaminated leachates (mg/L concentrations) and the contamination of groundwaters used as drinking water sources ($\mu\text{g/L}$ concentrations). Currently, each of the two common treatment techniques, air stripping and granular activated carbon (GAC) adsorption have problems, particularly for remote sites and small drinking water utilities. Thus, an alternative, a simple treatment technique for organic contaminant control was sought.

The overall objective of this project is to develop the $\text{H}_2\text{O}_2/\text{Vis-UV}$ Chemical Oxidation Process for the destruction of waterborne hazardous substances that occur primarily in leachates and groundwater. The method is general, and, thus could be applied to municipal and industrial waste streams as well. The work proposed herein, PHASE II, is a flow-reactor study, following the completed batch-reactor study on eight selected chemical compounds. PHASE II is important because the ultimate embodiment of the process will be in a continuous-flow system. The specific objectives of PHASE II are as follows: (1) Use of the mathematical-flow model and ten benzene runs to determine the effect on conversion of benzene of four primary variable as follows: space velocity (contact time), initial oxidant/reactant mole ratio, photon flux, and temperature; (2) Tests on the seven other compounds; (3) Tests on mixtures and real water; (4) Correlation of reaction rates for purposes of a design model; and (5) Development of a predictive model for mixtures and real waters.

A continuous-flow reactor has been constructed in which organic compounds can be exposed to H_2O_2 and visible and ultra-violet (Vis-UV) light. Two major variables of the flow-through reactor (2.56 L of nominal volume) are fluid flow rate and irradiation intensity. To date, each test has a pre-irradiation period (lamps(s) off) for about three detention times, followed by the irradiation period, more than three more detention times to ensure steady-state conditions by the end of the test. Data collected during the pre-irradiation period is used to calculate the diffusion coefficient, and the data collected during the irradiation period is used to calculate the reaction rate constants of the contaminant (initially benzene) and TOC (POC-purgeable organic carbon + NPOC-non-purgeable organic carbon) for several different runs. Variation in the feed water composition, the flow rate, and the irradiation intensity will provide the variable to be studied.

Characteristics of incidents involving transportation of hazardous substances

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Abstract – Project number 110UCF0161

A survey conducted by the U.S. Department of Transportation in the mid seventies showed that 5–15% of all the trucks on the road at any time carry hazardous materials or waste. In a recent study, trucks carried 24.9% hazardous materials and were responsible for 57.3% of the property damages. Hazardous material shipments are expected to double every ten years which creates potentially more volatile accident situations.

The main objective of this study is to have a better understanding of the characteristics and causes of highway incidents involving trucks transporting hazardous substances and, if possible, to identify countermeasures to reduce the probability of occurrence and potential risk to public safety.

- (1) Review the literature on the U.S. in general, and Florida.
 - (2) Collect data on highway truck incidents in Florida.
 - (3) Analyze and provide statistical analysis of the data.
 - (4) Utilize data to determine the correlation, or lack thereof, between accident rates and measure of highway design.
 - (5) Identify countermeasures that could reduce accident occurrence and severity of damage.
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Active municipal solid waste landfill operation: A biochemical reactor

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Abstract – Project number 100UCF0202

Landfills remain the most frequently used method of municipal solid waste (MSW) disposal. Landfills are designed and constructed to prevent contact between the waste and the environment. Modern designs include hydraulic barriers to collect and control liquids to be treated and disposed. Gas production from MSW landfills also requires collection and control. Landfill management alternatives and options must consider the potential uses of these landfill outputs.

Active Landfill Management (ALM), as used herein, includes management of a waste disposal facility to minimize risk to human health and the environment while optimizing landfill volume by promoting decomposition of landfilled waste, reducing the potential health risks by immobilizing constituents in the waste mass, and optimizing the quality and quantity of decompositional gases, such as methane.

In order to identify design, construction, and operational requirements for ALM, and recognizing the need to avoid duplication of ongoing or past related efforts, the objective of this research is to support studies necessary to initiate a full scale demonstration of ALM to optimize solid waste stabilization, leachate control, and gas production.

The principal investigator, Dr. Debra R. Reinhart, as contracted by the Gulf Coast Hazardous Substance Research Center, will provide support to a United States Environmental Protection Agency funded project with the above described objective.

Toxicological and chemical monitoring of microbial degradation of oil-based sludge in liquid-solid contact reactors

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Abstract – Project number 100LSU3127

Production of hazardous waste in the United States exceeds the capacity available for storage and treatment of these wastes. While onsite bioremediation of oil-based sludges may be a viable alternative to offsite shipping and storage of wastes, concerns regarding the possible production of more toxic intermediates during degradation have been raised. In this study, bioremediation of oil-based contaminated sludges was conducted in a laboratory reactor in concert with two short term mutagenicity bioassays (Ames assay and Prophage Induction assay) and a mammalian toxicity assay (Chinese hamster ovary cells, CHO) to monitor changes in the waste during degradation. Following eight weeks of bioremediation of contaminated soil, an enhanced mutagenic response in both the Ames and Prophage assays was obtained after 30 days of incubation. The Prophage induction assay was more sensitive than the Ames assay in detecting mutagens. In the Ames assay, an increase in mutagenic compounds causing frameshift mutations was more marked than compounds eliciting base-pair mutations. Only one of the extracts was toxic in the CHO assay. The identification of the active organic components eliciting these responses is being pursued. This approach using biomonitoring concurrently with bioremediation will assist in the determination of the feasibility of this technology in future large scale cleanup procedures.

Preliminary investigation of continuous flow reactor treatment of contaminated soils

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Abstract – Project number 100MSU0076

Biological treatment of various hazardous substances has been shown to be a viable option. However, when these materials contaminate soils, bioremediation can become prohibitively difficult due to problems in development of needed microorganism populations. *In situ* technologies experience limitation due to nutrient addition while removing the soil for above ground treatment is controlled by an often excessive time for microbial acclimation and an extensive surface area requirement. These limitations are typical of batch-type treatment regimes.

The proposed two-year research project will be an initial study of the feasibility and benefit of developing a continuous flow reactor regime for treating soils contaminated with hazardous materials. During the first year, a series of bench-scale reactors will be used. Pseudo-continuous loading of the reactors will be achieved by daily addition of small portions of silty sand saturated with fuel oil. Removal of treated soil in amounts equal to this addition will be performed to maintain a constant reactor volume. The amounts will be varied between reactors to provide variation in the mean cell age of the microbial population. Moisture content in the reactor will also be varied. Supplemental nutrients will be added and monitored so as to assure that carbon contained in the contaminant is the only limiting nutrient. Upon achieving steady-state removal, the reaction kinetics will be determined and evaluated to define optimum conditions. During the second year, kinetics will be evaluated in similar fashion for different soil types and fuel contaminant levels.

Development of bioreactors for the destruction of chlorinated solvents

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Abstract – Project number 100UTA3131

Biological treatment of groundwaters contaminated with chlorinated solvents is a promising alternative to conventional treatment technologies. Biodegradation is advantageous because the contaminants are destroyed in place rather than transferred to another phase. This project builds on recent observations that many aerobic microorganisms, when grown on substrates that induce nonspecific oxygenase enzymes, can cometabolize chlorinated solvents. The goal of this research is the development of cometabolism based treatment processes for the destruction of compounds such as 1,1,1-trichloroethane, chloroform, and trichloroethylene (TCE) at concentrations below 1 mg/L.

The suitability of several microbial cultures was screened for and evaluated, with emphasis placed on mixed cultures grown with simple aromatic substrates. A consortia of phenol-utilizing organisms was selected for further study based on its rate of trichloroethylene degradation, its reliability of degradation, and its ability to rapidly form cohesive biofilms. In batch studies of a chemostat culture, pseudo first-order TCE degradation rate constants were typically in the range of 10 to 80 L/g_{TSS}/day. Greater than 95% removal and 80% mineralization of TCE were obtained in batch incubations lasting a few hours. The culture could transform greater than 12 $\mu\text{g}_{\text{TCE}}/\text{mg}_{\text{TSS}}$ at a TCE concentration of 1 mg/L. Phenol at concentrations of 5 to 10 mg/L strongly inhibited TCE degradation.

Continuous-flow column experiments and mathematical modeling of column performance with existing biofilm reactor computer models were conducted. TCE and phenol were fed simultaneously to columns packed with glass beads. TCE removals over time were sporadic and low, ranging from 0% to 20%. In short term continuous-flow tests without phenol present, TCE removals improved to about 40%. When the reactors were continuously fed phenol, they plugged with biofilm in the inlet region after several days of growth.

Modeling indicated that elevated flow rates during phenol feeding would provide more biofilm activity and better distribution of biomass throughout the reactor. However, because the TCE degradation rate is lower than that of

phenol and high TCE removals are desired, feedwater with TCE must be fed at a flow rate about ten times less than the phenol feedwater flow rate. To accommodate this, our recent research has focused on sequencing biofilm reactors, which cycle between growth on phenol followed by removal of TCE. This type of operation provides a practical means of dealing with the differences in kinetics, controls plugging by limiting growth and avoids enzyme competition between phenol and TCE.

With the sequencing biofilm reactor, average TCE removals of greater than 90% at an empty bed contact time of 35 minutes have been sustained for one week. Average TCE removals greater than 70% have been sustained for up to one month. Reactor modeling has determined that initial rate constants greater than 50 L/mg_{TSS}/day are being obtained in the reactors, which are significantly higher than other reports for biofilm reactors. Several combinations of feeding frequency, duration, and phenol concentration have been examined. Ongoing and future work will address other important factors related to increasing and sustaining the cometabolic activity in sequencing reactors. Bed fluidization during growth, more efficient media, and enzyme competition between several chlorinated solvents will be examined.

The feasibility of *in situ* treatment of soil to promote desorption of hazardous wastes, thus permitting capture and treatment

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Abstract – Project number 100UHH3008

Hazardous wastes are frequently fixed on soil particles by adsorption. Final destruction of these wastes is limited, because they are not available for treatment without removal of the soil itself. If some technique could be found to desorb these materials from the soil particles *in situ*, then they would be mobilized, and could be intercepted, captured, and treated. Treatment alterna-

tives could be either *in situ* biodegradation or "pump and treat" chemical oxidation. Neither of these processes would be effective on adsorbed organics, however. Thus, some method of freeing the organics bound to the soil must be found.

This project has begun by 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. Four 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 sodium hydroxide as a source of hydroxide ions, (3) the addition of lime as a source of calcium and hydroxide ions to alter the surface properties of the soil and (4) the addition of surfactants to competitively displace the sorbate.

The study is employing six special flexible-wall permeameters designed and built by the University of Houston. To start a desorption test, a clayey soil, mixed with sand to adjust permeability, is contaminated with the organic to be tested on a batch basis, then is compacted wet of or at optimum liquid content to simulate a saturated condition and placed in a permeameter. As the *in situ* mobilization process is applied, the effluent is examined for the organic compound under study. As this effluent stream is monitored over time, the quantity of material leaving the column is calculated, and the extent of desorption is determined as compared to a control that is flushed with plain deionized water. This allows a comparison of the treatment process to simple flushing. Environmentally contaminated soils will be tested later; however, the batch contamination step above will not be employed. Each test is performed in replicate so that any differences in performance of the treated sample compared to the flushed samples can be tested statically.

Solidification/stabilization of hazardous waste substances in latex modified portland cement matrices and ultrasonic pulse velocity and echo attenuation as a evaluation tool

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Abstract – Project number 041LUB3205

Immobilization of hazardous waste substances in a portland cement matrix is considered a major solidification method due to the simplicity of the process and its low cost. However, relatively high porosity of the cement matrix, which could lead to considerable leaching, has created a demand for improving portland cement matrices. The main objectives of this study are twofold:

- (1) To develop alternative hybrid materials using portland cement modified with different admixtures to treat inorganic and organic wastes.
 - (2) To develop a non-destructive test method using ultrasonic pulse velocity and echo attenuation, for evaluating the performance of solidified/stabilized inorganic wastes.
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***In situ* treatment for cracked and contaminated clays and permeable soils: Seepage control and long-term performance**

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Abstract – Project number 100UHH3176

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. There is also growing concern about deep aquifers being contaminated due to the seepage of hazardous organic permeants through confining clay barriers. However, little is known about repairing clay barriers or reducing the hydraulic conductivity of permeable local soils *in situ* to control seepage and satisfy the EPA limit of 10^{-7} cm/s. The hydraulic conductivity of clay is affected by the interactive nature of local defects (desiccation cracks, fissures, faults and fractures), chemical wastes and *in situ* stresses. Since field tests are expensive, time-consuming and, in many instances impractical, reliable laboratory permeability tests have been developed where the field conditions including cracks are closely modeled. These cracked clay samples are being used to evaluate effect of cracks on the hydraulic conductivity of cracked soils *in situ*. Preliminary studies show that the hydraulic conductivity of cracked clay ($> 10^{-7}$ cm/s) and contaminated soils ($> 10^{-4}$ cm/s) can be reduced to below 10^{-7} cm/s by treating with grouts, but the long-term durability of such treatment has to be verified.

In this study, the long-term performance of treated cracked clays and contaminated soils under various chemical environments will be evaluated. Permeant list will be expanded to include chlorinated organics and actual field leachate and field clays obtained from the Gulf Coast region. The compatibility of grouts with the organic permeants and the soils will also be studied in a fundamental way. performance of various grouts such as sodium silicate, cement, lime, fly ash and bentonite grouts or their mixtures thereof will be evaluated for longer periods of time under various chemical environments. A field study is proposed to demonstrate the laboratory findings. These findings will improve the current repair practice for leaking clay barriers, control seepage through contaminated soils and increase the use of permeable local soils with *in situ* treatment as impermeable barriers at future waste disposal sites.

Leaching mechanisms and performance of solidified/stabilized organic hazardous waste substances in modified cementitious and polymeric matrices

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Abstract – Project number 100UHH3160

Solidification/stabilization (S/S) is one of the treatment technologies with the potential to meet the cleanup standard outlined by SARA and, in recent times, it has been used at numerous CERCLA sites to reduce waste toxicity and/or mobility. However, the primary concern of the current S/S technology using cement and pozzolanic systems is the interfering effects of organic contaminants which affect setting, chemical stability and long-term durability. 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% to 20%. Hence, alternative binder materials for S/S treatment of non-volatile organic hazardous wastes must be developed to meet the current demand in treating organic wastes and mixed wastes. Recent studies at the University of Houston and Lamar University were limited to cement-phenol and polymer-phenol systems and it was concluded that (1) even 0.1% of phenol concentration will affect the performance of cement and the phenol leached (TCLP test) from the cement matrix exceeds the regulatory level, and (2) the polyester polymer is very effective in rapidly treating much higher concentrations of phenol.

It is being proposed to develop alternative hybrid materials using a combination of additives (sorbents), cement and polymers (organic and inorganic) for effectively S/S phenolic wastes in particular and non-volatile organic hazardous wastes in general. The additives will include sorbents such as organophilic clay, activated carbon, silica fume, fly ash, lime and clay. Organic waste list will be extended to include halogenated phenolic derivatives such as 2-chlorophenol, pentachlorophenol and polychlorinated biphenyls (PCBs). The interaction between the wastes and the modified binders will be studied in a fundamental way from the time of mixing to final solidification and there after (up to 2 years) using chemical analysis, leachate tests and microstructural studies. Using at least two representative industrial organic sludges, the capabilities of the new modified cement-additive-polymer binder systems in solidifying/stabilizing the organic wastes will be demonstrated by bench scale process development.

Resolving the dilemmas of hazardous waste management: The why of NIMBY attitudes

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Abstract – Project number 100UCF3150

This plan describes our continuing investigation as to why people and communities oppose the siting of hazardous waste management facilities. Our preliminary research suggests that people may be more receptive to the idea of such facilities than is generally recognized, and that concerns of proximity and political cultural beliefs play a significant force in producing opposition attitudes and behavior. A majority of people appear to support hazardous waste facility siting, and only minorities see them as either health and safety or general environmental threats. The problem in understanding NIMBY (“not in my backyard”) attitudes remains a central research focus, as does the measurement of political culture attributes. We propose to measure these attitudes in more extensive and complex ways, following on the experience to date. The final result will be an analysis of what factors best explain the resistance to siting, and how those factors relate to conditions that can or cannot be changed. We will utilize a mass public random sample survey of Florida residents to better measure the variables, and give us a longitudinal basis for understanding attitudes. This is unique survey data not available elsewhere that will most likely attract wide interest. It will include measurement of demographic factors; cultural beliefs; attitudinal precepts; and questions concerning proximity, health and safety, environmentalism, and risk.

Application of ultimate Bingham material in hazardous spills

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Abstract – Project number 100LUB0090F1

This proposal is for a one-year exploratory investigation of adding solid particles to increase the gel strength of an ultimate Bingham material (UBM).

Such a material might be useful to mitigate pollution from hazardous spills on land and water. The material is a gel, and thus has a solid-like structure, but when given sufficient shear will liquify at a shear plane and immediately re-develop the gel when motion stops. Thus, the material can be mixed by a fire truck, pumped through standard hose to a spill and the material exiting the hose can form a dike to contain the spill. Or, it can be foamed to cover the spill and the foam will not drain. A combination of gel and foam might be used to protect shore lines (with a minimum of wave action) from oil spills. The material is a mixed metal layered hydroxide compound (MMLHC) that is added to a prehydrated bentonite in water mixture. It is not hazardous. As presently used in oil well drilling, the gel strength is too weak to build dikes but is adequate for foam.

The first step is to find how the gel strength varies with the concentration of prehydrated bentonite (in water) and concentration of MMLCH (in the prehydrated bentonite-water mixture). While high gel strengths can be obtained by high concentrations (and high costs) theory predicts that small particles may be able to produce the needed properties at much lower costs. The second step is to find how the concentration, size distribution, and shape of particles change the gel strength.

Hydrometallurgical treatment of hazardous waste for simultaneous detoxification and metal recovery

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Abstract – Project number 100UAL3103

Many industrial processes generate hazardous solid wastes containing heavy metals such as lead and cadmium. Flyash from municipal solid waste (MSW) incinerators and waste molding sand from brass foundries are two examples. This material is currently disposed of in hazardous waste landfills. Investigations address a potential hydrometallurgical process for (1) chemical dissolution (leaching) of the metal values from the hazardous waste, and (2) recovery of the dissolved metals from the aqueous leaching solution which can then be recycled. The process is flexible and has been applied here to MSW flyash.

The leaching of metal values from MSW flyash has been compared for var-

ious lixivants, including HCl, H₂SO₄, acetic acid, NaCl and HCl+NaCl. The maximum extractions observed for Pb, Cd and Zn were 89%, 98% and 74%, respectively in 1 M HCl. Chemical dissolution of Pb, Cd and Zn can be accomplished quickly and effectively in both HCl and HCl+NaCl solutions. Optimization of leaching conditions for effective detoxification and subsequent metal recovery can be achieved by controlling the pH of the lixiviant and the ratio of flyash to lixiviant. Significantly, Toxicity Characteristic Leaching Procedure (TCLP) tests have been conducted which show that residues can be produced which meet the toxicity limit for Pb and Cd. Furthermore, lead and cadmium can be recovered from the leaching solution by cementation with zinc dust. Experiments have been performed to determine the effects of pH, particle size of the zinc dust used, quantity of zinc added, and dissolved impurities on the cementation kinetics. The final solution obtained after leaching and cementation yields a dissolved zinc concentration of approximately 15 g/L or higher, a level suitable for direct electrowinning of zinc. Electrochemical experiments have been performed which are aimed at determining the critical parameters which affect the cementation and electrowinning steps.

Many MSW incinerators use lime to reduce SO₂ emissions in the flue gas. The flyash generated by such incinerators cannot be economically treated with acidic leaching solutions, since unreacted lime would consume excessive quantities of acid. Recent experiments have been aimed at determining the feasibility of leaching out Pb, Cd and Zn in basic solutions, pH > 11, using CaO, Na₂CO₃ and NaOH. Results indicate that Pb is much more leachable than the Cd or Zn under these conditions.

The NIMBY syndrome: Exploring the relationship between public education and siting opposition

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Abstract – Project number 100LUB3135

Studies of NIMBY indicate that opposition to or acceptance of new hazardous waste facilities may be related to the level of public education about the issue. The role of knowledge or information has not been adequately studied. Statements by industry representatives often reveal assumptions that link level of knowledge with support for new sites or facilities. Yet these assumptions

remain untested. Environmentalists also make assumptions that informed persons are more likely to oppose current methods and technologies. These assumptions are untested as well (public opinion polls demonstrating attitudes favorable to environmental issues are measuring opinion not level of knowledge). Neither side is willing to claim the ignorant or uninformed since each party in the siting impasse feel they are allied with better information and the best solution to the waste problem. Therefore, more research is needed to clarify the role of public awareness and knowledge. Two surveys are proposed to evaluate the relationship between public education and siting opposition/acceptance.

Water solubility and Henry's Law constant for crude oil hydrocarbons

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Abstract – Project number 100LUB0101

The contamination of water with crude oil hydrocarbons (primary compounds in gasoline, diesel, jet fuel, heating oil, etc.) is an important issue that will intensify in the future. It is especially important to have quantitative data on how such hydrocarbons and related compounds distribute or partition themselves in the environment between air, water and soil.

The solubility (S) of a crude oil hydrocarbon in water is an indication off how much off the hydrocarbon will dissolve in water. Knowledge of the waste solubility is very helpful in environmental studies. As an example, solubility data is very helpful in determining the assessment and distribution of a hydrocarbon spill upon its contact with water. Unfortunately, data for solubility of crude oil hydrocarbons in waste are very limited and nonexistent for many compounds. Additional data are needed.

Henry's Law constant (H) for a compound in water is an indication of how the compound will partition or distribute between air and water. Knowledge of Henry's Law constant (i.e., air-water distribution coefficient) is also very helpful in environmental studies. Unfortunately, data for Henry's Law constant for crude oil hydrocarbons in water are very limited and nonexistent for many compounds. Additional data are needed.

The objective off this research is to provide additional data and expanded results for water solubility and Henry's Law constant for crude oil hydrocarbons:

- Part 1 Paraffins (alkanes) (year 1)

- Part 2 Naphthenes (cycloalkanes) (year 2)
- Part 3 Aromatics (benzenes) (year 3)

The results issuing from this research for water solubility and Henry's Law constant for crude oil hydrocarbons may be used by process and environmental engineers in initial engineering and environmental studies.

Applications of materials handling approaches and systems to remediations on Superfund sites

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Abstract – Project number 100LUB0102M1

Very few Superfund project managers have a particular expertise in the technologies available for materials handling in general or hazardous materials handling in particular. This study will result in a manual and user friendly software package which will provide Superfund site managers the information necessary to make materials handling decisions which are cost effective, in compliance with applicable regulations and utilize "current best" technologies.

A case study approach will be utilized in the first year of this project. It will involve inspection, documentation, analysis and improvement of materials handling technologies at Superfund sites in Region VI. Approximately six sites will be visited by members of the research team. Process flow analyses will be performed and documented. Special emphasis will be placed on the movement and handling of hazardous materials. Documentation may include videotape process flow charts and narrative explanations.

A survey of superfund sites outside of Region VI will be conducted by telephone or written survey form in order to gather additional information regarding materials handling technologies and problems at Superfund sites. This survey data will be used to decide on whether or not to visit sites outside the region which may present special problems or opportunities.

A review of the documentation on all six sites visited as well as survey information will be conducted and three sites will be revisited in order to gather more indepth and quantitative data and measurements regarding materials flows and materials handling problems and/or bottlenecks. A report will be prepared outlining the status of materials handling technologies at Superfund sites visited. This report will provide a baseline of knowledge from which additional research and development tasks will be defined.

The second year of the project will involve development of a taxonomy of materials handling technologies and a database system for analyzing the hazardous materials handling requirements of Superfund sites and relating those

requirements to existing technologies. This analysis will form the basis for two major research thrusts: the first being the development of a quality function deployment (QFD) model for hazardous materials handling systems design and the second being the development of a knowledge based expert system for hazardous materials handling system selection. The third year of the project will involve completion of the QFD model and further development of the expert systems model. Additionally, a handbook to aid Superfund site managers in making material handling decisions will be developed in year three of this project.

Potential new technologies such as robotics, artificial intelligence and artificial vision will also be examined. Finally, a taxonomy of the myriad types of material handling equipment categories will be developed.

Removal of hazardous organic contaminants to purify water

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Abstract – Project number 100UHH2011

Experiments done to date on water deliberately contaminated with organic compounds, widely accepted as environmentally dangerous, have resulted in a promising method for reducing such pollutants to acceptable levels from a health hazard viewpoint. The method appears to offer simplicity, low cost, and ability to be regenerated, thus allowing extended reusability.

We utilize the unusual permeability to many organic compounds we have observed for certain stable, silicone polymers, in the form of tubing, through which the polluted water is pumped.

The data we have accumulated to date has provided us with sufficient engineering parameters to permit the preliminary design of a purification system, comprised of tubing "bundles", each capable of delivering 500 gallons (1900 L) per day of purified water. The influent water is presumed to contain 1-2 parts per million of chloroform, trichloroethylene and benzene (prime targets of pollution control), while the effluent water can be reduced to levels at or below the presently accepted values of 50 parts per billion.

We believe that the additional data we propose to obtain will permit the firm design of units exceeding these quality goals. We propose to make such a module, measure its performance over a range of influent contamination, flow rate (laminar vs. turbulent flow), total water gallonage decontaminate and regeneration procedures, ranging from simple air flushing to more complex approaches.
